To Piero Lunghi. We miss you a lot.
To you our gratitude for ever.


Piero made significant contributions in the field of fuel cells in the course of his too short career. He was the leading figure in the formation of the fuel cell research group at the University of Perugia and several activities and research projects initiated by him are still ongoing. This means that, thanks to Piero, many young people are working in this exciting research field and are coming to Rome to present their results. Therefore, Piero’s memory is in the conference name but Piero’s contribution is still in the contents of this book.

The memory of our friend Piero, his great personal generosity and energy, survives in our hearts, his contribution and his tenacity survive in the work of young people who carry on his vision throughout the world.
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Fuel Cells 2000 is an activity of the Breakthrough Technologies Institute (BTI), a non-profit 501(c)(3)) independent, environmental educational organization, with the mission to promote the commercialization of fuel cells and hydrogen by supplying accurate, unbiased information and developing and disseminating summary materials accessible to a general audience. Fuel Cells 2000 is independent and non-aligned, and supports fuel cells of all types for all applications.

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Please feel free to contact us!
Andreas Frömmel (afroemmel@fces.de; +49 351 2553 7390)
SOFCpower has placed at the center of its research program a micro-cogeneration with fuel cells (Solid Oxide Fuel Cells), an innovative technology focused on the development of power modules for the cogeneration of electricity and heat.

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Authors of selected extended abstracts will be invited to submit a full paper for publication within the special issue of the International Journal of Hydrogen Energy fully dedicated to EFC13.

Submissions for publication in the Journal are upon invitation only.
Dear Participant,

Welcome to Rome and to the 5th edition of the European Fuel Cell Technology and Applications “Piero Lunghi” Conference. It is an honour for us to host you and we are pleased to say you will be enjoying the company at this event of over 250 colleagues and leading experts in the wide field of fuel cells. Covering the entire spectrum of research, development, demonstration and deployment, 137 lectures and 100 posters have been selected for presentation of the latest achievements and updated perspectives in fuel cell technology.

Fuel cells are improving unstoppably, not only in terms of efficiency but also in durability and reliability, and are now decidedly edging into the market. EFC13 reflects this as can be seen from the increased number of reports from real-life applications of fuel cells and fuel cell-based products. Also the increasing research activities on the use of fuel cells for producing chemicals taking advantage of anode and cathode local conditions to enhance specific reactions for the production of H2, CO, H2O and so on are widely represented.

The core part of the event stays focused on material development, lab tests and modelling as well as looking at innovative fuels, fuel processing and system design. Environmental issues specifically addressed in certain fuel cell applications will be part of the "decarbonizing society" track. Once again, many new ideas and concepts are offered for presentation at EFC13, with a special full-day session dedicated to the evolving world of microbial fuel cells.

EFC13 constantly strives to increase the awareness of fuel cells in society at large as well as to push forward the boundaries of research and development in the field. Complementary side-events will be held in conjunction with this 5th edition of EFC13: the international workshop "Integrating Numerical and Experimental Approaches for the Design of Next Generation Fuel Cells" on 10th December 2013; the national event (in Italian) "Hydrogen and Fuel Cells: what opportunities for Italy?" on 13th December 2013; as well as the Microbial Fuel Cells Session on 12th December 2013.

To combine the compulsory dissemination activities of European projects (e.g. FCH-JU) with the benefits of networking and the leisure of an evening drink, the "project cocktail" session has been introduced to allow the presentation of project progress and comparison of results, scheduled after the lectures of 12th December.

Finally, our beautiful congress location will give you immediate access to the very heart of the Eternal City, making up an unparalleled backdrop to what we hope will be a profitable stay for you and a successful meeting.

The conference Chairman
and Organizing Committee
Abstract
FUEL CELL MICRO-CHP IN EUROPE: A PEMPTY PROMISE, OR A SOLID BET?

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Abstract – What is ‘success’ for fuel cell micro-CHP (FC m-CHP) in Europe? According to the industry, it equates to annual sales of 70,000 to 100,000 units by 2020. This research examined what is needed to achieve such sales – paying particular reference to the base market of Japan – to determine if such ‘success’ can be achieved. Our findings were that volumes will struggle to reach industry targets of 70,000 to 100,000 units a year given the current drivers, commercialisation plans, and the expected scale of cost reductions. The growth rate required for Europe to achieve this target (from zero sales today) would mean market growth in excess of that which Japan has experienced for FC m-CHP over the last few years. There is simply a lack of signals that, today, make this credible. We do expect a market to emerge however, and we identify a number of wildcards that could enable ‘success’ to be reached.

Index Terms – Europe, fuel cell, markets, micro-CHP.

I. NOMENCLATURE
BoP = balance of plant
m-CHP = micro combined heat and power
FC m-CHP = fuel cell micro-CHP
PEM = Proton Exchange Membrane
SOFC = Solid Oxide fuel cell

II. INTRODUCTION

The next few years will prove critical for the creation of a market for fuel cell micro combined heat and power (FC m-CHP) appliances in Europe. In particular, for Proton Exchange Membrane (PEM) and Solid Oxide (SOFC) types. A widely-shared industry goal is to reach 70,000 – 100,000 unit sales per year by the end of this decade. This stems from forecasts by the IEA1 [1] and German NIP2 [2]. Yet, with fully-commercialised product still unavailable, and launch targets repeatedly being pushed back, investor confidence has lullled. Some in the industry feel it is “now or never” for the technology.

Several national and multinational field trial projects are taking place over the next few years and developers are amassing a body of experience. Thus, there persists a justifiable expectation for a wave of products coming to market. The earliest may well come within the next year, and there are numerous developers vying to be amongst the first to retail a FC m-CHP system in Europe.

Before deciding whether their goal (market success) is possible, answers to several questions were required:

a) What, exactly, does ‘market success’ mean?
b) Is the growth required to achieve it realistically achievable?
c) Can product costs fall fast enough to enable the volumes necessary for ‘success’?
d) What could improve the odds for FC m-CHP reaching this goal?

III. ACHIEVING MARKET SUCCESS

As part of this research we tested the forecasts and potential sales numbers from our company’s own database of market statistics and forecasts [3] with against the experience of key industry players.

4. Criteria for the emergence of a successful market

With regard to how product developers/integrators/vendors will accomplish it, our research uncovered which key criteria FC m-CHP providers must meet in order to attract the volume of customers needed. These were:

i. ‘Products that work’ – meaning have at least a 40,000 hour stack life (a managed stack replacement programme could make shorter stack lifetimes acceptable);

1 International Energy Agency
2 National Hydrogen and Fuel Cell Technology Innovation Programme, co-funded by the Federal Ministry of Transport, Building and Urban Development and industry partners. Its forecast is based on FC m-CHP gaining 15% share of the residential heating market.
ii. ‘Offer a strong value proposition to end-users’ – it is critical FC m-CHP fares well in comparison to competing options for residential customers. To attract utility interest, products must give a solution for securing continued gas sales and / or customer retention and new acquisition; and

iii. ‘Have strong backing from commercial partnerships and the wider heating industry’ – to help secure route to market channels and access installers – and fore mostly give robust, reliable products.

B. The scale of the task in Europe

We calculated the growth experienced in the FC m-CHP market in Japan – the first country to establish a commercial market. The industry there has benefitted from sizeable subsidy support and so has expanded rapidly. To assess the feasibility of the European target, we compared this to the rate at which sales of current micro-CHP (m-CHP) products have developed here. This is illustrated by Figure 1.

We applied learning rates theory to analyse the progression of product costs. This indicated that the volumes required to drive substantial cost reductions exceed what we believe to be achievable within the short time frame out to 2020.

The more novel parts of FC m-CHP products – the fuel cell stack, the desulfurizer, the fuel reformer – are where the greatest potential for cost reduction lies. Balance of Plant (BoP) contributions to lowering costs will be minor, given how most are mass manufactured already.

Fig. 1. Past and future growth of micro-CHP and FC M-CHP sales in Europe and Japan.

We conclude that our product performance criteria for FC m-CHP will largely be met in the period up to 2020. Yet, our key finding is that volumes of 70,000 – 100,000 sales per year will be highly challenging, given the current state of market drivers, manufacturer’s plans to commercialise and the expected product cost reductions. The growth required for Europe to achieve this market size requires market growth (assuming 1,000 sales in year 1; 2015) in excess of that which Japan has experienced since 2009.

There is simply a lack of signals that, today, make this credible. Slow sales of engine-based m-CHP in recent years support this viewpoint. Given the comparatively high number of entrants expected (likely over 10) and the initially high prices (we estimate €35,000+ fully-installed), volumes to the end-user will struggle to increase in time to facilitate enough demand by 2020.

We do fully expect a market to emerge, however. What is less clear though is how FC m-CHP’s vendors will grow early sales beyond the small numbers of innovators who willing to pay the high prices. Subsequently, the race to volume and associated lower costs will be a tough one – and will require substantial investments.

We stress that there are a number of wildcards (unpredictable factors/’Black Swans’) that could enable ‘success’ as defined here to be reached. Innovative business models and routes to market are in the early stages of exploration, and we agree these will be necessary in the creation of a more mainstream market.

Ultimately, the question is if these can be implemented in time (and add enough value) to become a viable mechanism to bridging the gap to higher uptake.

Other factors which could open up the market faster than we expect include: the emergence of an anomalously low-cost product, or energy companies and governments suddenly deciding to throw their weight (budget) behind the technology.

ACKNOWLEDGMENTS

We would like to extend our thanks to all our industry contacts we consulted during this study. We also thank Jon Slowe for his insight and guidance throughout.

REFERENCES

ACCELERATED STRESS TESTING OF POLYBENZIMIDAZOLE BASED HT-PEM FUEL CELLS FROM DIFFERENT SUPPLIERS

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Abstract – In this work, 25 cm² MEAs from different suppliers were investigated in a high temperature polymer electrolyte membrane fuel cell. The accelerated stress tests consisted of current density cycling between open circuit voltage (4 minutes) and 0.3 A/cm² (16 minutes) for ~1000 h of operation. Electrochemical characterization with polarization curves, EIS, CV and LSV was carried out once per week. It was observed that OCV, performance and electrochemical active surface area decrease. Moreover, hydrogen crossover and charge transfer resistance increases were also detected. Degradation decline was strong in the first two weeks but then deceleration took place.

Accelerated Stress Test, Commercial MEAs, HT-PEMFC, Degradation.

I. INTRODUCTION

In the recent years, different fuel cell research groups are focusing their efforts on the development of high temperature PEM (proton exchange membrane) fuel cells for high efficiency electrical power generation. This technology shows a number of desired features that low temperature technology does not provide. Among all the desired features, fuel impurities tolerance, generated heat utilization or enhanced electrode kinetics can be highlighted. One of the promising candidates to be used as electrolyte material in this kind of high temperature technology is the phosphoric acid doped polybenzimidazole (PBI). When PBI is doped with H₃PO₄, it shows good proton conductivity, virtually zero electro-osmotic drag coefficient and good chemical, thermal and strain resistances. Nevertheless, the high degradation rate compared to low temperature PEM fuel cell is one of the key issues to be solved for H₃PO₄ doped PBI-based PEM fuel cells. That fast degradation is due to the high operation temperatures, the acidic environment and high electric potential that the elements of the membrane-electrode-assembly (MEA) in the fuel cell are exposed to [1-3]. In this work, PBI-based MEAs from two suppliers have been evaluated electrochemically in 1,000 hours accelerated stress tests (AST) with the aim of determining the state-of-the-art of this kind of technology. Thus, this work can also be considered as starting point for the development of the European Project CISTEM funded by the Joint Undertaking FCH-JU where a CHP system will be developed with improved HT-PEM MEAs. An AST utilizes a defined load cycling mode which allows driving the fuel cell degradation mechanisms in higher rates than with a long-term testing at constant load. So these ASTs provide results in a shorter period of time for an understanding of the fuel cell degradation. Various electrochemical measurements were carried out to identify and classify the different degradation mechanisms shown by the MEAs investigated.

II. EXPERIMENTAL

A. Membrane Electrode Assembly

Celtée®-P1100W MEAs (BASF Fuel Cell, Germany) with an active area of 20.25 cm² were used. The MEA consists of a polymer gel membrane with PBI and phosphoric acid. The acid content is about 95 wt % which accounts for 70 phosphoric acid molecules per PBI repeat unit. The GDL is made of woven carbon cloth. The membrane thickness is about 50-75 µm, the catalyst utilized is a Pt-alloy with 0.75 mg Pt/cm² for the cathode and 1 mg Pt/cm² for the anode [4]. According to the supplier [5], the cathode side uses graphitized carbon for better corrosion resistance.

Dapozol®-G55 MEAs were provided by Danish Power Systems (Denmark) with a nominal active surface area of 25 cm². This type of MEA consists of polymer material and carbon paper as GDL material. The acid content of this type of MEA is between 8 and 9 phosphoric acid molecules per repeat unit of PBI.

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B. Cell Compression Units and Fuel Cell Test Stations

A cell compression unit (CCU) from Pragma Industries (France) was used to apply a constant contact compression of 0.75 MPa to the MEA during the experiments. The fuel cells were operated with five-fold serpentine and grid flow field geometry bipolar plates (BBP). A displacement sensor on the CCU allowed the recording of thickness changes during the experiments. MEA thickness changes presented in this work have been recorded at constant contact pressure mode.

The CCU was operated with a commercially available fuel cell test station Evaluator C50-LT from FuelCon AG (Germany). Constant stoichiometry conditions were selected for operation. Thus, hydrogen supply was fixed with a stoichiometric factor of 1.2. In case of the cathode, both air and oxygen supplies were used and stoichiometric factors of 2 and 9.5 were selected, respectively. The difference between oxidant oxygen supplies were used and stoichiometric factors of 2 and 0.5 were selected, respectively. The difference between oxidant stoichiometries provides the same volume flows on the cathode side.

C. Fuel Cell Test Procedure

An external potentiostat (Modulab 2100A, Solartron Analytical, U. K.) was used to record cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). Polarization curves were performed with the fuel cell test station. The CV scan started from 0.05 V up to 1.0 V with a sweep rate of 100 mV/s. LSV was performed with a potential between the initial rest one and 0.5 V and a sweep rate of 2 mV/s. Potentiostatic mode was kept for EIS measurements and hence an alternating voltage was applied with an amplitude of 10 mV r.m.s. The frequency range studied was recorded from 100 kHz to 100 mHz.

All MEAs under investigation followed the standard break-in procedures recommended by the respective suppliers. After the break-in procedure, the MEA was initially characterized. MEA characterization procedure consisted of polarization curves and EIS measurements carried out with H2/air and H2/O2. Then, the gases were changed to H2/N2 in order to perform CV and LSV experiments. Thereafter, the gases were reset to H2/air and the AST was started. Approximately once per week, the current density cycling was interrupted for MEA characterization. One AST cycle consisted of applying a current density load of 0.3 A/cm2 for 16 minutes which was followed then by 4 minutes at open circuit voltage (OCV). Therefore, three cycles per hour had taken place. The test was conducted for ~1,000 h of operation.

III. RESULTS

Figure 1 shows cell voltages, MEA thickness change and current density as function of time for a BASF P1100W MEA operated with grid flow field BPPs.

IV. CONCLUSION

The AST can help to identify the degradation mechanisms that occur within the fuel cell during long term operation. Most of the fuel cell degradation occurs during the first 300 h of operation. After this point, degradation declines. This work establishes the basis of the European Project CISTEM where more stable and efficient HT-PEM MEAs will be developed.

ACKNOWLEDGMENT

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REFERENCES

Description of a pilot plant for biogas valorization by means of PEMFC

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Abstract - Mitigation of global warming is a major priority in energy and environmental policies of the European Union (EU). Besides contributing to these objectives, production and use of biogas allow to create many economic and environmental benefits. The project BIOCELL aimed to demonstrate the feasibility and economic viability of energy production from biogas via Polymeric Exchange Membrane Fuel Cells (PEMFC) and Solid Oxide Fuel Cells (SOFC), adapted to WWTP. This paper describes in detail the experimental plant built in Murcia-Este Waste Water Treatment Plant (WWTP) for the valorization of biogas via PEMFC.

Index Terms - biogas, cleaning, PEMFC, reforming

I. INTRODUCTION

Mitigation of global warming is a major priority in energy and environmental policies of the EU. Besides this, production and use of biogas allow to create many economic and environmental benefits, as the use of a renewable energy, reducing the dependence on fossil fuels and reducing the volume of waste generated.

Biogas is a mixture of methane (CH₄) and carbon dioxide (CO₂) generated in WWTP as a byproduct of the process of sludge stabilization by anaerobic digestion (AD) [1].

The biogas valorization through different methods (boilers, cogeneration plants, micro-turbines and upgrading for use as fuel or for injection to grid) is widely developed. Due to its high electrical efficiency and reduced environmental impact, fuel cells (FC) are destined to become an interesting alternative for implementation in biogas production facilities [2, 3].

From 2009 to 2012; Aguas de Murcia, company that manages the water cycle in Murcia municipality, has participated in the project BIOCELL (http://www.life-biocell.eu), funded by the LIFE + program of the EU, aimed to demonstrate the feasibility and economic viability of energy production from biogas via low and high temperature(Tª) fuel cells (FC) are destined to become an interesting alternative for implementation in biogas production facilities [2, 3].

The project BIOCELL aimed to demonstrate the feasibility and economic viability of energy production from biogas via Polymeric Exchange Membrane Fuel Cells (PEMFC) and Solid Oxide Fuel Cells (SOFC), adapted to WWTP. This paper describes in detail the experimental plant built in Murcia-Este WWTP, managed by Aguas de Murcia, for the valorization of biogas by PEMFC.

The study has involved a high degree of technological innovation due to the absence of background information about industrial plants operating this kind of technologies such as the lack of commercial equipment suitable for integration into the demonstration plant.

II. PLANT DESCRIPCION

The composition of the biogas produced during AD of WWTP sludge can vary greatly, depending mainly on the characteristics of wastewater. In order to comply with the stringent inlet requirements of PEMFC, a previous biogas cleaning step is necessary including: (i) caustic scrubbing (absorption of hydrogen sulfide (H₂S) by chemical washing with a solution of sodium hydroxide (NaOH)) and a polishing stage, make up of (ii) cooling, for removal of water (H₂O) and siloxanes (Si), and (iii) adsorption in a bed of activated carbon, to eliminate H₂O, H₂S and Si. The purity requirements are determined by the reforming catalyst sensibility: [H₂S] < 0.1 ppm, relative humidity, RH < 2.5% and siloxanes, [Si] < 0.2 mg/Nm³.

The experimental fuel processor generates a hydrogen (H₂) rich stream to feed two FC. The off gas and the excess of reformate gas produced are recirculated to a burner, providing the thermal energy needed to carry out the process.

The processes that take place into the fuel processor are [4]: the catalytic reforming (REF, CH₄(g) + CO₂(g) ←→ 2H₂(g) + 2CO(g)) and the oxidation of carbon monoxide (CO) in two steps: Water Gas Shift (WGS, CO(g) + H₂O(g) ←→ CO₂(g) +
H₂(g) and CO preferential oxidation (COPROX, CO(g) + ½ O₂(g) ↔ CO₂(g)) aimed at eliminating, almost entirely the CO in the stream feeding the stack [5] because this compound is a poison for PEMFC [6]. Fig. 2 shows the flow chart of the process of energy production from biogas via PEMFC:

![Flow chart of energy production via PEMFC.](image)

The input to prototype should be 4.4-5.5 m³/h of a mixture of CH₄/CO₂ 1:1, at pressures 3.4-5.5 bars. To ensure these conditions there are a booster (Adicomp, BVG2.2-4.30LD-(WP) (EEex nL)) and a mass flow controller. The biogas booster includes an internal drying system, which would guarantee the fulfillment of quality requirements even in case of pretreatment faults. Normal composition of biogas at pretreatment output is: [CH₄] = 68-74%, [CO₂] = 24-34%, [O₂] = 0, [H₂S] = 0-45 ppm, [Si] = 0–0.1 Si/Nm³ and RH = 100%, while biogas cleaned was: [CH₄] = 68-74%, [CO₂] = 24-34%, [O₂] = 0, [H₂S] = 0-45 ppm, [Si] = 0–0.1 Si/Nm³ and RH = 6.80% Later investigations concerning the performance of reforming catalyst demonstrate that it tolerates higher water contents. It would possible to feed a biogas stream with moisture content up to 50%.

The pilot plant construction was completed at the end of July to December 2011 and has been running fueled by WWTP biogas intermittently from December 2011 to May 2012 in Murcia-Este WWTP for a total of 385 h. Previous laboratory trials allowed identifying operating conditions at: REF (T>700°C, CH₄ conversion≈75%), WGS (ratio H₂O/CO=7, T= 300-350°C, CO conversion≈98%) and COPROX (T=118-150°C, CO conversion close to 100%). If CO conversion is lower than 99.5%, it is necessary to recycle the stream to the burner; CO content should be less than 10 ppm at the PEMFC input.

Under laboratory conditions were reached [CO]<4 ppm, which means better performance than initially expected and during the field tests were recorded [CO]< 50 ppm, not enough to feed the FC. Due to several technical problems, mainly related to commercial equipment, it was not achieved the steady state operation regime and therefore the PEMFC units were not operated powered by reformate gas. PEMFC units have been operated under synthetic gas prior to processor assembly in Murcia. Test bench results show that, using pure H₂ as fuel it is possible to achieve performances of 86.67% and fed by H₂:N₂ 1:1, at input pressure of 0.65 bar, a maximum power of 800 W has been achieved, which means a rate of 26.67% of nominal power.

IV. CONCLUSIONS

Available data state that fuel processor is energetically self-sustainable by burning the off-gas. The design is highly versatile and would allow taking advantage of each reactor output. Field tests probes that T and pressures are highly critical factors; any slight change in operation conditions leads to unexpected plant shut downs.

Results show that the plant operation is feasible, although the process is energetically expensive and is in an early stage of development.

Further work is necessary to optimize the system in order to develop catalysts less sensitive and high capacity stacks that support reforming gas as feedstock.

ACKNOWLEDGMENTS

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REFERENCES

PALLADIUM-BASED ELECTROCATALYSTS FOR OXYGEN REDUCTION AND HYDROGEN OXIDATION IN INTERMEDIATE TEMPERATURE POLYMER ELECTROLYTE FUEL CELLS

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Abstract - Carbon supported Palladium electrocatalyst have been investigated for oxygen reduction and hydrogen oxidation in polymer electrolyte fuel cells operating at intermediate temperatures (110-130 °C) and low relative humidity (33%). The materials consisted of both bare and composite Pd electrocatalysts with ultra-low Pt loadings. Bare Pd/C catalyst showed low overpotential for hydrogen oxidation whereas its performance as cathode was significantly lower than a benchmark Pt3Co1 catalyst. A composite Pd electrocatalyst consisting of a surface layer of Pt (5% wt.) supported on a core Pd3Co1 alloy (95% wt.) and dispersed as nanoparticles on a carbon black support (50% wt. metal content) showed a significant increase of performance for the oxygen reduction reaction as the temperature was increased to 110 °C bridging most of the gap with respect to benchmark PtCo catalysts. The composite Pd catalyst demonstrated sufficiently stability after electrochemical cycling.

Index Terms - Pd catalysts, Oxygen reduction reaction, Polymer electrolyte membrane fuel cells, Intermediate temperature.

I. INTRODUCTION

Highly dispersed carbon supported nanosized Pt particles are presently the benchmark electrocatalyst for polymer electrolyte fuel cells (PEMFCs) [1-4]. Yet, the continuous increase of the cost of Pt has made less effective such progresses. In the transition process from Pt to cheaper non Pt-group (NPG) metals or non precious catalysts, Pd-based electrocatalysts appear as a proper compromise[5]. Pd shows a suitable electrocatalytic activity for the oxygen reduction reaction, even though lower than Pt, whereas its cost is at the present significantly lower than Pt and its reserves much wider. Pd-based electrodes may represent a consistent way to reduce the Pt content in PEMFCs and provide a performance that is not significantly lower than Pt/C or Pt-alloys. One interesting approach to reduce the Pt loading while maintaining proper activity and stability is to form a Pt monolayer on Pd or Pd-alloys [5]. Various procedures have been used for preparing Pt and Pd fuel cell catalysts. One of the main drawback is the increase of particle size passing from Pt-rich to Pd-rich catalysts. The approach pursued in this work is based on the synthesis of an inorganic salt of Pd (Pd-sulphite complex) which is then decomposed on the surface of a carbon black support in solution forming colloidal amorphous nanoparticles which are easily impregnated by a Co precursor. After a thermal treatment, PdCo nanoparticles surface-enriched in Pd are obtained. These are successively covered by a Pt layer using a colloidal solution obtained from a similar Pt-sulphite complex. Most of the recently investigated Pd-based catalysts have been studied in rotating disc configuration at room temperature or under PEMFC at the conventional temperature of 80 °C. Whereas, for automotive applications, operation at intermediate temperatures such as 110 °C-130 °C can mitigate the constraints concerning with thermal and water management simplifying the fuel cell system, reducing its volume inside the car with a strong impact on costs and reliability. In order to assess the performance of Pd-rich catalysts under conventional and automotive relevant (high temperature and low relative humidity), a comparison with a Pt3Co1/C benchmark characterised by the same crystallographic structure has been made.

II. RESULTS AND DISCUSSION

Carbon supported Palladium electrocatalyst have been prepared by the sulphite complex route and investigated for oxygen reduction and hydrogen oxidation in polymer electrolyte fuel cells operating at conventional conditions (80°C, 100% R.H.) and intermediate temperatures (110-130 °C) with low relative humidity (33%).
The materials consisted of both bare 30% wt. Pd/C and composite Pd electrocatalysts (50% wt. \([5\%\text{Pt-Pd}_3\text{Co}_1]/\text{C}\)) with ultra-low Pt loadings.

It was observed that formation of a core \(\text{Pd}_3\text{Co}_1\) alloy followed by deposition of a Pt overlayer in the composite catalysts prepared by two different reduction steps produced an enrichment of Pt in the outermost layers and a lower degree of interaction with carbon functional groups. This gave rise to an increase of the electrochemically active surface area despite a larger particle size with respect to a Pd-based catalyst prepared in a single step.

Bare Pd/C catalysts showed low overpotential for hydrogen oxidation whereas its performance as cathode was significantly lower than a benchmark \(\text{Pt}_3\text{Co}_1\) catalyst.

A composite Pd electrocatalyst consisting of a surface layer of Pt (5% wt.) supported on a core \(\text{Pd}_3\text{Co}_1\) alloy (95% wt.) and dispersed as nanoparticles on a carbon black support (50% wt. metal content) was prepared and the activity for oxygen reduction compared to the pure Pd electrocatalyst as well as to a benchmark \(\text{Pt}_3\text{Co}_1\) catalysts. The composite catalyst performed better than the bare one.

At 80 °C, the mass activity at 0.9 V RHE of the composite catalyst, normalised by the total noble metal content, was lower than the \(\text{Pt}_3\text{Co}_1\) alloy catalyst (65 vs 360 mA/mgPt+Pd). However, after normalising by the Pt content only (Pd is significantly cheaper than Pt), the mass activity at 0.9 V RHE of the composite catalyst reached more than 1.1 A/mgPt.

The electrocatalytic activity of the two-step Pd-based catalyst increased considerably by increasing the temperature from 80° to 110 °C at low relative humidity (R.H. 33%). Whereas, an opposite effect was observed for a conventional PtCo alloy catalyst with similar crystallographic structure but characterised by finer particles.

The composite Pt-PdCo catalyst thus showed a significant increase of performance as the temperature was increased to 110 °C whereas the \(\text{Pt}_3\text{Co}_1\) showed a decrease due to a prevailing effect of ionomer dry-out in the catalytic layer.

The composite catalyst appeared sufficiently stable after \(10^4\) electrochemical cycles between 0.6 and 0.9 V at 110 °C and 33% R.H.

III. CONCLUSION

Bare 30% wt. Pd/C and composite 50% wt. \([5\%\text{Pt-Pd}_3\text{Co}_1]/\text{C}\) catalysts obtained from sulphite complex preparation routes were investigated for the oxygen reduction reaction in PEMFCs. It appears that the strong temperature activation for the composite Pd-based catalyst at low current densities where catalytic effects are important compensates the negative effect of ionomer dry-out at intermediate temperatures that is instead prevailing for the PtCo catalyst. At high current densities where mass transport phenomena are relevant, catalyst morphology probably influences the performance at intermediate temperatures and low R.H. operating conditions in a manner different than at conventional operating conditions (80 °C, high R.H.). However, a systematic investigation of catalysts with different morphologies but with the same structural and surface characteristics is necessary to confirm this conjecture. The bare Pd/C catalyst shows excellent performance for the hydrogen oxidation reaction and may represent a cheaper alternative to Pt for polymer electrolyte fuel cell anodes.

ACKNOWLEDGMENT

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REFERENCES

CISTEM – CONSTRUCTION OF IMPROVED HT-PEM MEAS AND STACKS FOR LONG TERM STABLE MODULAR CHP UNITS

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Abstract – In this work, the Fuel Cells & Hydrogen Joint Undertaking (FCH JU) project CISTEM (Construction of Improved HT-PEM MEAs and Stacks for Long Term Stable Modular CHP Units) and its concept will be introduced. The improvement of the performance on one hand and of the lifetime of the cells, stacks and system on the other are important targets within this project. Next to an improved stack design and the modular CHP system design, the development and integration of a modular designed natural gas reformer is a necessary task.

CISTEM, CHP system, HT-PEMFC.

I. INTRODUCTION

The new FCH JU project CISTEM was started in June 2013. The vision of the CISTEM project is to develop a new fuel cell (FC) based CHP technology, which is suitable for fitting into large scale peak shaving systems in relation to wind turbines, natural gas and SMART grid applications. The technology should be integrated with localized power/heat production in order to utilize the heat from the FC via district heating and should deliver an electrical output of up to 100kW. Additionally the CHP system should be fuel flexible by use of natural gas or use of hydrogen and oxygen which can be provided by electrolysis. This gives the additional opportunity to store electrical energy in case of net overproduction by production of hydrogen and oxygen for use in the CHP system and gives an additional performance boost for the fuel cell.

The main idea of the project is a combined development of fuel cell technology and CHP system design. This gives the opportunity to develop an ideal new fuel cell technology for the special requirements of a CHP system in relation to efficiency, costs and lifetime. On the other hand the CHP system development can take into account the special advantages and disadvantages of the new fuel cell technology to realize an optimal system design.

The purpose of the CISTEM project is to show a proof of concept of high temperature PEM (HT-PEM) MEA technology for large combined heat and power (CHP) systems.

II. CONCEPT

CISTEM develops a new generation of HT-PEM based combined heat and power (CHP) systems. A CHP system of 100 kWel will be set up and demonstrated. This CHP system size is suitable for district heat and power supply. It will be build up modularly, with FC units of each 5 kWel output. This strategy of numbering up will achieve an optimal adaption of the CHP system size to a very wide area of applications, e.g. different building sizes or demands for peak shaving application.

Within CISTEM at least two 5 kWel modules will be implemented as hardware; the remaining 18 modules will be implemented as emulated modules in hardware in the loop (HIL) test bench. The advantages of the 5 kWel modular units are: suitable for mass production at lower production costs, higher system efficiency due to optimized operation of each unit, maintenance “on the run”, stability and reliability of the whole system. With the help of the HIL approach different climate conditions representing the European-wide load profiles can be emulated in detail. Furthermore, interfaces to smart grid application will be prepared. The CHP will be implemented for demonstration within a modified energy storage concept following the usage of hydrogen and oxygen production with electrolyzer from wind energy.

Increased electrical efficiency of the FC will be obtained by improved operational conditions with new materials and the additional use of air enriched with oxygen from the electrolyzer, which is normally wasted, on the cathode supply will also lead to better HT-PEM FC efficiencies. In addition to this a highly efficient reformer unit will be developed and implemented allowing the use of natural gas as backup energy.
source for of the CHP operation. This unit will use the most efficient steam reforming technology with respect to the modular system design of the numbering up strategy.

The development of the modular HT-PEM CHP design includes various work tasks with intense interactions. CISTEM will improve and optimize materials including membrane and bipolar plate materials to achieve operation up to 40,000 hours. The performance of the catalytic material will be revised in terms of reducing platinum loading or even using non-precious catalysts. A desirable heat management has also to be considered. Therefore, very much care has to be taken on the design of the stacks to follow the modular concept. Fully identical stacks are needed for evaluation to verify such modular design ideas. All development steps will be supported by state-of-the-art modeling. As a final step a CHP system, consisting of several stacks, reforming unit and heat supply units combined with hardware in the loop test bench, is supposed to show its operating capabilities within the end-user operation. This will verify the proof-of-concept and evaluate the capabilities.

Important part of the project is the validation of the design targets. The complete HT-PEMFC system, including the reformer, is designed for an operation temperature of 160 °C with an efficiency improvement of more than 20 % compared to currently available HT-PEM systems. Lifetime tests with defined accelerated ageing procedures on single cells and short stacks will allow the verification of the desired stack lifetimes. In all development processes the partners have agreed to a design-to-cost approach. This includes the production in series production processes. A cost assessment will indicate the cost savings by the less complicated modular system. Figure 1 shows a visual exposure of the concept of the CISTEM project.

Figure 2, showing the basic tasks for components and assembling the stacks up to complete modular CHP unit.

III. SUMMARY

The project CISTEM can be summarized in the following key points:
1) Concept and testing of large area pressurized HT-PEM FC for large scale systems;
2) Improvement of the HT-PEM FC technology for performance and lifetime;
3) Optimization of the effect of cathode air enrichment by pure oxygen for efficiency;
4) Development and integration of a modular designed natural gas reformer;
5) Improved stack design for modular concept approach;
6) Modular CHP system design for a 100 kWel CHP unit based on 5 kWel units;
7) Proof of concept for the modular CHP system design for a 100 kWel CHP unit based on 5 kWel units using a hardware in the loop test bench;
8) System modeling provides detailed specifications for the CHP system numbering up from 10 kWel up to 100 kWel;
9) General design rules for efficient operation of a modular HT-PEM based CHP system using fuel flexible conditions with respect to smart grid applications.

The consortium is extremely well balanced along the whole supply chain. Component suppliers and system designers are backed by research institutions and an end-user. High quality of the development process is of top priority to all partners. Therefore the consortium will agree at the beginning of CISTEM on specific quality and management procedures - including contingency planning measurements.

ACKNOWLEDGMENT

The authors would like to thank the European Commission for supporting this work by the FCH-JU through the project CISTEM (01.06.2013-31.05.2016, Project Number 325262).
Abstract - The development of a polymer electrolyte membrane (PEM) fuel cell utilizing a coplanar bipolar plate on which the anode reactant gas and coolant flow fields are integrated onto the same plate surface is presented. This work was carried out to demonstrate lower cost, thinner unit cells having higher function-to-part ratios. Polarization performance tests of a single cell showed a 0.31 V (63%) performance drop at 2.4 A/cm² and an 8.9 psig (30x) increase in fuel pressure drop compared to a baseline cell made up of a conventional bipolar plate, and are a result of the alternating flow fields nature of the coplanar configuration. An ohmic loss is also present as the clamping pressure of the cell was not optimized for the new seal used. Lessons learned from this initial operational cell will be applied to future development of the coplanar concept.

Index Terms - Bipolar plate, Coplanar flow field, Integrated flow field, PEM fuel cell

I. INTRODUCTION

Reducing cost is a key requirement to commercializing fuel cell vehicles, with material and space usage of fuel cell components being key drivers. Conventional bipolar plates utilize two plate halves to contain the fuel, coolant and oxidant flow fields, and necessarily require more material and space as compared to a single-layer plate design using coplanar flow fields [1, 2]. A coplanar flow field design puts both reactant gas flow field and coolant flow field on the same plate surface [1, 3-4], thereby enabling bipolar plates to be made of one piece.

In this paper we examine the polarization performance of a polymer electrolyte membrane (PEM) fuel cell utilizing a coplanar flow field bipolar plate on which the anode reactant gas flow field and coolant flow field are integrated onto a common plate surface. This work was carried out as part of the development of a coplanar concept to demonstrate lower cost, thinner unit cells having higher function-to-part ratios.

II. EXPERIMENTAL

A. Materials and Equipment

Coplanar bipolar plates were machined from carbon composite blanks. The active area region of the anode face of the bipolar plate was comprised of parallel, alternating fuel and coolant flow fields, as shown in Figure 1, while the cathode face of the bipolar plate contained a conventional parallel oxidant flow field. A thin, non-porous perforated material was used on the anode face of the bipolar plate as a barrier layer to separate fuel and coolant circuits, confining the coolant to the bipolar plate while allowing access for hydrogen gas to pass from the fuel flow field to the membrane electrode assembly (MEA).

Fig. 1. Optical cross-section of anode face of coplanar bipolar plate.

A single cell PEM fuel cell stack, having an active area of 42.7 cm², was assembled using an in-house baseline MEA, and air-actuated pneumatic hardware for cell compression.

B. Polarization and Compression Sensitivity Measurements

The single cell was conditioned for 16 h at a current density of 1.0 A/cm² before conducting polarization performance tests. The first polarization test point was done at a current density of 1.2 A/cm², corresponding to a fuel pressure of 15 psig, with subsequent points done at progressively lower current densities. This starting point was chosen as the experimental cell was only proof pressure tested to 15 psig at beginning of life.

Following this initial polarization test, performance sensitivity to cell clamping pressure was evaluated by...
varying the supply air pressure to the pneumatic hardware. Bladder pressure was gradually raised from 63 psig to 100 psig at a current density of 1.0 A/cm².

A further polarization test was carried out, beginning at 1.2 A/cm², with subsequent points at progressively higher current densities and fuel pressures in order to evaluate cell performance until cell burst.

III. RESULTS AND DISCUSSION

Polarization performance of the coplanar cell is shown in Figure 2. Performance is improved over earlier coplanar prototypes, and remains significantly below a baseline cell having conventional bipolar plates, a difference of 0.31 V, or 63 %, at 2.4 A/cm². The alternating nature of the fuel and coolant flow fields results in an increased diffusion path for anode reactant, leading to increased mass transport losses compared to the baseline. Another consequence of the flow field arrangement is an increase in fuel pressure drop (Figure 3) as the number of fuel channels for a given active area is reduced.

The cell ultimately developed a leak at a current density of 2.4 A/cm², corresponding to a fuel pressure of 27 psig.

IV. CONCLUSIONS

Polarization performance tests of a single coplanar cell showed a significant performance gap compared to an incumbent baseline. Tremendous progress was made in developing the coplanar concept from small, ex-situ test plates towards a larger, operational cell. Failure modes in prototypes showed the importance of balancing design, materials and manufacturing process. Future development of the coplanar bipolar plate fuel cell will look at improving the barrier layer and bipolar plate designs to maximize fuel cell performance and durability.

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REFERENCES

IMPEDANCE STUDIES OF POROUS ELECTROLYTE WITH MIXED ION CONDUCTIVITY


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Abstract - In this study mixed ion conductivity of a composite material based on proton conducting BaCe$_{0.85}$Y$_{0.15}$O$_{2.925}$ (BCY15) and oxide ion conducting Ce$_{0.85}$Y$_{0.15}$O$_{1.925}$ (YDC15) electrolytes has been investigated by Electrochemical Impedance Spectroscopy in relation to its application as a membrane (named central membrane CM) in an innovative design of a high temperature Dual Membrane Fuel Cell (DMFC). The key-point of the DMFC development is the design and fabrication of the porous CM, which has to combine high mixed ion (proton and oxide ion) conductivity with sufficient porosity necessary for the evacuation of the water produced in this layer. The obtained results show that a composite central membrane with 50 v % BCY15 and 50 v % YDC15 and porosity about 35-40 % obtained by addition of pore former (graphite) could be used for the fabrication of the first (Proof of the Concept) generation Dual Membrane Fuel Cell.

Index Terms - central membrane, composite electrolyte, impedance spectroscopy, mixed ion conductivity.

I. INTRODUCTION

The need for systematic studies of mixed ion (proton and oxide ion) conductivity in materials applied for solid oxide fuel cells (SOFC) operating in intermediate temperature (600-700°C) is related to the development of a new fuel cell concept named Dual Membrane Fuel Cell [1, 2]. It combines the advantages and eliminates the disadvantages of both SOFC and proton conducting fuel cells (PCFC) in respect to the water formation on the electrodes. The main idea consists in connecting the anode part of a PCFC with the cathode part of a SOFC by porous mixed ion conducting ceramic junction named central membrane (CM) where the water is part of a SOFC by porous mixed ion conducting ceramic junction named central membrane (CM) where the water is produced and evacuated. Thus the cell consists of three independent chambers for hydrogen, oxygen and water which could be separately optimized.

The key factor for the performance of the new concept is the central membrane, which has to ensure high anionic and protonic conductivities in the presence of sufficient porosity. The proper connectivity among the different phases (proton conductor, oxide ion conductor, open porosity for water evacuation), should avoid tortuous and resistive paths. Both solid phases (BCY15 and YDC15) must percolate towards their respective electrolyte, and porosity must percolate towards the periphery of the CM where water is evacuated. Thus each triple phase boundary (TPB) segment should be connected to both electrolytes.

The aim of this study is impedance characterization and optimization of the CM which has to combine high proton and oxide ion conductivity, thermochemical and mechanical stability and porosity needed for the evacuation of the water.

II. RESULTS AND DISCUSSION

For evaluation of the YDC15 and BCY15 conductivity, measurements of half cells with dense electrolyte support obtained in the absence of pore former and optimized sintering temperatures respectively 1350 and 1450°C were performed.

The application of starch and graphite as pore formers influenced the microstructure of the composite CM. The results obtained by Scanning Electron Microscopy (SEM) show that starch caused big cracks which make the samples mechanically fragile. The addition of about 2 % graphite ensures mechanically stable structures with sufficient porosity (Fig. 1).
The impedance measurements of the CM were performed in O₂ and H₂. The data obtained in oxygen ensure information about the conductivity of the YDC15 phase in the real structure, i.e. in the presence of the proton conducting phase and the pores. Measurements in hydrogen separate the conductivity of the proton conducting BCY15 phase. The Arrhenius plots of the CM with different porosity are presented in Fig. 2. Results show that the increase of the porosity leads to decrease of the conductivity. This effect is more pronounced for the proton conducting phase which, however, has higher conductivity (Fig. 3), confirmed also by measurements of dense BCY15 and YDC15 samples.

The comparison of the conductivities for the two ceramic phases in the porous composite CM with data from the literature obtained for dense materials shows that the registered conductivities for samples with about 30 % porosity are in the frames characteristic for applied electrolyte materials [3]. Thus for composite central membranes with 50 v % BCY15 and 50 v % YDC15 and porosity about 30 % obtained by graphite pore former good compromise between conductivity and porosity is obtained.

III. CONCLUSION

The impedance studies of the new functional CM layer of the innovative DMFC concept ensured the design and fabrication of appropriate membrane combining sufficient mixed ion conductivity with optimal porosity and good mechanical and thermal stability. It has been used for the construction of the first model cell with which the new concept has been successfully proved [4, 5].

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REFERENCES

STUDY OF A PHOTOSYNTHETIC MFC FOR ENERGY RECOVERY FROM INDUSTRIAL FRUIT JUICE WASTEWATER

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Abstract - Microbial Fuel Cells (MFC’s) are electrochemical devices that use microorganisms as catalyst to generate electricity from organic matter. In this system, a photosynthetic bio-cathode has been coupled. This bio-cathode consists of a pure culture of Chlorella vulgaris which provides the oxygen (electron acceptor). No external catalysts or electron shuttles have been added.

Some experiments were conducted in order to determine the best flow-mode for feeding the anode chamber. It was found that working under continuous-flow mode the system reaches quicker and steadier output power in comparison with semi continuous-flow mode. Also, a substrate-load characterization was performed. It was determined that substrate concentration up to 1000 ppm can be successfully treated in the system. In addition, two different inorganic carbon (IC) sources for feeding the bio-cathode were under study.

Index Terms: MFC, wastewater treatment, biocathode, bioelectricity.

I. INTRODUCTION

Microbial Fuel Cells (MFC’s) are electrochemical devices that use microorganisms as catalyst to generate electricity from organic matter [1]. These new technologies are to substitute for traditional activated sludge treatments, due to their interesting advantages: electricity production from a wastewater stream together with less sludge production and energy input, since aeration at the cathode chamber is no longer needed.

Bio-cathodes can be included successfully in MFC’s. In this system, a photosynthetic bio-cathode has been coupled, in which a pure culture of microalgae Chlorella vulgaris produces oxygen using light and CO₂. This bio-cathode has many advantages, since it is not necessary to pump air into the cathode and it works as a CO₂ sink.

II. SET-UP

The set-up used consisted of a two chambered (800 cm³ each) MFC, using a proton exchange membrane (PEM, by Sterion®) to separate the electrodes. Both electrodes were built of Toray carbon cloths with 10%. The active area of each electrode was 8 cm². Both electrodes were connected by an external resistance (Rₑₒ) of 120 W.

A digital multimeter (Keithley 2000 multimeter) was used to monitor continuously the cell. Dissolved oxygen of the cathodic compartment was monitored continuously with an Oxi538 WTW oxyimeter.

The initial inoculum of anodic compartment was an activated sludge from urban wastewater treatment plant, after 25 days the biofilm of microorganisms was formed on the surface of the anodic electrode [2]. These microorganisms were fed in continuous mode with a synthetic fruit processing industry effluent containing 322 mg/dm² of sugar (50 % of fructose and 50 % of glucose) and nutrients. The composition (shown in literature [2]) is very similar to the composition of wastewater from the fruit juice industry, taking into account the organic composition of the fruit juice [3]. The cathode compartment contained a culture of Chlorella vulgaris. This compartment was illuminated for approximately 12 h a day (from 8:00 h to 20:00 h) and it was fed feed with inorganic carbon and nutrients.

III. EXPERIMENTAL RESULTS

3.1 Comparison of flow mode

Two different flow modes for feeding the anode chamber were compared: semicontinuous and continuous. Operating
under the continuous-flow mode implies feeding the anode at a steady flow rate of 1.4 mL/min. Under semicontinuous-flow mode, the anodic suspension was removed, emptying and refilling the chamber every two days.

The Figure 1 shows the maximum power density at different hours of day (at 13:00 and 17:00 h along the light cycle and at 9:00 and 20:00 h along the dark cycle). A significant difference is observed at 13:00 h (15.44 mW/cm² vs. 22.67 mW/cm²). In this way, the maximum power density is similar at 13:00 h (22.67 mW/cm²) and 17:00 h (23.97 mW/cm²) under continuous mode.

**Fig. 1. Maximum power output**

Considering these results, there be certain microorganisms along the solution which produce soluble exogenous mediators that shuttle electrons from cells to electrode through diffusion [4]. Furthermore, chemical oxygen demand (COD) removal was slightly higher (78.28±7.64% vs. 70.26 ±6.68%) operating under continuous-flow mode.

In this way, the best flow mode for operating the system is the continuous one because it reaches quicker and steadier output power.

### 3.2 Substrate-load characterisation

A chemical and electrochemical characterisation under increasing/decreasing substrate loading conditions was performed, monitoring a wide range of parameters.

In Fig. 2 the output voltage during light/dark cycle for each substrate load is shown.

**Fig. 2. Output voltage for different substrate loads**

According to the results, the more substrate load, the more output voltage, except for the highest. These results point out that there is a certain substrate load which cannot be exceeded; otherwise electricity production is interrupted.

When organic load is high, other microorganisms grow, consume substrate and produce acid. In this way, pH dropped down to 5.5 as load increased, which is responsible for the low performance of electrogenic microorganisms at high substrate concentrations. Other experiments obtained the same low performance in electricity production at low pH’s [5].

### 3.3 Inorganic carbon source

This system can also be used as a CO₂ sink. Hence, two different inorganic carbon (IC) source were tested, CO₂ gas and HCO₃⁻. No difference was found in the performance of the cathode when HCO₃⁻ or CO₂ was fed; same O₂ production was obtained at both cases. However, electricity production was not interrupted due to stripping of dissolved O₂ caused by bubbles of CO₂ when HCO₃⁻ was fed. Table I shows the obtained results.

**Table I. INORGANIC CARBON CONSUMPTION AND VOLTAGE PRODUCTION**

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Bubbled CO₂</th>
<th>Sodium bicarbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Voltage (mV)</td>
<td>Voltage (mV)</td>
</tr>
<tr>
<td>10:00 (feeding IC)</td>
<td>6,2890</td>
<td>16,0178</td>
</tr>
<tr>
<td>18:00</td>
<td>16,8239</td>
<td>16,6072</td>
</tr>
</tbody>
</table>

In conclusion, sodium bicarbonate is a better inorganic carbon source in terms of electricity production.

### IV. CONCLUSIONS

Continuous-flow mode is the best way of feeding the anodic chamber in terms of both producing electricity and removing COD.

Higher substrate loads at the anodic chamber increases energy production. Too high substrate concentrations (1000 ppm for this system) inhibit the metabolism of electrogenic microorganisms because of the low pH.

As far as electricity production is concerned, sodium bicarbonate is a better inorganic carbon source.

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EXTRUSION AND OPTIMIZATION OF CARBON RESISTANT TUBULAR IT-SOFCS.
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Abstract - Extrusion is a fast and reliable way to shape moldable pastes into long tubes with constant cross section. This technique can be applied to the fabrication of the anodic layer of small tubular Solid Oxide Fuel Cells (SOFC). In this work the composition and preparation of pastes for the extrusion, the deposition via dip coating of electrolytic layer and co-sintering of the anode supported half-cell have been optimized to obtain a porous conductive anode and a dense and well adherent electrolyte. 10mol% gadolinia doped ceria ceramic powder (CGO10) was employed as ionic conductive phase in both the anodic and electrolytic layer. To avoid the carbon deposition reaction but insure the electronic conductivity, copper oxide is added to the anode composition. Considering the low melting temperature of copper oxide compared to the required temperature for full dense sintering of GDC10, the electrolyte powder is doped with various amount of transition metal oxides (TMO) as cobalt, iron, manganese and lithium, which act reducing the temperature for full densification of the electrolyte and allow the co-sintering of the half cell.

Index Terms – Carbon resistant anodes, Extrusion, Tubular IT-SOFC.

I. INTRODUCTION

Among the many challenging objectives along the way of SOFCs development, the resistance to coking is still one of the major. Considering that more than 50% of Hydrogen is produced by natural gas and naphtha steam reforming or partial oxidation, feeding directly with hydrocarbons would reduce by one step the production of fuel for the cell. Also, it would decrease the issues regarding the Hydrogen storage for mobile application, which is seen as one of the most promising field of interest for SOFCs. Unfortunately, among the many chemical reactions observed when fuelling with hydrocarbons, some of them produce carbon that deposits on the catalytically active nickel sites at the anode, blocking the conversion and leading to the failure of the cell.

Decreasing the operating temperature has also many benefits related to the less restrictive requirements for materials selection and heat management systems of the cell. Also, at intermediate temperatures (700-750°C) the carbon deposition reactions are less favorable [1] and, coupled with the employment of nickel free anodes [2], this could lead to the development of a carbon tolerant IT-SOFC.

II. EXPERIMENTAL

Tubular anodes are produced from extrusion of a ceramic plastic mass through a ram extruded connected with a MTS mechanical testing machine. The solid phase of the paste is composed by 40:60 v/v of GDC10 (Treibacher Ind.) and Cu2O (Sigma Aldrich) powders. To achieve the required plasticity and moldability for extrusion, the powders are mixed with a liquid phase composed by water, HPMC as binder and PEG (Sigma Aldrich) as lubricant using a kneading hook on a vertical shaft mixer. Once the paste is homogeneous, it is transferred into the extrusion barrel and extruded at a constant speed in a tubular shape of 5mm external diameter and 500um wall thickness. The extrudates are collected on a polyurethane sponge and dried in a highly humid environment to reduce risks of bending and breaking. Finally the tubes are cut at the desired length and further dried at 100°C overnight to remove the remaining water.

Electrolyte slurries for dip coating are produced mixing CGO10 powder differently doped with TMOs in form of nitrates. The dry powders are stirred in ethanol until its complete evaporation, grounded and ball-milled in α-Terpineol (Sigma Aldrich) with solid loading of 30wt%. The anodic tubes are coated with the obtained slurry and the half-cells are then dried at room temperature for 24h. The half-cells are then co-sintered in controlled atmosphere to avoid further oxidation of copper oxide at temperatures higher than 1100°C. Anode reductions are performed in 2vol% Hydrogen flux at 500°C for 2 hours.

Dilatometry and TG-DTA analysis are used to evaluate the sintering behavior of the individual functional layers. Porosity is evaluated by the Archimedes water uptake method.

III. RESULTS

A. Anode: Porosity and conductivity

The main requirements of a SOFC anode are its mechanical and chemical stability together with a well-developed ionic and electronic conductive network and a porosity value sufficient to allow the gaseous fuels to reach the reaction sites at the triple phase boundary. The substitution of nickel oxide with copper oxide imposes to lower the sintering temperature below 1100°C, above which the coarsening and migration of the conductive network leads to the breakage of the tube during cooling. At these temperatures the GDC10 network is far from being sintered but, due to the considerably large pressures produced during the extrusion process, the anodes posses a notable mechanical resistance compared to the other fabrication...
technique usually employed. As showed by Fig.1 the anodes are regular, homogeneous and lacking of pinholes and defects.

**Fig. 1. Sintered anode longitudinal view and section.**
The porosities of the sintered and reduced anodes are reported in Fig.2 for different sintering temperatures. The anodes possess already more than 25vol% of open porosity after sintering and the reduction of the copper oxide results in an additional 10-15vol%.

**Fig. 2. Open porosity after sintering and reduction.**
The anodes resulted to be electronically conductive when checked with a simple tester. The SEM micrograph of the anode section (Fig.3) confirms the correct distribution of the metallic and ceramic phases.

**Fig. 3. SEM micrograph of anode section.**

### B. Electrolyte: Effect of sintering aids

Due to the requirements on maximum sintering temperature imposed by the copper oxide in the anode, the co-sintering of the half-cell can be achieved only decreasing the full densification temperature for the electrolytic layer. This can be obtained by doping with TMOs [3]. Different dopants are reported in literature to be effective for CGO10. The effect of 1mol% doping of the most referenced on the sintering behaviour of the electrolyte is reported in Fig.4. Among the dopants tried, only lithium oxide allow full densification below 1050°C.

**Fig. 4. Dilatometric analysis of GDC10 1mol% doped with different TMOs.**

**Fig. 5. Section of the co-sintered half-cell.**

### IV. CONCLUSION

Optimizing the type and concentration of sintering aid in the GDC10 electrolyte, the co-sintering of an extruded ceria based anode with copper conductive phase and a thin dip-coated electrolyte resulted in a half-cell attaining the mechanical and functional requirements. The anode layer is porous and conductive and the electrolytic layer is dense and well adherent to the substrate as shown in Fig.5.

### REFERENCES

TOWARDS DISPOSABLE MICROBIAL FUEL CELLS: NATURAL RUBBER GLOVE MEMBRANES

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Abstract - Natural rubber from laboratory gloves (GNR) was compared to cation exchange membrane (CEM) in microbial fuel cells (MFC). GNR-MFCs produced an immediate working voltage (50mV) indicating the availability of pathways for proton transfer. Their performance improved and power was 5 times higher after three weeks. Bi-directional polarisation experiments during this period showed a power increase (22%) for GNR-MFCs during the backward sweep compared to the forward, which is contrary to CEM-MFCs where power dropped by 42%. After 6 months, GNR-MFCs produced 26% and 20% higher power than CEM-MFCs, when connected to 100Ohm and 1kOhm loads respectively, and reduced COD by 82% (1kOhm) and 88% (100Ohm) compared to 46% and 73% (CEM-MFCs). Under composting conditions, GNR samples degraded 100% after 268 days whilst GNR-MFC membranes were still intact and operational after a year. This innovative research could lead the way in producing inexpensive, disposable MFCs with controllable degradation.

Index Terms – Microbial fuel cell, natural rubber, proton exchange membrane, biodegradation.

I. INTRODUCTION

Microbial fuel cells (MFCs) produce power by employing bacteria to breakdown organic pollutants from undesirable waste sources making the technology attractive as a new green source of energy. However, materials are rarely compatible with the environment and are expensive, in particular the proton exchange membrane (PEM). Recently, alternative and inexpensive PEM materials have been tested including j-cloth [1] and ceramic [2]. To further increase the accessibility of the technology, waste materials could be utilised, as was recently demonstrated using prophylactic natural rubber (NR) PEMs [3]. Alternative sources of NR and their use as PEM requires further investigation because manufacturers incorporate constituents to improve protection against biological damage [4] and the treatments vary for different products. Furthermore, laboratory gloves are a considerable source of waste [5] and so the current study investigated NR laboratory gloves as PEM in MFCs.

The specific aims were: (i) to look at short-term stability, (ii) to analyse performance over batch-cycles in terms of power, anolyte chemistry and external resistance, and (iii) to compare the biodegradation of the GNR membrane with samples in a composting facility.

II. EXPERIMENTAL

MFCs with 25mL anode chambers along with mature, established pre-colonised anode electrodes were used. On Day 1 of the experiment, the already existing PEM from four working MFCs was removed. GNR (cut from the palms of new laboratory gloves [110µm dry film thickness, 5 x 6cm]) was inserted into two MFCs and off-the-shelf CEM (160 µm dry film thickness, 5 x 6cm) inserted into the other two MFCs. The MFCs were batch-fed with synthetic wastewater (tryptone [1%] and yeast-extract [0.5%]) and were tested in real-time under varying external resistances. Anolyte COD, pH and conductivity were monitored. Biodegradation of the NR within the MFC was compared to compost field trials using photography and SEM imaging.

Periodically, bi-directional polarisation experiments were performed using an automated variable resistor where 60 resistance values were applied from 1MOhm down to 3Ohm (sample rate: 5 min) before being swept back up to 1MOhm. To assess short-term stability, the maximum power point (MPP) produced during the forward sweep was compared to the MPP generated over the reverse sweep. One day before the polarisation sweeps, the MFCs were drained and fed with fresh feedstock, whilst the cathodes were hydrated immediately before each experiment.
III. RESULTS

Performance of the GNR-MFCs initially dropped (indicated by arrow in Fig. 1) but after just a few hours, a working voltage of 50mV (1kOhm) was produced. This differs from previous work using NR (prophylactic) as PEM in MFCs [4], where a working voltage was not produced until 3 weeks. SEM images of GNR indicated a lattice-type structure in cross section samples and proton transfer could have been taking place through this tortuous matrix. Power output was higher for CEM than GNR in power curves produced after 3 weeks. However, CEM displayed instability reflected by a 42% drop in the MPP produced during the reverse sweep compared to the forward sweep (Fig. 2a).

Fig. 1 Start-up of two GNR-MFCs under 1kOhm. Arrow indicates the point when the conventional membrane was replaced with GNR.

GNR-MFC on the other hand exhibited a 22% increase in MPP during the second (reverse) sweep as the material matured (Fig. 2b). Following a further 5 months of operation, CEM again produced higher power than GNR but continued to demonstrate instability, reflected by a 31% decline in performance over the reverse sweep (Fig. 2c). The GNR-MFCs were very stable, with bi-directional curves almost identical (Fig. 2d). After 6 months, MFCs were analysed under fixed loads (1000Ohm and 1kOhm) during 96hr batch cycles. CEM initially produced higher power but after 24hrs GNR improved and outperformed CEM over both periods (Fig. 3).

Fig. 2 Bi-directional power curves produced after 3 weeks: (a) CEM, (b) GNR and 5 months; (c) CEM, (d) GNR. (mean and range, n=2)

These findings demonstrate that MPP produced during forward polarisation sweeps can be a misleading parameter particularly when analysing membrane materials. Anolyte conductivity increased almost 8-fold for CEM-MFCs but less than 3-fold for GNR-MFCs. Protons have a higher conductivity contribution than other cations [6] and so the dramatic increase could be linked to pH, which dropped more steeply for CEM than GNR under all external resistances tested. During the 96hr periods, GNR-MFCs reduced COD by 82% (1kOhm) and 88% (1000Ohm) compared to 46% and 73% for the CEM-MFCs. The GNR-MFCs rely on the degradation of NR to generate pores for proton exchange but too much deterioration could result in short-circuiting. Under composting conditions, macro-sized holes were first observed in GNR samples after 88 days and by day 268 the samples had degraded 100%. The GNR-membranes in MFCs on the other hand remained intact and operational after 1 year of operation.

IV. CONCLUSION

This work demonstrates the suitability of GNR as PEM material. GNR-MFCs reduced COD more efficiently, produced comparable power and displayed a more stable performance than CEM-MFCs. This innovative research could lead the way towards the production of a new generation of inexpensive, disposable, soft MFCs with controllable degradation behaviour.

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DURABILITY STUDY OF HT-PEMFC THROUGH CURRENT DISTRIBUTION MEASUREMENTS AND THE APPLICATION OF A MODEL

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Abstract - In this work, a life study of a single 50 cm² single high temperature proton exchange membrane fuel cell HT-PEMFC has been carried out. It includes a study of the influence of the catalyst load and the deposition technique on the lifetime. The single cell was characterized along the period of time by means of impedance spectra, cyclic voltammetries (CVs) and hydrogen crossover measurements. Moreover, the durability study was also assessed through current distribution measurements. Once, the durability tests were finished, the MEA was divided into 16 pieces and the phosphorous and the platinum contents were measured and related with the current distribution results. The behavior of these single cells was analyzed by means of a model developed by our group. It was modeled each of the 16 pieces and this lets us know which parts of the single cells are more degraded.

Index Terms: High Temperature PEMFC, Lifetime, Modeling, PBI, Platinum.

I. INTRODUCTION

Fuel cells are presented as a possible alternative to the looming energy crisis. The cost and durability of a high temperature proton exchange membrane fuel cell (HTPEMFC) are one of the major obstacles to overcome for the application of these electrochemical devices in motor vehicles, portable devices, etc. Compared with other types of fuel cells, HTPEMFCs based on PBI have a significantly lower lifetime, which advises against commercialization at the present moment. A number of different reasons for the fast degradation are suggested, although the origin of performance decay seems to lie in two processes. One is catalyst agglomeration, the second is the oxidative degradation of the polymer. Corrosion of the carbon support and loss of ionic conductivity due to H₃PO₄ condensation at high temperature are other reasons mentioned in literature to explain this decay [1].

An optimum loading of Pt in the electrodes is not common to all the systems, since depends on the features of the different elements of the fuel cell and on the operating conditions. The optimization works aim at improving the design of one or several components of the fuel cell which allows reducing the ideal amount of catalyst added in the electrodes without compromising the fuel cell performance. Optimization of the catalyst layers includes the enhancement of their properties with new deposition techniques. In this work, electrospray and airbrushing methods are evaluated.

The effects of current distribution on the durability of a PBI-based PEM fuel cell can give significant information, such as a potential increased degradation in any of the inlet of the cell or the appearance of a huge temperature gradient. Current distribution measurement gives information about the current density profile generated under the operating conditions, which makes possible to detect and diagnose failures and to eventually associate them with the phenomena occurring inside the fuel cell. In addition, if modelling is employed to support and complement experimental measurements, it is expected that the reasons of deterioration can be identified [2].

II. EXPERIMENTAL PROCEDURE

Four PBI based MEAs were prepared according to the procedure described elsewhere [2]. The total Pt loading was 0.5 mg Pt cm⁻² (0.25 mg cm⁻² for both electrodes, MEAs 1) and it was reduced to 0.25 mg cm⁻², being the cathode loading 0.15 mg cm⁻² and the anode 0.10 mg cm⁻² (MEAs 2). Airbrushing was used to built-up the electrodes of one of the assemblies, whereas others were prepared by electrospray.

A life study was performed to all MEAs, which consisted of the operation of the fuel cell at 150 °C and at a constant potential of 0.60 V, while the average and local current density values were recorded. CV tests were carried out at operating temperature by purging the cathode side with 100 sccm humidified N₂. Crossover measurements were performed under the same conditions and fixing a constant potential of 500 mV until the current density was stable. Local current measurements were performed by a sensor plate formed by 100
sensors placed on the cathode. A post-mortem assessment was performed by dividing the degraded MEA in 16 pieces, analysing their Pt and P content by ICP.

III. EXPERIMENTAL RESULTS

3.1 Changes in the current density measurements

Figure 1 shows the average current density measured during the life tests performed. It can be observed, neither the global fuel cell performance nor the stability is affected by the reduction of Pt loading by 50%. Regarding the two assemblies prepared by electrospray, the assembly with low Pt loading (Electrospray 2) performs even better than the assembly with high loading (Electrospray 1). This fact suggests that lower loadings could be employed successfully, decreasing the investment cost of the HTPEMFC.

![Fig. 1. Evolution of the average current density.](image)

3.2 Results obtained in off-line electrochemical tests

From the polarization curves it can be said that the current density yield by the MEAs with lower Pt content showed, at least, the same performance as their equivalent with higher one. In Fig. 2 the evolution of charge transfer resistance from EIS analyses is shown. The reduction of Pt loading slightly increases the charge transfer resistance of the MEAs prepared by airbrush. The opposite effect was achieved with the MEAs prepared by electrospray, despite the important decrease in the available reaction area according to the ESA vs time plot. The membrane resistance was constant along the life test and the crossover current density as well, except for the Airbrush 2 in which a sudden increase was observed at 120 h.

3.3 Post-mortem analysis and Modeling

The electrodes were not homogeneous, but not relationship between the Pt and P distribution and the local current density profile can be established. In the case of the electrospray MEAs, it seems clear that the automatic method spreads the catalyst irregularly but always following the same pattern, which creates a reproducible and uneven Pt distribution that defines the local current density profile measured at 0.60 V (Fig 3). The $i_{\text{Pt}}^2$ and the porosity were higher for the MEAs prepared by electrospray. The lower the average current density, the more similar to the $i_{\text{Pt}}^2$ distribution is the current density profile as it can be observed in Figure 3.

![Fig. 2. Charge transfer resistance evolution](image)

![Fig. 3. Results at 227 h for cathode prepared by electrospray 2. a) Current density distribution at $=0.60 \text{ V}$ in the cathode, expressed as relative deviation from the average. b) profile of estimated by the model.](image)

IV. CONCLUSIONS

The reduction of Pt content from 0.5 to 0.25 mg Pt cm$^{-2}$ does not significantly affect the average current density. The ESA of the electrode is more affected by a Pt loading change when the MEA is prepared by electrospray than by airbrush.

The randomness of manual airbrushing makes the Pt distribution non-reproducible whereas the electrospray spreads the Pt with a particular pattern characterized by higher concentration in the center of the electrode. The simulation tools estimations agree with the diagnostics performed with the experimental techniques.

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MODEL-BASED PROCESS ANALYSIS OF A SOFC MICRO-CHP UNIT WITH REDUCED OPERATING TEMPERATURE

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Abstract – In the collaborative project “LOTUS - Low Temperature SOFC micro-CHP system” a 1 kWel system prototype is developed and tested. A dynamic model is established for in-depth investigation of the novel system concept, referring to transient and critical system states. For this purpose the Modelica modeling language is used in combination with the simulation tool Dymola. By means of a software state machine, the start-up procedure is analyzed and the control logic of the prototype can be developed.

Index Terms – Dynamic System Model, System Start-Up, Software State Machine, Control Logic

I. INTRODUCTION

The collaborative project LOTUS aims to develop and test a micro-CHP system prototype that is operated with grid quality natural gas. The concept is based on new SOFC technology leading to a significantly reduced operating temperature compared to the state-of-the-art systems. By lowering the thermal stress on the SOFC stack and peripheral components it is expected that a number of materials and manufacturing techniques become available, which are supposed to provide considerable cost reductions and extended durability.

For the system integration of anode-supported cells (ASC) operated at 650°C a thorough process layout and component design was developed, because a number of conversion steps, e.g. fuel processing and electrochemical oxidation, show special characteristics at decreasing operating temperatures. Moreover, the system integration of ASC requires some special precautions during start-up and shutdown procedures, which is addressed in the system design. Based on stationary calculations, a dynamic model is established to analyze transient system behavior and critical states in detail.

II. STATIONARY PROCESS MODEL

In order to meet the requirements for the LOTUS system with anode-supported cells, an appropriate system concept had to be developed, see [1]. Figure 1 shows the LOTUS system concept by means of a process flow diagram.

With the help of a fuel bypass at the reformer, controlled stack internal reforming is possible and the steam reformer is downscaled, thus ensuring fast heat-up. Thereby, reformate can be provided at the anode side of the stack in an early stage of the start-up procedure, assuring a reducing atmosphere at 300°C stack operating temperature and above, avoiding unwanted nickel oxidation. Moreover, an additional air path to the steam reformer allows for oxidative steam reforming to control the electricity to heat ratio during system operation, independently.

III. DYNAMIC SYSTEM MODEL

Literature shows that a variety of modeling approaches is used for dynamic models [2]. Besides specialized commercial software, independent programming languages (FORTRAN, C++) are used. Modeling languages, either signal oriented (SIMULINK) or object oriented (e.g. ASPEN, Modelica), provide a great degree of freedom during model development, ena-
ble modeling of different physical domains and easy interfacing of different model types.

Object oriented languages turn out to be suitable for dynamic models of fuel cell systems. In contrast to signal flow oriented modeling, a-causal models are closer to the physical problem and more intuitive, since physical potential and flow variables serve as connector signals and discrete volume formulations allow for a better representation of reactor geometries.

For the LOTUS model, the Modelica language [3] in connection with the simulation tool Dymola is used. In a first step, basic classes such as fluid and heat connectors, fluid and solid volumes and physical blocks had been developed. With these classes, basic system components like heat-exchanger, evaporator and steam reformer have been built up. For the calculation of the chemical equilibrium and SOFC stack modeling proprietary function libraries (dynamic link libraries) of the IKTS were integrated into the Modelica LOTUS library.

Based on data input from hardware development and testing, the component models were implemented and tuned to meet the actual performance. Connecting the component models and introducing fluid sources and sinks as well as heat losses and controls leads to a complete system model as shown in Figure 2.

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Based on data input from hardware development and testing, the component models were implemented and tuned to meet the actual performance. Connecting the component models and introducing fluid sources and sinks as well as heat losses and controls leads to a complete system model as shown in Figure 2.

IV. USE OF THE DYNAMIC SYSTEM MODEL

A software state-machine is implemented in Dymola to model different system states. Transition conditions and set points for each state are defined, see Figure 3. In the first stage (start-up mode A) the burner provides hot exhaust and heat is transferred to the cathode air to preheat the stack. Starting at 300°C stack temperature, the fuel input to the burner is reduced and the steam reformer is put into operation, to provide reformate at the anode side. When the stack reaches nominal temperature, an adequate current ramp is used to reach the nominal stack performance at rated fuel and air input. Other operational states of the LOTUS system, such as part-load and hot stand-by, are considered additionally. An emergency shut-down is required from each state and a controlled cool-down procedure will be developed finally.

V. CONCLUSION

A dynamic process model was coupled with a software state machine in order to investigate operational procedures of an SOFC micro-CHP system, like start-up, shut-down, load changes, etc. Modelica and the simulation environment Dymola was used for system modeling. By the end of the LOTUS project the dynamic process model will be validated and parameterized using measurement data from prototype testing and characterization.

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A SELF-STARTING POWER MANAGEMENT DEVICE FOR MICROBIAL FUEL CELLS

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Abstract - In this work, we present a system that harvests energy from a Microbial Fuel Cell (MFC), stores the harvested energy in a capacitor, and supplies an electronic load when the storage element has been charged. The system consists of an MFC as an electrical source, a generic load, and an ultra low-power front-end circuitry able to manage the energy delivered by the cell.

Index Terms – Boost converter, Energy Harvesting, Microbial Fuel Cell (MFC), Power Management System.

I. INTRODUCTION

An MFC is a particular kind of fuel cell that exploits the electrochemical reactions carried out by some species of bacteria, during their metabolic cycle, to produce electricity [1-2]. Although MFCs are a very appealing power source, especially where other renewable energy sources are unavailable (e.g. dark places, underwater, etc.), they have a big limit: they yield low levels of both voltage and current [3].

The voltage available from an MFC is typically on the order of hundreds of mV, and is therefore insufficient to directly supply an electronic load. Moreover, the current produced by an MFC is few mA or less, whereas a load such as a wireless transmitter consumes tens of mA. For these reasons, a specific front-end circuitry is required to interface an MFC with the load. This electronic circuit has to boost the voltage of the MFC, accumulate energy over long time periods, and enable the load only when an adequate amount of energy has been stored. In this work, we propose a front-end circuit for the above purpose. This circuit is self starting (to this end, only a low-voltage low-power external voltage source is needed), requires an ultra-low input current from the MFC, and ensures operation of the MFC with very limited output voltage ripple. First, the structure of the MFC used is described, then the design of the front-end circuitry is presented, and, finally, experimental results are reported and discussed.

II. MFC PROTOTYPE

The prototype used to test the device is a home-made single-chamber, membraneless MFC operating in batch mode with an open air cathode. The cell (basically, a pipe) is built in a hydraulic circuit in which the water to be depurated is kept moving by means of a low-flow pump. The internal volume of the cell is about 7 litres. The anode is made of carbon cloth (non wet proofed), wrapped around a stainless steel bar and placed inside the pipe. The cathode is made of carbon cloth (wet proofed) inserted between two stainless steel supports and placed at the upper end of the pipe. The cathode surface is 75 cm²; the distance between electrodes is equal to 3 cm. The cell is filled with raw wastewater from the local treatment plant with a Chemical Oxigen Demand (COD) of 300 mg/l. The temperature is stabilized at 23° C by means of a thermostat. The electric behavior of the MFC is shown in Fig. 1.

![MFC characteristic curve](image)

Fig. 1. MFC characteristic curve (circles) and output power (dots).

The polarization curve was obtained by using a variable resistor as an external load and measuring the output voltage with a
Keithley multimeter (Model 2000). The open-circuit voltage is 500 mV and the short-circuit current is 2.5 mA. The maximum power available from the cell is delivered at an output voltage of about 200 mV.

III. POWER MANAGEMENT CIRCUITRY

The output current of an MFC depends on the electrodes surface, and in most practical situations this current may be insufficient to directly supply a low-voltage boost converter. Some authors [4-5] suggest to use a combination of two cascade DC/DC converters in order to reach the voltage level required by the load. The solution proposed in this work consists in using a single boost converter and keeping it disabled while the MFC is charging a supercapacitor, thus avoiding any current consumption except the capacitor leakage. The block diagram of the whole system is shown in Fig. 2.

![Block diagram of the proposed system.](image)

The MFC is directly connected to the energy storage component (supercapacitor C1). When the voltage across this capacitor has reached a predetermined level, set by a voltage divider, a network of MOS transistors (SW1) is switched on and the DC/DC boost converter is connected to C1. Boost operation is enabled by an N-channel transistor (M1) that connects the converter to ground. The supply voltage applied to the gate of this transistor, which is controlled by SW1, is provided by an external voltage source, such as a solar cell or a rechargeable battery (the latter can be recharged by the DC/DC converter). When boost operation is enabled, the DC/DC converter charges the high-side capacitor (C2) by extracting the required energy from the pre-charged capacitor C1. As C2 is much smaller than C1, the voltage drop at the cell output is kept to very small values, thus ensuring that the MFC works with a very limited output voltage ripple. Once the high-side capacitor has been charged at the predetermined voltage level, a second network of MOS transistors that acts as a threshold switch (SW2) enables the load. The time required to enable the load functions has to be taken into account when choosing the size of capacitors. Boost operation remains enabled until the voltage across C1 falls below a predetermined threshold: when this level is reached, SW1 is switched off, boost operation is disabled, and the charging phase of the super-capacitor starts again. The proposed system was implemented on a printed circuit board by using the following components: the supercapacitor is a 1F Cooper Bussmann PowerStor, the boost converter is a Linear Technology LTC3108, the output capacitor is a 470 µF Nichicon low-leakage series, and MOS transistors are Si2329DS (P-channel) and Si2342DS (N-channel) by Vishay. The measured working cycles of the system are shown in Fig. 3 (load consumption: pulsed 12 mA). The waveforms were acquired with a Tektronix DPO4104 Digital Phosphor Oscilloscope.

![Measured working cycles of the system: voltage across C1(circles, right horizontal axis) and C2 (line, left horizontal axis).](image)

IV. CONCLUSION

In this work, we presented a system that can make an MFC suited to supply a high-voltage electronic load. The interface between the MFC and the load accumulates energy over long time periods in a supercapacitor and enables the load only when enough energy has been stored. The key advantage of this solution is that the only load connected to the MFC is the supercapacitor and the only current drawing element is its parasitic resistance: this allows implementing circuits, specific for low-voltage sources, where the input current can be as low as 20 µA, whereas the current consumption of the load is as high as some mA. In this way, it is possible to scale down the dimensions of the cell and/or work with wastewater where COD levels are lower than 100 mg/l. Experimental results were presented to validate the proposed approach.

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SULFONATED POLYBENZIMIDAZOLE-POLYETHERSULFONE MEMBRANES FOR HIGH TEMPERATURE PROTON EXCHANGE MEMBRANE FUEL CELLS

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Abstract - Polymer electrolyte membrane (PEM) which is the core component of fuel cells has attracted considerable attention for the limit of usable materials. In this paper, a series of phosphoric acid (PA)-doped blends of SPBI and PES (PA/SPBI-PES) membranes for high temperature proton exchange membrane fuel cells (HT-PEMFCs) were prepared by a microwave synthesis method and the result showed that at 180°C and anhydrous conditions, the membrane PA/SPBI-PES with 7 wt.% of PES has showed high proton conductivities (45 mS/cm).

Index Terms - Proton exchange membrane, fuel cell, polybenzimidazole, high temperature

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have operated at no higher than 80 °C because the perfluorinated sulfonic acid membranes are highly dependent on water-based proton conductivity. Besides, the high production costs and large fuel transmission of these membranes as well as CO catalysts poisoning and water-heat management may reduce the effectiveness of PEMFCs. Elevated temperatures (> 100 °C) and anhydrous operations not only can overcome these shortcomings but also can increase the electrode kinetics and efficiency of heat recovery [1, 2]. Therefore, more and more researchers have turned to developing novel PEMs to improve the performance of PEMFCs upon 100 °C and low humidities. One of the most prominent PEMs is the phosphoric acid (PA) doped polybenzimidazole and its derivatives membranes, in which PA acts as the proton conducting carrier and no water is needed for the conduction of protons in the membranes [3, 4].

In our previous study, we found that H₃PO₄ or H₂SO₄ doped in OPBI membranes were easily to run off resulted in the nonstable proton conductivities at high temperature [5], and this problem can be improved by adding some inorganic oxides or organic high-polymers into the membranes [6]. Some studies have confirmed that sulfonated polybenzimidazole (SPBI) has better performance in PEMFCs than PBI [7, 8], but the synthesis of SPBI is also very slow by the traditional solution polycondensation. So in this study, we prepared SPBI in less than 2.5 hours by a microwave synthesis method with simple operation, and we also try to maintain the high proton conductivity and mechanical performance with the incorporation of sulfonated polybenzimidazole (SPBI) and polyethersulfone (PES).

2. Synthesis of SPBI

SPBI was synthesized by a solution polycondensation method under microwave irradiation, according to literature method with some changes [5], and the synthetic scheme is shown in Fig.1. Firstly, PPA and P₂O₅ were added into a 100-mL four-necked round bottom flask under microwave irradiation and mechanical stirring at 120 °C in nitrogen atmosphere. Secondly, after P₂O₅ dissolved in PPA and the system cooled down to room temperature, DAB and SIPA-Na were added into the flask, and the mixture was heated at 40 °C for 10 min, then at 90 °C for the same time and at 120 °C for 30 min for thorough mixing. Thirdly, the mixture was heated to 170 °C for 30 min and then at 200 °C for 60 min to react thoroughly. Finally, the product was isolated by pouring the solution into ice water, and then neutralized by the saturated solution of NaHCO₃. The SPBI product was filtered and washed several times until the pH is about 7 and dried in a vacuum oven at 80 °C for 48 h.

Fig. 1. Synthetic scheme of direct polymerization of SPBI from SIPA-Na and DAB
3. PA/SPBI-PES membrane preparation

The SPBI-PES membrane was prepared from casting of 2 wt.% SPBI and 0.5 wt.% PES’s solution in DMSO in an ultra flat petri dish and the solvent was slowly evaporate at 80 °C. Then the resulting membrane (see Fig.2) was dried under vacuum at 120 °C for 48 hours to remove the excess solvent. Acid doping of the membranes was conducted by immersing the membranes in 85 wt. % H₃PO₄ solutions at room temperature. The acid doping levels (ADLs) of a membrane is defined as the molar number of H₃PO₄ per mole of the repetitive chain unit of SPBI molecules and was calculated from mass changes of the membrane sample before and after doping [5].

4. Proton Conductivity of PA/SPBI-PES membrane

The through-plane proton conductivities of the PA/SPBI-PES membranes up to 180°C at dry conditions were measured according to the method mentioned by reference [6] and the results are shown in Fig.3. For comparison purpose, the data of Nafion 112 membrane are also listed in this figure. Though Nafion 112 has higher proton conductivity below 100 °C, PA/SPBI-PES membranes show higher performance at elevated temperature when the ADL is 9.63 mol of phosphoric acid for SPBI per repeat unit.

5. Conclusions

A series of phosphoric acid (PA)-doped blends of SPBI and PES (PA/SPBI-PES) membranes for high temperature proton exchange membrane fuel cells (HT-PEMFCs) were prepared for the time less than 2.5 h. At 180°C and anhydrous conditions, the membrane PA/SPBI-PES with 7 wt. % of PES has showed high proton conductivities (45mS/cm).

ACKNOWLEDGMENT

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NOVEL GLASS-CERAMIC COMPOSITIONS FOR APPLICATION AS SEALANTS FOR SOLID OXIDE FUEL CELLS AND SOLID OXIDE ELECTROLYSIS CELLS


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Abstract - The development of sealants for solid oxide fuel cells (SOFCs) and Solid Oxide Electrolysis Cells (SOECs) is a significant challenge as they must meet very restrictive requirements. They must withstand the severe environment of the SOFC and SOEC devices (high oxygen partial pressures and reducing gas environments) and be thermo-chemically and thermo-mechanically compatible with the materials to which they are in contact with (at 750-800°C). This study focuses on the preparation and characterization of two barium-free glass compositions with self-healing behavior based on the Ca-Al-Na-Si-O system. The glasses were characterized by heating stage microscopy, differential thermal analysis, dilatometer, X-ray diffraction, and Vickers micro hardness. Both new glass-ceramic sealant compositions showed excellent compatibility with Crofer22APU coated with Mn$_{1.5}$Co$_{1.5}$O$_4$ and anode supported electrolyte (YSZ) cells, as revealed by SEM and EDS measurements. Sealants were also tested in short stack configuration.

Keywords - glass-ceramic, Mn$_{1.5}$Co$_{1.5}$O$_4$, solid oxide cells.

I. INTRODUCTION

Sealing for solid oxide fuel cells (SOFCs) and Solid oxide electrolysis cells (SOECs) is still a major challenge to advancing these technologies. The development of sealants for solid oxide cells present a significant challenge since they must meet very restrictive requirements; they must withstand the severe environment of the stack (i.e., be resistant to oxidative and reducing environments, high oxygen partial pressures) and be thermo-chemically and thermo-mechanically compatible with the materials to which are in contact [1]. For a successful long-term stable operation the joints between the ceramic electrolyte and the metallic interconnect is a critical issue. Five main approaches have been pursued for sealing SOCs: brazing, compressive seals, glass, glass–ceramic and glass–composite seals. Glass–ceramics, which are prepared by the controlled crystallization of glasses, are considered advantageous as sealing materials because, by carefully choosing the glass composition, glasses and glass–ceramics meet, in principle, most of the requirements of an ideal sealant. Moreover the presence of residual glassy phase in the sealant is beneficial, since cracks eventually formed due to thermal cycling (during stack operation) can be healed by viscous flow.

The application of a protective coating on the interconnect surface has been proven as a viable and effective method to inhibit Cr volatilization and cathode poisoning in SOFC operating condition (i.e. short stacks). Mn$_{1.5}$Co$_{1.5}$O$_4$ spinel coating is one of the most promising ones due to its high electrical conductivity and good CTE match with the stainless steel substrate.

This study focuses on the preparation and characterization of two barium-free glass compositions with self-healing behavior based on the Ca-Al-Na-Si-O system and on the interaction between the sealants and both the Mn$_{1.5}$Co$_{1.5}$O$_4$ coated Crofer22APU and YSZ electrolyte.

II. EXPERIMENTAL

The heat resistant metal alloy used for this study was Crofer22APU (Cr 20-24, C 0.03, Mn 0.30-0.80, Si 0.50, Al 0.50 max, Fe balance, wt %) manufactured by ThyssenKrupp, Germany. The anode-supported-cell (ASC) (electrolyte: 8 mol% yttria stabilized cubic zirconia, 8YSZ; anode support + anode functional: NiO-YSZ; cathode: Lanthanum Strontium Manganite, LSM-YSZ) were purchased from H.C. Starck GmbH, Germany. Mn$_{1.5}$Co$_{1.5}$O$_4$ thin coatings were prepared on Crofer22APU by thermal co-evaporation technique; experimental details are reported elsewhere [2]. The sealants, labelled as KMBY and SACNKMg, were produced as glasses by melting the appropriate raw materials in different proportions at 1500°C for 1 hour in a platinum crucible; the melts were cast on a metal plate and the transparent glasses were ground for differential thermal analysis (DTA) (Perkin-Elmer, DSC7).
Elmer DTA7) and hot stage microscopy (HSM) experiments (Leitz GmbHAI). Sealants were composed of SiO2, Al2O3, CaO, Na2O and K2O, MgO, B2O3, Y2O3 additives that were mixed in different proportions.

Joined Mn1.5Co1.5O4 coated Crofer22APU/sealant/YSZ structures were processed by thermal treatment from room temperature to 850 °C at a heating rate of 5 °C/min and a dwell time of 30 minutes at 850 °C. The cooling rate was 5 °C/min. Before and after the tests in a SOFC short stack configuration at 800°C, microstructures of Mn1.5Co1.5O4 coated Crofer22APU/sealant/YSZ samples were examined by SEM (FEI Inspect, Philips 525) EDS (SW9100 EDAX) and FESEM (Model ZEISS Supra 40); analyses were performed in order to detect element diffusion into and away from the Mn1.5Co1.5O4 coating into sealant and Crofer22APU.

III. RESULTS AND DISCUSSION
Sintering vs crystallization behavior of both sealants was carried out by heating stage microscopy and DTA coupled experiments. Fig. 1 shows the sintering behavior recorded from RT to 1080°C. For both glass compositions, the pellet densification occurred between Tg (transition temperature) and 850°C. A good sintering capability was obtained for both glass-ceramic compositions.

Figure 1. HSM experiments and sintering behavior for SACNKMg and KMBY

Figure 2 shows SACNKMg pellet images at characteristic viscosity points deduced from HSM experiments with HSM during non-isothermal heat treatment from RT to the flowing of the glass.

Figure 3 shows a SEM cross section of KMBY glass-ceramic /Mn1.5Co1.5O4 coated Crofer22APU after the joining process at 850°C, 30 min. The interface between the KMBY glass-ceramic sealant and the Mn1.5Co1.5O4 spinel coating on Crofer22APU (figure 3) was found to be continuous and crack free, due to a good thermal expansion coefficient match between the glass ceramic sealant (11.5×10−6 °C−1) and the Mn1.5Co1.5O4 spinel (10.8×10−6 °C−1). EDS mapping (not reported here) revealed no diffusion of Mn and Co from the Mn1.5Co1.5O4 into the KMBY sealant as well as no Fe and Cr transport from the steel into the glass ceramic sealant.

IV. CONCLUSION
New sealant compositions with good sinterability and self-healing properties for Solid Oxide Cells were designed and characterized in this study; this work demonstrated a good chemical and thermo- mechanical compatibility between the sealants and the Mn1.5Co1.5O4 coated Crofer22APU, thus making these new compositions promising candidate as sealants for solid oxide cells stacks.

REFERENCES
PEM FUEL CELL SYSTEM EXPERIMENTAL PERFORMANCE ANALYSIS WITH EVALUATION OF UNREACTED HYDROGEN, CROSSTRAVEL AND AGEING

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Abstract - A procedure for the evaluation, after laboratory tests, of the unreacted H₂ in a Proton Exchange Membrane (PEM) Fuel Cell (FC) is developed. The unreacted H₂ has been elaborated, a numerical analysis on the impact on efficiency has been carried out and the crossover phenomenon has been estimated. The investigation is based on the fuel utilization factor obtained with an in-house developed programming logic of the stack purging. This improved methodology and the resulting H₂ unreacted fraction are used to assess the PEMFC degradation and the ageing effects.

Index Terms - Ageing, crossover, H₂ utilization factor, PEMFC

I. INTRODUCTION

Lifetime and degradation of PEMFCs are still limits of this technology [1-3]. Many studies investigated modes of degradation [3,4]. One of the main causes of the membrane/electrode assembly degradation is the H₂ crossover phenomenon, i.e. a diffusion of H₂ from anode to cathode side, through membrane. It involves a loss of H₂, which does not participate in the electrochemical reactions, causing performance loss over long periods. In this paper an analysis on the PEMFC performance loss at low loads is carried out. The H₂ crossover effect and system ageing are investigated.

II. THE TESTED FUEL CELL SYSTEM

An experimental test bench described in a previous work [2], has been used. This integrated system is based on a micro-CHP FC system for stationary application. The FC generator is able to provide 4.5 kW of electric power and 4.8 kW thermal output, at low temperatures (65°C) at full load. The heart of the system is a H₂ fuelled PEMFC stack, consisting of 80 cells, electrically connected in series, with an active area of 275 cm² each.

III. THE FUEL UTILIZATION FACTOR ANALYSIS

In a previous work [1] a purge process optimized strategy was introduced (by managing the outlet control valve (OCV) opening), to improve FC efficiency, by reducing the purge time (Tₚₑ) at part load, but the resulting fuel utilization factor, Uᵢ, was optimal only for the high-medium load (4.5-2.5 kW). Instead, at lower load, even if a substantial improvement was obtained, Uᵢ was still not remarkable [1]. Further improvements in Uᵢ are difficult to achieve by further modifying the purge logic at part load conditions (3.5-1.5 kW and below). Moreover, the max Uᵢ is far from the ideal value of 100%. In order to understand the causes of reduced H₂ utilization at low loads an analysis has been carried out, considering the FC as a black box. An experimental campaign was conducted at various FC power output level (Pₑ). For each set of Pₑ values the flooding time (Tₚₕ) was varied up to the optimized purge programming logic value found in [1]. The results of the campaign show that, at medium loads Uᵢ increases with Tₚₕ and it assume the max value at the optimal flooding time. Instead, at low loads, the max Uᵢ is reached for a value of Tₚₕ lower than the optimal one. To investigate the causes of Uᵢ behavior at low loads, the H₂ unreacted, mₙᵢₑ, has been analyzed.

IV. UNREACTED H₂ EVALUATION

Different paths can lead to H₂ lost; thus, the unreacted H₂ can be decomposed as: mₙᵢₑ = mₚₑₚₜ + mₐ, where: mₚₑₚₜ is the unreacted H₂ mass flow, evacuated during the opening of the dead-end valve, and mₐ (hereinafter referred to “other”) is the quantity of H₂ not-reacted for other causes, such as leakage through membrane, seals, etc. These phenomena are both in the Tₚₕ and Tₚₑₚₜ time. Uᵢ can be rewritten as: Uᵢ = (mₚₑₚₜ + mₐ)/mᵢₑ = 1 - Xₚₑₚₜ - Xₐ where the X terms are the fractions of inlet H₂ mass flow rate. To determine Xₚₑₚₜ and Xₐ from the experimental data, an algorithm has been developed. The H₂ mass flow rate introduced to the anode side, (Fig. 1, blue line), and the DC current generated in the stack are acquired. By analyzing the mass flow rate plot, the OCV opening and closing times are identified, namely the Tₚₑₚₜ and the Tₚₑ. Then, the number of purges for each fixed Pₑ and Tₚₑ are calculated and the instantaneous amount of reacted H₂ is evaluated through the

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Nernst equation. Hence, the values of the mass flow rate reacted, \( m_a \) (Fig. 1, green line) and the \( \text{H}_2 \) introduced, \( m_{\text{H}_2} \) (blue line) is calculated averaging the instantaneous values over the purge and the flooding time-interval previously determined, while \( m_{\text{H}_2,\text{fl}} \) (orange line) is calculated as difference between the \( \text{H}_2 \) introduced into the FC and the \( \text{H}_2 \) that actively makes up in the electrochemical reactions. The \( m_a \) value coincides with the amount of unreacted \( \text{H}_2 \) due to "other" causes, since during flooding the purged \( \text{H}_2 \) through the OCV is zero: \( m_a(T_f)=m_{\text{H}_2}(T_0) \). The unreacted \( \text{H}_2 \) during \( T_{pu} \) due to "other", \( m_{\text{H}_2,\text{OCV}}=m_a(T_{OCV}) \), is calculated as the average of mass flow in the purge under examination and in the previous one (purple line). Finally, the \( \text{H}_2 \) mass values are calculated by multiplying the flow rate values by the corresponding time window extents.

**Fig. 1.** The \( \text{H}_2 \) mass flow rate components at constant \( P_{FC} \) & \( T_p \).

V. ANALYSIS OF EFFICIENCY USING \( X_{DE} \) AND \( X_{A} \)

Using the developed \( U_j \) algorithm, \( X_{DE} \) and \( X_A \) have been determined and analyzed. The quantity of \( \text{H}_2 \) expelled through the OCV vs \( T_p \) for different \( P_{FC} \) values (Fig. 2a) reaches the min. value at the optimal \( T_p \). Instead, the trend of \( X_A \) vs \( T_p \) (Fig. 2b) is not monotonic. The unreacted \( \text{H}_2 \) due to other causes is particularly significant, especially at low loads. Based on literature survey, the \( \text{H}_2 \) crossover phenomenon can be seen as main cause. The rate of \( \text{H}_2 \) crossover can be calculated as \([4]\):

\[
J_{\text{H}_2}=(\psi_{\text{H}_2}/I)P_{\text{H}_2,a}
\]

where: \( \psi_{\text{H}_2} \) is permeability, \( l \) membrane thickness and \( P_{\text{H}_2,a} \) the anodic side \( \text{H}_2 \) partial pressure. It can be possible to associate \( X_A \) to this phenomenon. Thus, the apparent loss of FC performance at low load is due to \( P_{\text{H}_2,a} \) fluctuations.

**Fig. 2.** Unreacted \( \text{H}_2 \) a) due to the purge, \( X_{DE} \) b) due to the \( \text{H}_2 \) crossover, \( X_A \).

VI. THE PEMFC AGEING ANALYSIS

The developed methodology is here applied to investigate the PEMFC degradation and the effect of ageing. The FC ageing analysis is carried out by considering about 50 hours of discontinuous operation of the system. The polarization curves at \( t=0 \) after 50 h show differences at medium/low loads. To identify components affecting power output, efficiency and performance loss of the system, the PEMFC components have been taken into account: a significant drop in stack efficiency is obtained comparing the FC performance before and after 50 h, while inverter and auxiliaries losses do not significantly affect the system energy balance, being less than 2%. Using the developed \( U_j \) calculation procedure, the \( \text{H}_2 \) flow rate introduced at the anode side (reacted and unreacted) and corresponding mass have been calculated for different FC power values. \( T_p=20s \) and \( T_{pu}=2.5s \) have been assumed. A large contribution to ageing is given by \( U_j \) with a high drop at low/medium loads. The unreacted \( \text{H}_2 \) due to purging, \( X_{DE} \), and crossover, \( X_A \), have been analyzed. An effect on unreacted \( \text{H}_2 \) due to purging (Fig. 3a) occurs, but it is limited. Instead other effects (Fig. 3b), even after only 50 h of discontinuous operation, cause evident degradation particularly at low loads. Hence, the main cause of ageing is to be attributed to \( \text{H}_2 \) crossover phenomenon (Fig. 3b).

**Fig. 3.** Unreacted \( \text{H}_2 \) due to purge a) & to crossover b).

VII. CONCLUSION

An analysis on the part load performance of a PEMFC has been carried out. A procedure for the evaluation of the unreacted \( \text{H}_2 \) fraction has been developed. Using this algorithm and an optimized purge programming logic, the \( \text{H}_2 \) crossover phenomenon has been identified for different FC power levels adjusting the flooding time. This methodology is applied to assess the PEM degradation and the effect of ageing. The experimental results show the link existing between crossover, performance loss and ageing, especially at low power values.

REFERENCES


METHANOL REFORMER DEVELOPMENT AND TESTING FOR INTEGRATION WITH A HIGH TEMPERATURE PEM FUEL CELL

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Abstract – This paper describes the development work of a methanol steam reformer test bench and the reformer design work. The newly developed reforming catalyst will operate at 180 °C, which enables the use of the waste heat from a high temperature PEM fuel cell for the reformer process. The structure and functionalities of the modular test bench are described. The reformer design work is presented, including the limitations brought by the heat transfer and low operation temperature. Based on this work the steps needed to produce a fuel cell – reformer integrated prototype are identified and presented.

Index Terms – High temperature PEM fuel cell, methanol steam reformer, reformer design, test bench development.

I. INTRODUCTION
High temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) have advantages compared to conventional PEM fuel cells. Due to the higher operation temperature, the kinetics are faster and the tolerance to CO is up to several percent, which enables operation with reformate fuels without CO removal. Methanol (MeOH) would be an attractive fuel for FC system since as a liquid fuel, it is easy to store and handle. The maximum operating temperature for HT-PEMFC is approximately 180 °C, limited by the accelerated degradation of the polymer membrane. At the same time, the conventional Cu-based MeOH steam reforming catalysts are commonly operated at temperatures around 250 °C for full conversion [1].

A first version of a new type of catalyst operating at a notably lower temperature has been developed for this study. It operates efficiently in lower methanol steam reforming catalyst temperatures, attaining as low as 180 °C, which corresponds to the HT-PEMFC operating temperature. Therefore thermal integration of these two devices is possible. The fuel cell produces heat in the cathode reaction and the reforming reaction is endothermic. By integrating the reformer and the HT-PEMFC, the system efficiency can be increased. Consequently no additional catalytic burner is required since the fuel cell produces the required heat for the reformer.

In this study the development work and testing of the methanol steam reformer to be integrated with a HT-PEMFC is presented. The test bench developed in this study enables both testing the reformer by itself, and integrated with the HT-PEMFC. The first stage reformer design is a packed bed reactor which has been optimized in terms of heat exchange with the fuel cell.

II. DESIGN AND EXPERIMENTAL WORK
A. Test bench development
The test bench contains hardware and software instrumentation as well as control and measurement system. The MeOH reformer test bench has been designed and built in order to test a MeOH reformer that will be combined with a 350 We HT-PEMFC stack. The test bench also contains the control and monitoring of the fuel cell stack enabling the testing of both devices simultaneously.
The MeOH reformer test bench has been built with commercial and in-house made components in a way that it is flexible and easily modified according to specific needs. The test bench developed in this study contains the fuel feeding system, the reformer, thermal fluid circulation, temperature and pressure monitoring, product gas analysis and optional fuel cell controls and measurements for reformer operation coupled to a HT-PEMFC. The control and measurement system is built using National Instrument’s Compact FieldPoint hardware and Labview based program. The main part of the test bench is the reformer subsystem, Figure 1.

B. Reformer development

In this study the aim is to heat the MeOH steam reformer with the product heat from the fuel cell stack. The reformer development is based on the new Cu-based catalyst which operates at 180 °C, opposed to the conventional Cu-based MeOH steam reformer catalysts operating around 250 °C. The low temperature and limited available heat create challenges to the heat transfer with conventional reformer designs, such as tubular geometry [1,2]. Due to similar temperatures of the stack and the reformer, the heat gradient is small and heat transfer thus limited. The heating effect of the fuel cell stack on the thermal fluid is approximately 5 °C. In the reformer this heat is consumed by the reactions. The material of the MeOH steam reformer is SS316L which has good heat conductance.

To enhance the heat transfer, the heat transfer distance must be minimized and the contact surface area maximized in the reformer geometry. Due to these conditions, a microchannel reactor was considered as a feasible option. At the moment the needed amount of the novel catalyst working at 180 °C is approximately 5 times higher than in MeOH reformers with conventional catalyst operating at higher temperatures. To minimize the reformer volume and weight, the microchannel geometry was replaced with cross flow plate heat exchanger type geometry. The reformer is built of stainless steel plates with a constant 1 mm gap between adjacent plates. Every other gap is filled with catalyst particles, size of app. 100 µm, and every other gap is for thermal fluid circulation.

There is a possibility to increase heat with a catalytic burner using the fuel cell stack exhaust hydrogen, in case the reforming rates are not sufficient.

III. CONCLUSION AND FUTURE WORK

In this study it has been noted that the reformer’s physical size is not compact enough for a practical device. The reformer development work will continue from the results obtained with the current design. The catalyst development is a continuous process and the reformer development has to follow it. In the future the reformer weight and volume will be decreased and the integration with the fuel cell stack will be improved. In the next stage of the study a cell-type modular reformer, assembled in between cells in the fuel cell stack, will be developed. The final objective of the development work is to produce a prototype for a reformer-fuel cell integrated system.

ACKNOWLEDGMENT

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INNOVATIVE FLUORINATED POLYURETHANE BASED GAS DIFFUSION MEDIA FOR PEM FUEL CELLS

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Abstract – Polytetrafluoroethilene (PTFE) is a widely used compound in the PEM-FC field, where it is usually used to make gas diffusion media (GDM) hydrophobic in order to improve electrochemical performance. Due to the polymer properties, it is necessary to work with high PTFE concentration as well as to achieve high temperature in heating processes. In order to overcome these problems, a new polymer (Fluorolink P56, an anionic, segmented polyfluorourethane with high molecular weight) has been investigated as alternative to PTFE for both making Gas Diffusion Layer (GDL) hydrophobic and producing Micro-Porous layer (MPL). Samples were tested in a single cell in order to evaluate electrochemical properties. During test, temperature was set at 60 °C, while relative humidity (RH) was held constant at 80% on anode side and 100% on cathode side. Micro-porous layer properties were estimated by using Electrochemical Impedance Spectroscopy (EIS) of the running cell.

Index Terms - PEM-FC, perfluoropolyethers, Electrochemical Impedance Spectroscopy, micro-porous layer.

I. INTRODUCTION

Among the sustainable energy systems, fuel cells assume a crucial role considering their peculiar flexibility, modularity and “zero-emission” output. In particular, Polymer Electrolyte Membrane Fuel Cells (PEM-FCs) are considered one of the most promising devices due to the low operating temperature and fast start-up [1]. Water management is a well-known issue regarding PEM-FCs. Substantial performances improvement may be induced by preventing flooding both on anode and cathode side [2]. This result is achieved mainly by introducing both a macroporous gas diffusion layer (GDL) and a microporous layer (MPL), forming the so-called Gas Diffusion Medium (GDM), and by making them hydrophobic using PTFE [3]. The aim of this work was to evaluate a new diffusion medium completely based on Fluorolink® P56 (Solvay Solexis, Italy), an anionic, segmented polyfluorourethane with high molecular weight.

II. EXPERIMENTAL

A. Preparation of Gas Diffusion Media

An untreated carbon-cloth GDL (SCCG 5N, Seal Group) portion was dipped for 10 minutes in a Fluorolink P56/water emulsion (1%w), previously homogenized my magnetic stirring (10 minutes at 500 rpm); then it was drawn and heat-treated at 120 °C for 30 minutes to remove water and sinter the polymer.

In the procedure applied to produce GDM, the weighted quantity of carbon black (CB, Vulcan XC-72 R), wetting medium (IPA, isopropyl alcohol) and Fluorolink P56 were strongly mixed at 8000 rpm for 10 minutes by using Ultra Turrax (IKA, T25 homogenizer). The ink prepared was blade coated on the Fluorolink P56-treated GDLs, leaving a layer of the thickness needed (40 μm).

The speed of the lab-scale coater (K Control Coater) was set at 153.8 mm/s, corresponding to a shear rate of about 350 s⁻¹. The samples were treated at 120 °C in order to remove the solvent and to bind the polymer.

GDM 5 and 8 share the same CB/IPA ratio (7.72 w/w) and differ in terms of Fluorolink P56 content (12% and 6% respectively). A previously produced [4] sample containing PTFE (STD PTFE) is used as term of comparison for new samples; the latter is prepared with a different procedure, as described in elsewhere [5].

B. Physical characterization

Rheological properties of slurry prepared were evaluated by using a lab-scale rheometer (Reologica Instruments AB, Stresstech 500). Dynamic viscosity was measured varying the value of the shear rate applied in the range 10⁻³ s⁻¹ - 10³ s⁻¹.
Taking account the importance of hydrophobicity [3], static contact angle (CA) analyses were performed on each sample by using a OCA 20 Dataphysics Instrument in order to measure water repellence.

Surface properties of the samples were observed with a Stereo Zoom Microscope (Olympus SZ40).

C. Electrochemical characterization

In order to evaluate electrochemical properties, all samples were tested in a lab-scale single cell assembly where a commercially catalyst coated membrane (CCM) was used. Tests were performed using constant flow rates: 0.2 Nl/min for anodic hydrogen and 1 Nl/min for cathodic air. Polarization curves were obtained in galvanostatic conditions, from OCV to high current density (1.14 A/cm²), with steps of 0.088 A/cm². Electrochemical Impedance Spectroscopy was employed to assess ohmic resistances and the different nature of voltage losses by using an equivalent circuit model [6]. For further details about the electric test refer to [4].

III. RESULTS AND DISCUSSION

A. Physical characterization

CA values obtained for the samples before cell testing (BCT) and after cell testing (ACT -A and ACT -C for anode side and cathode side respectively) are reported in Table I.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BCT</th>
<th>ACT -A</th>
<th>ACT -C</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD PTFE</td>
<td>145.18 ± 4.08</td>
<td>145.67 ± 1.83</td>
<td>146.47 ± 2.30</td>
</tr>
<tr>
<td>GDM 5</td>
<td>148.11 ± 3.91</td>
<td>150.35 ± 2.31</td>
<td>146.45 ± 5.27</td>
</tr>
<tr>
<td>GDM 8</td>
<td>150.80 ± 1.80</td>
<td>147.14 ± 5.31</td>
<td>148.87 ± 2.78</td>
</tr>
</tbody>
</table>

All samples show nearly a super-hydrophobic behavior. The change in polymer doesn’t affect hydrophobicity both before and after cell testing.

Rheological properties of the inks used are reported in Fig. 1.

B. Electrochemical characterization

Results of electrochemical tests are reported in FIG. 2; the polarization curves obtained with Fluorolink P56 are similar to the one of the PTFE sample.

IV. CONCLUSION

Results obtained lead to the following conclusions:
- Fluorolink P56 doesn’t affect GDM hydrophobicity;
- inks display still shear thinning and are then suitable for blade coating deposition;
- performance are comparable with PTFE;
- temperature during MPL heat-treatment decreases from 350 °C (PTFE) to 120 °C (Fluorolink P56).

REFERENCES


Fig. 1. Flow curves of inks used for deposition

Switching from PTFE to Fluorolink P56 the ink keeps the shear-thinning behavior and only a small increase in viscosity values can be observed. Therefore, blade coating remains a good deposition technique even for Fluorolink P56 slurries.

Fig. 2. Polarization curves at 60 °C and high RH condition (80-100)

Power density and polarization curve tendencies are validated by EIS analysis; for the sake of brevity, EIS analysis is not reported in this paper.

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KINETIC MONTE CARLO MODELLING OF ION DIFFUSION. EXAMPLE: CERIA

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Abstract – Development of theoretical tools allowing us to study diffusion in solids at different scales is important for rational materials design. One of the effective approaches is a combination of Kinetic Monte Carlo technique with first principle electronic structure calculations. The KMClib program developed by us is a robust and flexible tool for studying diffusion, in particular, in ion-conducting materials. The code has unique features such as on-the-fly custom rate calculations, simulation of electrical bias and possibilities for on-the-fly analysis. It can be used in conjunction with ab initio calculations or just providing it with rates estimated from experiment or obtained in any other way. As an example of the code performance we present a simulation of oxygen diffusion in ceria.

Index Terms – Ceria, Diffusion, KMS, KMSLibs

I. INTRODUCTION

Understanding of microscopic details of oxide ion diffusion in different structures is important for tuning the performance of solid oxide fuel cells. Modern theoretical methods enable us to model materials at different time/size scales. Detailed knowledge of the elementary atomistic diffusion processes, e.g. from first principles calculations, can be used within the kinetic Monte Carlo (KMC) method [ref. original KMC] to run simulations over times and system sizes approaching the experimental reality. Measurable quantities computed from these simulations can easily be compared with experimental values and be used as a guidance for further experimental investigations in the search for improved materials.

Due to the simplicity of the KMC algorithm together with the common need for custom modifications to the method for the investigation of particular systems there are only a handful of KMC programs publicly available. Most of these programs are furthermore specifically geared at studying reactions and diffusion at surfaces and are thus not particularly well suited to study diffusion processes within the bulk of materials.

To improve the software situation and make the KMC method more readily available to the study of ion-diffusion in solids we have put an effort into developing a general, publicly available KMC code, KMClib, that handles both surfaces and bulk diffusion. KMClib is written in C++ with a user interface in Python. It is fast and efficient, well documented and well tested, and can handle a vast range of geometries and elementary diffusion processes. We will here briefly describe the code and some of its key features in regards to studies of bulk diffusion, within the context of an ab initio KMC study of ion-diffusion in ceria.

II. METHODS AND RESULTS

A. KMClib

KMClib [2] (www.github.com/leetmaa/KMCLib) is a collection of Python front-end functions, classes and interfaces for performing efficient lattice KMC simulations, with all computationally heavy back-end functionality implemented in C++. The KMC simulations can be performed either with predefined rates for all possible processes, or the rates can be updated on the fly with any external code interfaced with KMClib via a well defined custom rate calculator plugin interface. Analysis of the simulation results are either performed on the fly via an analysis plugin interface, or after the simulation is finished by examining the produced trajectory file.

Elementary processes are defined by specifying the local geometry of a lattice site (the atom types at the lattice sites in the vicinity of a central site), before and after the process is performed. Additionally, vectors can be given that determines which particles should be considered to move to which new
lattice sites during the process. In this way any kind of elementary processes that can be described as two local configurations and the vectors connecting them can be used in KMCLib. The program itself thus puts very little constraints on the type of processes used or on the number of particles involved in a single process. The only constraint is that the geometry can be represented on a regular grid in space in 1, 2 or 3 dimensions.

To facilitate diffusion studies KMCLib implements an algorithm for obtaining the mean squared displacement (MSD) curve with correct error estimates for the diffusing particles [3]. Preliminary results from this method are presented in the next section for the case of ion-vacancy diffusion in Ceria.

B. Ion-diffusion in Ceria

We used the newly developed KMCLib package to study temperature and volume dependence of the oxygen diffusion coefficient. We present results obtained for vacancy concentration of about 1.5%. Diffusion barriers were calculated by first principle methods, with rates estimated from transition state theory with the constant pre-factor D=0.5e-12. The formation of oxygen vacancy is accompanied by electron localization at two cerium atoms [4]. The relative position of these Ce+3 atoms can be important for oxide mobility. In our model calculations two +3 atoms are placed in the x-y plane as nearest neighbours. Diffusing in the x-y plane vacancy mostly stays in the first coordination shell of +3 cations, whereas it can go a bit further from the +3 pair when diffusing in the z-direction. Figure 1a shows the MSD curve for the diffusion of oxygen in the x- and z-directions at 1073 K for the compressed volume with cell parameter a = 5.40 Å (black curves) with their corresponding standard deviations (gray curves). The MSD was calculated using KMCLib on-the-fly during a simulation of 1,000,000 elementary steps for a Ceria system containing 95 atoms and one vacancy in the oxygen sub-lattice. Diffusion constants were estimated from slope of straight lines fitted to the MSD data (red lines in fig 1a).

In Fig.1b we present the temperature dependence of diffusion coefficient for two lattice parameters around the equilibrium value: a=5.40 Å and 5.44 Å. The interesting feature to notice is that for smaller volumes the diffusion in the z-direction is faster than in the x-y plane up to ~800 K but above this temperature the trend is reversed. For larger volumes ion mobility is similar in all the directions.

III. CONCLUSION

KMCLibs is robust and efficient implementation of the KMC algorithms to treat bulk and surface diffusion. It has unique features and can be used together with theoretically or experimentally estimated rates. Results on ceria are presented as an example of KMCLibs application to an ion conductor.

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Dissipative Particle Dynamics Approach for Nano-Scale Membrane Structure Reconstruction and Water Diffusion Coefficient Estimation

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The membrane is often considered to be the heart of the proton exchange membrane fuel cell (PEMFC), and it is of pivotal importance to involved transport phenomena and performance of the entire PEMFC. In this paper, the nano-scale structure of the membrane is reconstructed using dissipative particle dynamics. The average water pore sizes of the equilibrated membranes are calculated by using the radial distribution function, and the reconstructed nano-scale membranes are then used to evaluate water diffusion within the membrane by calculating the mean square displacement. The tortuosity of the membrane is evaluated by comparing the diffusivity of the membrane to that of a limiting case of cylindrical channels. Important findings from this study are presented by membrane structures, water diffusivity at different water saturations, and calculations of the tortuosity within the membrane.

Dissipative Particle Dynamics (DPD), Nafion Membrane, Modeling, PEMFC

I. INTRODUCTION
Nafion is the industry standard membrane material commonly applied in proton exchange membrane fuel cells (PEMFCs) [1]. To study transport phenomena in the Nafion membrane, one must first consider how to correctly represent the microscopic structure of the material. In this paper, the structure of the Nafion membrane is obtained using the dissipative particle dynamics (DPD) method [2], with the Nafion molecule represented by coarse-grained beads as shown in Fig. 1. The three bead-types in Fig. 1 represent hydrophobic backbone, side-chain, and hydrophilic side-chain, respectively. The most important parameter in this evaluation is the ratio between the number of water particles in the domain per sulfonate group in the membrane, i.e., the so-called $\lambda$-value.

II. METHOD
The average pore sizes of the membrane are evaluated using the radial distribution function (RDF) [3]. When the membrane is equilibrated, the diffusivity of water within the membrane is calculated using the mean square displacement (MSD) method [4]. To determine the tortuosity of the membrane, the diffusivity inside the membrane is compared to that of a straight cylinder with the same diameter as the average water cluster pore size for a given water saturation.

III. RESULTS
Figure 2 shows the equilibrated membrane structure for three different water saturations, and it is found that the water pores of the membrane are increasing in size as the water saturation increases. It can also be seen that the hydrophilic side-chains align themselves between the water beads and the hydrophobic back bone, as expected. The calculated diffusivity in the membrane is compared to available data from the open literature [5-7] showing a reasonable agreement. The results of this comparison are shown in Fig 3. It is clear that the largest increase in diffusivity occurs for small values of $\lambda$, which is due to the water being more tightly bounded when the pores are small. Figure 4 shows the calculated tortuosity as compared to experimental results, empirical and analytical correlations [8-10] and it is found that the prediction in this study achieves better agreement with experimental data than other correlations available in the literature. On the other hand, the trend for higher values of water saturation (where measurements from the literature are sparse) is in good agreement with empirical correlations proposed by other authors.

IV. CONCLUSIONS
Dissipative particle dynamics simulations with coarse-grained beads of water and polymer with different repulsion parameters are applied to acquire the structure of the Nafion membrane. The water will form clusters within the membrane with the size of the pores increasing with increasing water content. How the
size of the simulation box, length of Nafion membrane chains and simulation time affects the structure of the membrane is discussed. Simulation of the diffusivity of water within the Nafion membrane using the DPD method produces results similar to those obtained by other methods, both from other simulation techniques and experiments. The tortuosity of the membrane is evaluated by comparing the diffusivity of the membrane to that of a limiting case with no tortuosity and the results show a better agreement than other tortuosity correlations for Nafion membranes, especially for low values of $\lambda$.

![Fig 2: Cross-section view of equilibrated structures for: a) $\lambda=5$, b) $\lambda=10$, and c) $\lambda=15$. The different colors correspond to different beads, such as water (blue), backbones (red), side-chains (pink and green), respectively.](image)

![Fig 3: Prediction of relative diffusion coefficient of water beads inside the Nafion membrane compared to other measurements and simulations](image)

**ACKNOWLEDGMENT**

The financial support from the European Research Council (ERC) is gratefully acknowledged.

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REVERSIBLE OPERATION OF PLANAR SOLID OXIDE CELLS WITH H2/H2O AND CO/CO2 MIXTURES: MODELING AND EXPERIMENTAL VALIDATION

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Abstract - A combined modeling and experimental study on the reversible operation of planar Solid Oxide Cells with H2/H2O and CO/CO2 mixtures is presented. Commercial electrode-supported cells were experimentally characterized by measuring current-voltage curves and impedance spectra in both fuel cell (SOFC) and electrolysis (SOEC) operation modes.

A 1-D full-cell electrochemical model has been developed and validated on the experimental data. The model simulates current-voltage characteristics of the cell in SOFC/SOEC operations taking into account the electrochemical processes occurring at the electrodes together with the mass transport of gaseous species.

The thermal behavior of the cell has also been simulated using a simplified 2-D finite element model of the cross section of the cell in order to investigate the spatial temperature distribution.

Index Terms - experimental, modeling, reversible solid oxide cells, validation.

I. INTRODUCTION

Reversible technologies capable of storing renewable electricity in the form of synthetic gaseous fuels and producing electric energy from stored chemical energy will play a fundamental role in the future for the balancing of energy systems with high share of renewable sources.

Solid Oxide Cells (SOCs) can be used directly as fuel cells to produce electricity from gaseous fuels with high efficiency or reversely, as electrolyzers, to produce synthetic gas using electricity.

II. EXPERIMENTAL

Two types of commercial planar circular-shaped electrode supported SOCs were characterized in reversible operation with H2/H2O and CO/CO2 mixtures. The cells are Ni/YSZ fuel electrode-supported, with YSZ electrolyte and air electrode made either by a functional layer of YSZ/LSM with an LSM current collector layer or by LSCF with an YDC barrier layer. Current-voltage curves and impedance spectra were measured for different temperatures and gas mixture compositions in SOFC and SOEC operations.

The cell with LSCF air electrode showed better performance than the LSM cell in both fuel cell and electrolysis operation for all the gas compositions investigated, as shown in Fig.1. The SOFC and SOEC polarizations of the LSM cell were almost symmetric, while the LSCF cell showed higher losses in electrolysis mode at high current density, in agreement with literature that reports asymmetric polarizations for LSCF electrodes [1].

The increase of temperature had a positive effect on the performance of the cells, reducing voltage losses for both types of cells in all the tested conditions.
Fig. 2. Experimental and simulated cell polarization curves in SOEC/SOFC modes with CO/CO₂ mixtures.

III. MODELING

A. Electrochemical modeling

A 1-D full-cell electrochemical model has been developed and validated on the experimental data. The model, implemented in Matlab®, calculates the mass flow rates of the chemical species in the electrodes and the overpotentials of the cell as functions of the local current density.

Butler-Volmer equation is applied to determine activation overpotentials. The exchange current densities of the electrodes are calculated applying semi-empirical equations with kinetic parameters derived from the fitting of polarization curves [2].

The mass transport through porous electrodes is described applying the Dusty Gas Model, which has been integrated between electrode surface and electrode/electrolyte interface, where the reactions are supposed to take place. Ohmic overpotentials were obtained from impedance spectra analysis.

The simulated polarizations are shown in Fig.1 and Fig.2 together with the experimental data.

The kinetic parameters of the Ni/YSZ electrode resulting from the fitting of H₂/H₂O polarizations are almost equal (relative standard deviation < 10%) for all the SOEC curves, independently of the gas mixture composition and the material of the air electrode. The same occurs to the parameters derived from SOFC curves. The kinetic parameters of the Ni/YSZ electrode in CO/CO₂ tests are about 3 times lower than in H₂/H₂O tests, as expected from the slower kinetics of CO/CO₂ reactions [3].

The activation kinetic parameters of the LSM electrode do not change from H₂/H₂O to CO/CO₂ tests, consistent with the fact that the reaction at the air electrode is fully independent of the fuel electrode reaction. The LSCF electrode shows kinetic parameters two orders of magnitude higher than the LSM ones, in agreement with literature that reports very low activation resistance for LSCF air electrodes [1].

B. Thermal modeling

The thermal behavior of the cell has been simulated using a 2-D finite element model of the cross section of the full cell. Porous electrodes are modeled as pure conductive homogenous media with distributed heat sinks/sources related to reactions and overpotentials calculated using the electrochemical model.

Fig. 3. Thermal simulation of the cross section of the cell.

The model-calculated temperature gradients between cell center and border are very small, as shown in Fig.3, and the temperature difference between anode and cathode surface is negligible. Temperature distribution has a minimum in the cell center in SOEC mode when the cell operates below the thermoneutral voltage, while has a maximum in the center in SOFC mode, as expected from sinks and sources distribution.

IV. CONCLUSION

The results demonstrate that the developed electrochemical model can successfully reproduce voltage-current characteristics of single SOCs in test conditions. The kinetic parameters evaluated from the fitting of polarization curves are capable of relating the current-voltage characteristics to electrode materials and reactions. Further work is ongoing to refine and validate the thermal model in order to apply the coupled models to dynamic simulations at the single-cell level.

REFERENCES

NOVEL HIGH TEMPERATURE PEM FUEL CELL MEMBRANES - COMPOSITE AB-PBI/CARBON BLACK, DOPED WITH PHOSPHORIC ACID

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Abstract - A series of novel composite AB-PBI/Carbon black (AB-PBI/CB) membranes, doped with phosphoric acid (PA), were prepared and characterized. The purity of the monomer – 3,4-diaminobenzoic acid - was crucial for the preparation of high molecular AB-PBI. The synthesis of the composite casting solution of AB-PBI/Carbon black was performed in situ using modified Eaton’s reagent as reaction media. Due to the introduction of oxidized carbon black filler during the synthesis of AB-PBI, the composite membranes, prepared from the casting solution and subsequently doped with PA, exhibit very high doping levels and very good mechanical properties. Doping levels up to 40 moles PA per AB-PBI repeat unit were achieved. Proton-conductivity was measured at 160°C and relative humidity (RH) from 5 to 20%. As expected the proton conductivity strongly depends on RH. The proton conductivity, measured at RH 5% was 362 mS.cm⁻¹, while at RH=20% it reaches 435 mS.cm⁻¹.

Index Terms – AB-PBI, carbon black, composite membranes.

I. INTRODUCTION

Polymer electrolyte membrane fuel cells (PEM FC) are considered as promising candidates for mobile and stationary power generation devices. The development of solid polymer electrolytes for such electrochemical devices has involved considerable efforts both from academia and industry. PEM FC generates electricity from an electrochemical reaction in which oxygen (air) and a fuel (e.g. hydrogen) combine to form water and heat. The polymer electrolyte membrane (PEM) is the heart of the fuel cell. It has to fulfill harsh requirements such as high proton conductivity, low gas permeability, chemical and mechanical stability, long term operation under severe conditions. A breakthrough was achieved when in 1995 polybenzimidazole (PBI) was first proposed for preparing proton conductive acid doped membranes [1]. Since then phosphoric acid doped PBI membranes (PBI/PA membranes) have been successfully developed and systematically characterized. The class of polyazol polymers has been developed in the sixties as thermally stable materials. As already mentioned, in 1995 it was found that poly 2,2’-m-(phenylene)- 5,5’-bibenzimidazole (meta-PBI) can be doped with strong acids, becoming in this way a solid polyelectrolyte. Considerable amount of polymers, containing benzimidazole rings have been prepared and their properties as PEM studied. At present only several such polymers (all usually denoted PBI), have found practical application, e.g. meta-PBI, para-PBI, AB-PBI and O-PBI. Meta-PBI is a commercial product and is usually prepared by Marvel’s method (polycondensation of diaminobensidine (DAB) and diphenylester of the isoftalic acid) or in polyphosphoric acid. Depending on the dicarboxylic acid used, different PBIs can be obtained. The simplest PBI is poly(2,5-polybenzimidazole) commonly denoted as AB-PBI. It can be synthesized from a single monomer (3,4-diaminobenzoic acid) (DABA, Scheme 1), which is relatively cheap, commercially available (e.g. used in the pharmaceutical industry) and non-carcinogenic as DAB is. The synthesis of AB-PBI has been performed in polyphosphoric acid [2] (Scheme 1) or in Eaton’s reagent (methansulfonic acid (MSA) containing P2O5).

Scheme 1. Synthesis of AB-PBI in polyphosphoric acid

As the unbalancing factor of stoichiometry is avoided, the synthesis should be less dependant on the purity of the monomer. It has been however shown that the use of monomer with high purity results in high molecular AB-PBI [2]. Using recrystallized DABA, Wainright et al. [2] synthesized AB-PBI with inherent viscosity as high as 7.33, which is essential for preparing membranes by direct casting from trifluoroacetic acid (TFA)-PA mixture. Asenio and Gomez-
Romero have prepared AB-PBI membranes by direct casting from MSA solution [3] or a MSA-PA mixture [4]. The most recent trends in carbon based polymer nanocomposites offer an exciting opportunity for very efficient reinforcement of polyazoles materials. Two papers report the preparation of polyoxadiazole (POD)/oxidized carbon black (OCB) composites [5]. There is no data for preparation of polybenzimidazole/ oxidized carbon black composite membranes for PEM FC’s.

II. RESULTS AND DISCUSSION

In the present work preliminary results for the preparation and characterization of AB-PBI/OCB composite membranes doped with PA are reported. The crucial step for the synthesis of the composite casting solution was the use of modified Eaton’s reagent, containing concentrated sulfuric acid as sulfonating and oxidizing reagent, which in situ oxidizes the CB filler and enriches its surface with carboxylic acid groups from which polycondensation can be started. As already mentioned, the purity of the starting DABA is of great importance for obtaining high molecular weight AB-PBI. Monomer purification was performed by flash chromatography with activated carbon. The solution from which membranes were cast (5 mas % AB-PBI/0.5 mas % CB) was obtained by polymerization of DABA in MSA, containing 10 mas % P2O5 for 48h at 130°C. After casting (casting knife, glass substrate) the membranes were kept in air for 24 h. Water was absorbed and sol-gel transformation took place. After that the membranes were washed with water and water/ammonia solution. The doping of the composite membranes with PA was carried out in two steps. In the first one the as prepared porous membranes were doped with 85% PA to doping level about 5 moles PA per repeat unit and then thermally stabilized by heating at 160°C for 6 hours. The second step was further doping with 70 % PA. Doping levels up to 40 moles PA per PBI repeat unit were achieved. Nevertheless the membranes are of very good quality (Fig. 1).

![Composite AB-PBI/CB 0.5 mas % membrane doped with PA](image)

The dynamic mechanical properties of the composite AB-PBI membrane with 0.5 mas % content of CB, doped with 40 moles PA, shows Young's modulus of 3.3 MPa and elongation at break 27% which result could be regarded as very good. Proton-conductivity was measured at 160°C and relative humidity (RH) from 5 to 20%. As expected the proton conductivity strongly depends on RH. For a composite AB-PBI/0.5 mas % carbon black membrane with doping level 40 moles PA per repeat unit the proton conductivity, measured at RH 5% was 362 mS.cm⁻¹, while at RH=20% it reaches 435 mS.cm⁻¹. Having in mind that these membranes will be operated temperatures 160°C and above by self-humidification (RH = 5 - 20%), the proton conductivity values achieved have to be regarded as extremely high. A Celtec P® type membrane – PA doped p-PBI (doping level 41 moles PA per repeat unit, kindly supplied by BASF Fuel Cell GmbH) was used as reference. It’s proton conductivity (measured at the same conditions) reaches 190 mS.cm⁻¹.

III. CONCLUSION

Due to the introduction of oxidized carbon black filler during the synthesis of AB-PBI, the composite membranes, prepared from the casting solution and subsequently doped with PA, exhibit high doping levels (up to 50 moles PA per PBI repeat unit) and very good mechanical properties. No polymer leakage (main drawback for AB-PBI membranes, doped with high amount of PA) was observed at 180°C. During the thermal treatment of the phosphoric acid doped AB-PBI/CB membranes reactions of cross-linking take place. The result is considerable improvement of the mechanical properties. Proton-conductivity was measured at 160°C and relative humidity (RH) from 5 to 20%. For a composite AB-PBI/0.5 mas % carbon black membrane (doping level 40 moles PA per repeat unit) the proton conductivity, measured at RH 5% was 362 mS.cm⁻¹, while at RH=20% it reaches 435 mS.cm⁻¹. The mechanical parameters (E module, elongation at break) of the new composite AB-PBI/CB composite membranes are better than these of the Celtec P® type membrane.

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NOVEL MIDDLE TEMPERATURE PEM FUEL CELL MEMBRANES – POLYBENZIMIDAZOLE CONTAINING IMMOBILIZED PHOSPHONIC- OR SULFONIC ACID GROUPS

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Abstract – An easy and efficient procedure for the preparation of semi interpenetrating networks, comprising polybenzimidazole (PBI) containing cross-linked polyvinyl phosphonic (Cr-PVPA) or polyvinylsulfonic (Cr-PVSA) acid, has been developed. It involves several steps: 1) Preparation of porous PBI films, filled with water; 2) Exchange of water from the film with vinylphosphonic acid (VPA) or vinylsulfonic acid (VSA) solution, containing initiator, cross-linker and co-solvent; 3) Polymerization/cross-linking of the acid in the PBI matrix, induced thermally or by UV irradiation. Using this procedure, two series of membranes of very good quality, containing very high concentrations of acidic groups have been prepared and their properties studied. Proton conductivity measurements were performed at 80 and 100 °C and relative humidity (RH) from 20 to 100%. The PBI/Cr-PVPA membrane, containing 15.4 mol VPA per PBI repeat unit showed the highest proton conductivity - 87 mS.cm⁻¹.

Keywords: membranes for PEM FC, membrane preparation, PBI, cross-linked polyvinylphosphonic/sulfonic acid

I. INTRODUCTION

At present the most widely used proton conductive membranes are based on perfluorinated polyelectrolytes with attached sulfo groups (Nafion®, Flemion®, HyflonIon®, Dow membrane). These materials have high proton conductivity, excellent chemical stability and mechanical strength and potentially long term durability. The main drawbacks of these materials are high cost and strong dependence of the proton conductivity on water contents in the membrane. Such membranes can function properly only in the highly hydrated state. In order to maintain high water content complex water management is needed and the operation temperature is usually limited to the boiling point of water. Various polymers, containing sulfonic acid groups have been developed during the last years – sulphonated polyetherketones, polyether-sulfones, polyimides, polybenzimidazoles etc. Despite of being relatively cheaper than the perfluorinated types, these membranes suffer the same restrictions – low operating temperatures and complex water management.

The most successful material for high temperature PEMFC is based on polybenzimidazole (PBI) doped with phosphoric acid (PA) (PBI/PA membranes). The basic character of PBI allows doping levels up to 40 PA molecules per PBI repeat unit, resulting in very high proton conductivity – over 2.10⁻¹ S.cm⁻¹ at 190°C. PBI/PA membranes have to be operated at temperatures above 100°C. Under this temperature the water, formed as product of the reaction dilutes the electrolyte. With the drained water PA is slowly removed. The result is a drop in cell performance. This problem could be solved by the immobilization of acid groups in the PBI. Different types of PBIs, bearing -PO₃H₂ groups have been described – phosphoneted, substituted with different radicals having phosphonic acid groups, cross-linked [1] and with grafted polyvinylphosphonic acid (PVPA) chains [2]. The efforts, involved in the preparation of membranes, containing high concentrations of immobilized VPA groups show that the higher contents of such groups leads to higher proton conductivities both in the anhydrous and fully hydrated state of the membrane. Here we report a new method for the preparation of PBI membranes, containing cross-linked PVPA. As this method has proved extremely easy and efficient, it has been also applied for the preparation of PBI membranes, containing cross-linked polyvinyl sulfonic acid (PVSA).

II. RESULTS AND DISCUSSION

For preparation of the membranes further described, m- and p-PBI were used as starting materials (Scheme 1).
In order to incorporate high concentrations of −PO3H2 or −SO3H groups in the PBI, a new method has been applied – polymerization/cross-linking of vinylphosphonic acid (VPA) or vinylsulfonic acid (VSA) in the PBI matrix (Scheme 2).

Scheme 2: Semi interpenetrating network m-PBI/cross-linked polyvinyl phosphonic acid

The procedure for preparation of PBI membranes, containing cross-linked polyacids includes the following steps:

1) Preparation of porous PBI films, filled with water.
Two approaches have been applied.

a) m-PBI: a dry film was swollen in phosphoric acid (PA) or mixture PA/vinylphosphonic acid (VPA), followed by washing with water.

b) p-PBI: a PBI membrane, doped with phosphoric acid (PA) (prepared from the reactions solution p-PBI/polyphosphoric acid, 40 mol PA per PBI unit) was washed with water.

2) Exchange of water from the film with vinylphosphonic acid (VPA) or vinylsulfonic acid Na salt (VSA-Na) solution, containing initiator (V 50), cross-linker (triallyl-s-triazin-2,4,6-trion) and co-solvent – 3-4h at RT.

3) The radical polymerization/cross-linking of the acid in the PBI matrix, induced thermally or by UV irradiation. After finishing the process, the membranes, containing −SO3Na groups were treated with 5% HCl (conversion to −SO3H).

m-PBI was used for the preparation of membranes, containing cross-linked PVPA and p-PBI – for these with cross-linked PVSA.

The amount of cross-linked polyacid in the membranes prepared was determined gravimetrically from the weight uptake according to the weight of the starting film (after abundant washing with water and drying).

The method used offers vast opportunities for varying different parameters during membrane preparation – in the first step: composition of bath, temperature and duration of the swelling, degree of swelling (up to 1000% weight uptake can be achieved); in the second step: concentration of the acid, initiator, cross-linker and co-solvent in the bath; in the third step: intensity and duration of the UV irradiation, duration of the thermal treatment.

It was found that UV irradiation is the better method for polymerization/cross-linking of VPA in the PBI matrix. Depending on irradiation time (10-30 min) up to 75% of the acid in the swollen film can be cross-linked. For cross-linking of VSA-Na best results were obtained by 1-2h UV irradiation and heating at 80°C for 2-4 days. In both cases films of very good quality (smooth, flexible, good mechanical properties) were obtained.

Proton conductivity measurements were performed at 80 and 100 °C and relative humidity (RH) from 20 to 100% (Tab.1), using the EasyTest Cell method [3]. Nafion® 117 was used as reference.

Table 1. Proton conductivity measurements of PBI/Cr-PVPA membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>VPA units per PBI</th>
<th>σ (mS.cm⁻¹) at 80°C</th>
<th>σ (mS.cm⁻¹) at 100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC 1</td>
<td>8.8</td>
<td>62.1</td>
<td>37.8</td>
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<td>11.4</td>
<td>65.0</td>
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<td>69.1</td>
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<td>80.8</td>
</tr>
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</table>

Nafion® 117 showed σ=105 mS.cm⁻¹ at 80°C and RH=100%.

A series of membranes, comprising PBI containing cross-linked polyvinylsulfonic acid has also been prepared. The contents of VSA groups is in the range 0.8 to 3.6 per PBI unit. The proton conductivity drastically depends on RH. The membrane with highest −SO3H contents showed the best conductivity – 46 mS.cm⁻¹ at 90°C and 100% RH.

III. CONCLUSION

Using a new original method for polymerization/cross-linking of vinylphosphonic and vinylsulfonic acid in a PBI matrix two series of membranes with very high contents of immobilized acid groups been prepared. The concentration of −PO3H2 groups in the final membranes ranges from 8.8 to 15.4 for PBI unit, while these of −SO3H groups is from 0.8 to 3.6 per PBI unit. At 80-100°C and 100% RH the PBI/Cr-PVPA membranes show proton conductivity comparable to that of Nafion® 117, while at lower RH (20-50%) their conductivity is still good (9-60 mS.cm⁻¹).

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Acknowledgement

The authors would like to thank the Bulgarian Science Fund (Project PemHydroGen, ЪТК 02/68) for funding the research and FP7 EU project POLINNOVA, № 316086 for funding the presentation of the results at Piero Lunghi EFC Conference 2013, Rome, Italy.

Copyright © 2013
BIOMASS TO FUEL CELLS STATE OF ART: A REVIEW OF THE MOST INNOVATIVE TECHNOLOGY SOLUTIONS


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Abstract - Fuel Cells coupled with biomass-derived fuel gas can convert renewable energy into electricity with high efficiencies, in an environmental-friendly and CO2-neutral manner. However, the coupling of biomass-derived gases and Fuel Cells is, at present, unviable. The presence in the raw product gas of condensable organic compounds, particulate, and inorganic impurities renders it unsuitable. Recently developed hot gas cleaning technologies could improve energy efficiency and lower operational costs for high-temperature utilizations of the biomass-derived gas. The conversion systems have to be analyzed from various perspectives including feedstock, processes, and plant configurations. The review shows how these systems can obtain a remarkable electrical efficiency, drastically reducing the biomass power plants emissions. However, further research and demonstration activities are required in order to improve power plant reliability and reduce global capital cost, especially in developing novel catalysts and supporting materials to improve their selectivity, activity, productivity and economy.

Index Terms – Biomass, Fuel Cells, Gas Conditioning.

I. BIOMASS AND CONVERSION PROCESSES

Nowadays there is a change in the biomass energy uses from traditional and non commercial (e.g. simple open combustion to produce heat) to modern’s one (e.g. advanced processes to produce electricity and bio-fuels integrated in food and biomaterials industries). The biomass technical and economic potentials are higher than the actual world energy consumption, thus, the challenge is in the viable and sustainable use not in the availability. Indeed biomass is a complex source that can be processed in many ways leading to a variety of products and by-products, as showed in figure 1.

II. GAS CONDITIONING

Each process results in different energy products (heat-fuel-electricity), by-products and waste. E.g. in biological processes about half of the mass and energy content of the primary material goes to by-products. Gasification and anaerobic digestion produce gas (syngas and biogas) which can be directly exploited in fuel cells, avoiding the limitation of the thermal cycle (Carnot efficiency) and decreasing the pollutant emissions. Thus the paper will focus on these two primary conversion processes.

Fig. 1. Biomass conversion processes

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However, adopting in-depth clean-up before the fuel conversion step, guarantees clean emissions downstream of the system with smaller volume equipment. The gas conditioning technologies can be divided in primary methods (inside the reactor) or secondary methods (downstream); or chemical-physical (catalytic purification, adsorption, scrubbing, membrane separation, condensation) or biotechnological (biofilters, bioscrubbers, etc.). The secondary methods can be subdivided into two main categories based on the working temperature: cold methods mainly divided in “dry” methods (bag and sand filter) and “wet” methods (scrubber), hot methods (cyclones, filters and catalytic tar reforming). The paper will focus on gasification and tar reforming due to the fact that they are still undergoing development. In a gasification process a high temperature induces high conversions of gaseous phase. Narvaez et al. [1] show a 74% decrease in tar content changing the bed temperature from 700°C to 850°C. Regarding the catalyst more used in the tar reduction, they are Ni-based catalysts, calcined dolomites, magnetite, and olivine. Corella et al. [2] reported that the use of calcined dolomite inside a gasifier could decrease the tar amount from 6.5 to 1.3 wt%. Rapagnà et al. [3] observed a tar reduction more than 93.5% by integrating a catalytic filter candle in the gasifier freeboard.

III. POWER PLANTS

Omosun et al. [4] investigated the integration of a SOFC and a fixed bed downdraft gasifier via a cold clean up system and a fluidized bed gasifier via a hot one (catalyst in the bed material). Results obtained stated that the hot respect to the cold process have especially higher global efficiency (23% electrical and 59% cogenerative instead of 21% and 34%) whereas the capital cost for the hot process is higher. Aravind et al. [5] reported that when gas cleaning is carried out at temperatures lower than gasification temperature, additional steam has to be added to raw gas in order to avoid carbon deposition. Fryda et al. [6] showed global electrical efficiencies of 26% (with SOFC current density of 3774 A/m² and fuel utilization factor of 75%). Bang-Møller et al. [7] provided a global electrical efficiency of 36% (with Uf= 85% and J = 300 mA/cm² at 800°C), but, with the SOFC + mGT configuration (251 KW.), with a pressure ratio of 2.5 (and a TIT of 697°C) a global electrical efficiency of 50.3% was reached. Di Carlo et al. [8], using a bundle of catalytic ceramic filter candles in the upper part of the gasifier as clean-up system, demonstrated that varying both the utilization factor and the percentage of oxygen purity in the air stream (from 0.25% to 0.95%) the global efficiency reaches values ranging between 36% to 44%, meanwhile oxygen purity variation provokes maximum efficiency decrease of 2%, making economically questionable the adoption of complex and energy consuming air separation units. Finally Morandin et al. [9] performed thermo-economic analysis of 9 different system configurations, stating that the choice of auto-thermal reforming instead of steam reforming can decrease the system costs, but only up to a certain level, after which the benefits of steam reforming on thermodynamics, let the system reach higher efficiency.

IV. CONCLUSION

Biomass fuel cells power plants can provide a high efficiency and low environmental impacts way to convert low-value waste biomass. Fluidized bed gasification with steam, indirect heat supply and primary conditioning method with catalysts could provide a promising way to improve the syngas yield and quality. In this way the system is more reliable (more annual operating hours, more different typologies of biomass to be used, more load variation, etc.), the electrical efficiency increases but the global capital cost increases to about 10000-15000 €/kWe (cost of about 1000 €/kWe can be envisaged when fuel cells will be widely developed). However, more research is needed to improve gas quality for its commercial uses in a high energy-efficient heat and power generator such as fuel cells, especially in developing novel catalysts and supporting materials to improve the selectivity, activity, productivity and economy of a catalytic process for syngas cleaning and downstream utilizations.

REFERENCES

SYNCHROTRON-BASED IN SITU CHARACTERIZATION OF PEMFC AND SOFC COMPONENTS

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Abstract - Notwithstanding the environmental appeal of fuel cells the widespread application of these promising devices is still hindered by problems mainly related to the limited durability of crucial functional components. Recent developments of synchrotron soft X-ray imaging and spectromicroscopy has allowed in-situ characterization of the fuel cell components at the functionally relevant length scales opening unique possibilities to shed light on the origin of degradation processes.

Index Terms – PEMFC, SOFC, SPEM, STXM

I. INTRODUCTION

Fuel cells are electrochemical devices providing efficient and pollution-free production of electricity directly converting the electrons exchanged in a redox reaction (such as a combustion) into electric current. One of the still unresolved issues that impedes their widespread applications is related to the limited durability of crucial components and mass transport events that deteriorate the performance. The authors have developed soft X-ray spectromicroscopy based methodology allowing detailed, chemical and morphology analysis of the cell components under operation conditions. The synchrotron-based X-ray microscopes, namely SPEM (Scanning PhotoEmission Microscopy) and STXM (Scanning Transmission X-ray Microscopy), provide correlative information about the processes at the interconnects, electrodes and electrode/electrolyte interface and also occurring under operation conditions.

II. PEMFC AND SOFC CHARACTERIZATION

This work summarizes some achievements of TwinMic and ESCAmicroscopy beamlines of the Elettra synchrotron radiation laboratory in characterization of different types of fuel cells obtained in close collaboration with University of Salento.

A. STXM – TwinMic beamline

The activities using STXM included: (i) cell development and demonstrative work; (ii) studies of catalyst electrodeposition and (iii) corrosion of PEM interconnects, see [1] and reference therein contained. In SXTM the microprobe is an X-ray beam, focused down to sub-micrometric spot size by zone plate diffractive optics, and the specimen is raster-scanned across for obtaining 2D images by monitoring the transmitted X-rays and/or fluorescence [1,2]. As representative example here we show the corrosion of metal interconnects that is critical for the performance of fuel cells. The corrosion products can lead to: (i) increase of the ohmic drop; (ii) clogging of the porous, gas-transfer zones; (iii) catalyst poisoning; (iv) electrolyte deterioration. One of our STXM-based investigations has evidenced the release of Ni and Fe from PEM interconnects in the presence of a hydrated Nafion film [3]. Figure 1 depicts the absorption images of the interfaces between the Fe (a) electrode and the electrolyte, XRF maps (b) and local XAS spectra (c). Panel (a) clearly show the complex morphology of Fe electrode due to the progress of the corrosion reaction. Fe distribution within the electrode is identified by XRF maps (b) and local XAS spectra (c). XAS analyses in different positions in the area originally occupied by the electrolyte show different Fe chemical states that can be correlated with the local electrochemical potential. Moreover the XRF maps (b) show diffusion of corrosion products within the Nafion film, a mechanism related to the PEM electrolyte deterioration.
B. SPEM – ESCAmicroscopy beamline

SPEM as a surface sensitive technique has been very important for shedding light on the events at the reagent gas surface interface, which is in fact controlling the chemical process that ‘produces’ electricity. Its principle is the same as STXM but the information is provided using X-ray photoelectron spectroscopy \[1,4\]. Changes in the status of the morphology and chemical composition of the surface due to deposition of contaminants, mass transport and mass loss are crucial for the performance and duration of the fuel cell devices as SOFCs operated at high temperatures. We performed a lot of experiments with externally driven SOFCs \[1\] and recently we got the first results with realistic self-driven devices monitoring simultaneously the chemical state and local potential at the electrodes during spontaneous conversion of the chemical into electrical energy \[5\]. The used planar single-chamber cells, sketched in Figure 2(a), consist of Mn cathode and Ni anode deposited on a YSZ(110) electrolyte under fuel and oxidant (H\(_2\)+O\(_2\)) mixture. The time-evolution of the oxidation state and local potential, resulting from the current flow are imprinted in the Ni 2p\(_{3/2}\) spectra in Figure 2(b), measured close to the Ni/YSZ interface. The Ni 2p\(_{3/2}\) spectra show that the on-going electrochemical reaction is accompanied by progressive partial reduction of the NiO electrode, evidenced by the growth of a metallic Ni\(_0\) component at the expense of the Ni\(^{2+}\) one, until a steady state is reached after ~25-30 minutes. The current-induced spectral shift and the progressing NiO reduction as a function of the reaction time were also monitored with higher temporal resolution using the imaging mode, tuning to the selected energy window to outline the potential-induced shift or the intensity changes of the metallic Ni component, reflecting the current changes and the reduction rate respectively, see Figure 2(c).

III. CONCLUSION

In situ soft X-ray microspectroscopy has been proved capable of following morphological and chemical effects of electrochemistry. We have thus demonstrated that SXTM and SPEM can contribute unique information to electrochemical materials science, in particular for energy-conversion devices, for example in terms of: (i) assessment of localization processes (chemical and overvoltage); (ii) rationalization of growth/damaging mechanisms.

REFERENCES

Abstract - A promising direction in the development of solid oxide fuel cells (SOFC) is the reversible approach in which the device operates as fuel cell and as electrolyzer. Reversibility is very important for coupling with RES. A serious problem is the asymmetry of the system when operating in the two modes. A definitive breakthrough is the separation of the water production/consumption from the two electrodes. For fuel cell mode this idea has been realized in the innovative concept of the dual membrane fuel cell (DMFC), recently developed and proved in a FP7 project. The cell consists of three independent chambers for hydrogen, oxygen and water. They can be separately optimized. This work presents reversibility studies of the DMFC. The first results are very promising. They show good reversibility without application of a special catalyst for enhancement of the water splitting. The electrolyzer mode has lower overvoltage and thus lower internal resistance.

Index Terms - dual membrane fuel cell, fuel cell/electrolyzer, mechanistic model, reversible mode.

I. INTRODUCTION

The integration of hydrogen as a storage medium and as a fuel will accelerate the use of sustainable primary energy sources in our future energy systems. A promising direction is the development of reversible solid oxide fuel cells (SOFC) which operate as fuel cells and as electrolyzers (SOEL), i.e. as energy conversion/storage devices.

SOEC and SOFC concepts are similar regarding materials and geometries. In spite of the fact that the same global chemical reaction is used, they are strongly asymmetrical systems, with the production/consumption of water at the electrodes. This may cause implications concerning materials, microstructure, design, ageing etc. which introduce some constraints in the development of reversible systems. A definitive breakthrough for the design would be the separation of the water production/consumption from the two electrodes. This idea has been realized for fuel cell mode in the innovative concept of the dual membrane fuel cell (DMFC), recently developed and proved [1]. The kernel of the new design is the introduction of a porous mixed (oxide ion and proton) conducting junction, named central membrane (CM), between the anode part of a proton-conducting SOFC (PCFC) and the cathode part of a SOFC, where the water is produced and evacuated (Fig. 1). Thus the cell consists of three independent chambers for hydrogen, oxygen and water. In electrolyzer operating conditions the steam should enter in the central membrane and split into protons.
Due to the registered high oxide ion conductivity of the typically accepted as protonic conductor \( \text{BaCe}_{0.95}\text{Y}_{0.05}\text{O}_{2.5} \) (BCY15), a new improvement of the dual membrane fuel cell, named “monolithic” design, has been offered [2]. It strongly simplifies both technology and construction. This work is focused on reversibility studies of the dual membrane fuel cell design.

II. RESULTS AND DISCUSSION

The electrolyte-central membrane assembly (ECMA) of monolithic button cells with thickness about 1 mm was prepared by single stage cold pressing and sintering. Pt electrodes were deposited. The cell was forced to operate periodically as fuel cell and as electrolyzer changing the operation mode and using the water accumulated in the CM under anodic current.

A. Mechanistic Modeling

A model for the mixed ion conducting monolithic CM was developed, taking into account the following species, identified as: oxygen in the lattice \( (O^2) \), oxygen vacancies \( (\text{V}^0) \), proton defects \( (\text{OH}^-) \) in the solid phase and gaseous water within the pores. The global reaction can be described as:

\[
2\text{OH}^- \leftrightarrow \text{H}_2\text{O}(g) + \text{V}^0 + O^{2+}
\]

Fig. 2 shows the simulated polarization curve of a monolithic BCY15 CM with thickness 50 µm. The model predicts a lower overvoltage in electrolyzer mode.

B. Measurements in fuel cell and in electrolyzer modes

Results of operation in reversible mode are presented in Fig. 2. They show good reversibility without application of a special catalyst or water vapor pressure for enhancement of the water splitting. The electrolyser mode of operation is characterized by lower overvoltage and thus by lower internal resistance, which is in agreement with the simulations.

III. CONCLUSION

The first reversibility results show that the operation of the monolithic DMFC in both fuel cell and electrolyzer mode is a very promising direction for further development. Optimization of the geometry towards increasing the water vapor evacuation/supply surface is necessary.

ACKNOWLEDGMENT

The research leading to these results has received funding from the European Community’s Seventh Framework Program (FP7/2007-2013) under grant agreement No 213389. Powders were fabricated and supplied by Marion Technologies (MT). The authors acknowledge Operational Program “Development of Human Resources”, scheme “Science and Business”, BG051PO001/3.3-05-001 for the financial support that made possible the presentation and publication of the results.

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A PARAMETRIC STUDY OF THE CATHODE CATALYST LAYER COMPOSITION BASED ON A TWO-DIMENSIONAL TWO-PHASE FLOW AGGLOMERATE MODEL

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Abstract – A two dimensional, across-the-channel, two-phase flow and isothermal model for a proton exchange membrane fuel cell is presented. Water transport through the membrane is described by the combined mechanism of electro-osmotic drag, back diffusion and hydraulic permeation. Water phase transfer between water vapor, dissolved and liquid water as well as the membrane swelling are included. The spherical-agglomerate structure is used for the catalyst layer, in which the membrane and liquid water partially occupy the void space and in turn form the membrane and liquid films surrounding the agglomerate. The effects of platinum loading, platinum mass ratio, dry membrane volume fraction and catalyst layer thickness on fuel cell performance and effectiveness are investigated by using an orthogonal design method. For the highest current density at lower cell voltages, the optimal values of platinum loading, platinum mass ratio, dry membrane volume fraction and catalyst layer thickness are 0.4 mg cm$^{-2}$, 0.4, 0.3 and 20 $\mu$m, respectively.

Index Terms – two-phase flow model, orthogonal test, optimisation, proton exchange membrane fuel cell.

I. NOMENCLATURE

\begin{tabular}{ll}
\(c\) & concentration, mol m$^{-3}$ \\
\(D\) & diffusion coefficient, m$^2$ s$^{-1}$ \\
\(F\) & Faraday’s constant, 96485 C mol$^{-1}$ \\
\(i\) & current density, A m$^{-2}$ \\
\(k\) & permeability, m$^2$ \\
\(L_M\) & volume fraction of membrane \\
\(l\) & thickness of catalyst layer, $\mu$m \\
\(M\) & molecular weight, kg mol$^{-1}$ \\
\(m\) & mass loading, mg cm$^{-2}$ \\
\(n_d\) & electro-osmotic drag coefficient \\
\(p\) & pressure, Pa \\
\(S\) & source term, mol m$^{-3}$ s$^{-1}$ \\
\(s\) & water saturation \\
\(u\) & velocity vector, m s$^{-1}$ \\
\(w\) & mass fraction \\
\(x\) & mole fraction \\
\(\epsilon_p\) & porosity of the catalyst layer \\
\end{tabular}

II. INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are promising candidates as power sources for portable and stationary applications due to their high energy conversion efficiency, power density and low pollutant emissions [1,2]. The slow oxygen reduction reaction (ORR) in the cathode catalyst layer (CCL) significantly affects the fuel cell performance as thus is the main focus of experimental and modeling research. The agglomerate models have been previously used to investigate the kinetics and transport processes in catalyst layers [3-4]. Water management is critical to successful fuel cell operation due to the strong relationship between the water content and the ionic conductivity of the membrane. When the fuel cell operates at a higher current density, liquid water formation cannot be avoided because the effect of electro-osmotic drag (EOD) leads to an accumulation of water at cathode side of the membrane, while the liquid water is generated through membrane desorption and water vapor condensation [5].

The properties of the gas diffusion layer (GDL) and catalyst layer (CL) play a vital role in controlling water content. The aim of this work was to develop a two-phase flow, two dimensional, across-the-channel model based on an agglomerate catalyst structure in conjunction with comprehensive water phase-transfer and transport mechanism. An orthogonal design method is used to investigate the effects of platinum loading, platinum mass ratio, dry membrane volume fraction and catalyst layer thickness on fuel cell performance and the effectiveness factor of the CCL. This model can give useful guidance for optimisation of the catalyst layer composition.
The governing equations are given as follow:

$$\nabla \cdot (\rho \cdot \mathbf{u}) = \nabla \cdot \sum_{j=1}^{M} S_i^j \tag{1}$$

$$\rho \cdot \mathbf{u} \cdot \nabla \rho - \nabla \cdot \left( \rho \cdot \sum_{j=1}^{M} \left( \nabla S_i^j \right) \right) = \sum_{j=1}^{M} S_i^j \tag{2}$$

$$\frac{\partial}{\partial t} \left( \rho \cdot \mathbf{u} \right) + \nabla \cdot \left( \rho \cdot \mathbf{D} \right) = \nabla \cdot \left( \mathbf{w} \cdot \nabla \rho \right) - \nabla \cdot \left( \mathbf{w} \cdot \mathbf{B} \right) = \sum_{j=1}^{M} S_i^j \tag{3}$$

$$\frac{\partial}{\partial t} \left( \rho \cdot \mathbf{u} \right) + \nabla \cdot \left( \rho \cdot \mathbf{D} \right) = \nabla \cdot \left( \mathbf{w} \cdot \nabla \rho \right) - \nabla \cdot \left( \mathbf{w} \cdot \mathbf{B} \right) = \sum_{j=1}^{M} S_i^j \tag{4}$$

$$\nabla \cdot \mathbf{u} = 0 \tag{5}$$

Eq. (1) and (2) are used to describe the multi-component diffusion and mass conservation of the gas species (H₂, O₂, N₂ and H₂O). Eq. (3) is used to describe the dissolved water transport through the membrane. Eq. (4) is used to describe the two-phase flow between liquid water and gas mixture and Eq. (5) is to describe the conservation of charge in catalyst layers of anode and cathode.

### IV. DISCUSSION

#### A. Orthogonal test

Four design parameters, platinum loading, platinum mass ratio, membrane volume fraction and catalyst layer thickness, were investigated. The maximum current density at a cell voltage of 0.3 V is applied as the design target. The orthogonal test results are shown in Table I.

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<th>TABLE I ORTHOGONAL TEST RESULTS WITH L_0(3^4)</th>
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The greatest cell performance is achieved by using the parameters of case 4 and platinum loading and the platinum mass ratio are the most and least sensitive parameter in determining the cell performance at 0.3 V, respectively. The thinnest thicknesses of membrane and liquid water film are obtained in case 4 and 7, respectively.

#### B. Effectiveness factor of the cathode catalyst layer

The effectiveness factors of the cathode catalyst layer were shown in Fig. 1. The highest effectiveness factor was obtained near the CCL-GDL interface and under the gas channel and it decreases along the oxygen diffusion direction. The parameters in case 4 result in the highest effectiveness factor.

#### V. CONCLUSION

A two-phase flow model coupled with the agglomerate model has been used to determine the thicknesses of membrane and water film surrounding the agglomerate. The thicknesses of the membrane and liquid water film depend on the composition of the catalyst layer and current density. The fuel cell performance can be improved by adopting an orthogonal design method. The optimal values of the catalyst layer components at the cell voltage of 0.3 V are: platinum loading of 0.4 mg cm⁻², platinum mass ratio of 0.4, volume fraction of dry membrane of 0.3 and catalyst layer thickness of 20 μm.

### ACKNOWLEDGMENT

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### REFERENCES


ADVANCED STUDY OF TRANSITION METAL OXIDE BASED CATHODE FOR PEFCS

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Abstract - We have tried to apply group 4 and 5 metal oxide-based compounds to the cathode catalyst. They were heat-treated at 800-1200°C. The catalytic activities of our materials strongly depended on the degree of oxidation (DOO). Among these materials, partially oxidized Ta complexes and Zr complexes those contain nitrogen had high catalytic activity for the ORR. The onset potentials of them were almost reaching 1.05 V vs RHE. In a single cell test using Zr oxide based cathode we could obtain over 300 mA/cm² at 80°C with hydrogen and oxygen. A significant cost reduction of a cathode might be possible using these Ta or Zr oxide based materials.

Index Terms - cathode, oxygen reduction reaction, polymer electrolyte fuel cell, transition metal oxide,

I. INTRODUCTION
Polymer electrolyte fuel cells are expected for the residential and transportable applications, due to their high power density and low operating temperature. The ENEFARMs (home co-generation system using 1 kW PEFC system) are operating more than 50,000 units in Japan. Fuel cell vehicles will be commercialized in 2015.

However, a significant cost reduction is needed especially for fuel cell vehicles. And the estimated amount of Pt reserve is too small to supply for the huge number of fuel cell systems. In order to commercialize the fuel cell systems widely, the development of a non-precious metal cathode is strongly required.

We think that new non-precious metal cathodes should have both high stability and high catalytic activity for the ORR. In particular, we believe that high stability in cathode condition is essentially required for the cathode catalyst. Some transition metal oxides could be used for the cathode of PEFC. However, most of the transition metal oxides are not stable in the acidic and oxidative atmosphere.

We started this study by searching stable materials in acid and in oxygen. Group 4 and 5 metal oxides, which are well known as valve metals, are stable even in acidic and oxidative atmosphere. However, these oxides are generally insulator. In order to get some electrical conductivity, these oxides should be modified by the formation of the oxygen vacancy and/or the substitution of foreign atoms.

We have reported that partially oxidized group 4 and 5 metal carbonitrides are stable in an acid solution and have definite catalytic activity for the oxygen reduction reaction (ORR) [1-5]. We have tried to apply group 4 and 5 metal oxide-based compounds to the cathode catalyst. In this paper we will report our recent results.

II. EXPERIMENTAL
Powders of transition metal compounds (carbonitride or metal complexes that contain carbon, oxygen and nitrogen) were heat-treated at 800-1200°C under different flowing rate of the H2/N2 gas mixtures that containing small amount of oxygen. After heat treatment, the compounds changed to oxides that contained small amount of carbon and nitrogen.

Heat treated powder was mixed with alcohol, Ketjen Black and Nafion. The mixture was dipped.
on a glassy carbon rod (5 mm diameter) and the working electrode was made. All electrochemical measurements were examined in 0.1 M H₂SO₄ at 30°C under atmospheric pressure using a conventional 3-electrode cell. The RHE was used for the reference in the same solution. Slow scan voltammetry (scan rate: 5 mVs⁻¹) was performed under O₂ and N₂ atmosphere to obtain the current for the oxygen reduction reaction (ORR). The onset potential was defined as the electrode potential at the ORR current density of -0.2 µA cm⁻². A single cell test was performed using oxygen and hydrogen at 80°C.

III. RESULTS AND DISCUSSION

The catalytic activity of our material strongly depended on the degree of oxidation (DOO) for these compounds. An appropriate oxidation is essential to have a definite catalytic activity for the ORR. The onset potentials of partially oxidized Ta carbonitrides and Zr carbonitride were 1.05 V vs RHE that is the onset potential of commercial Pt-C.

In order to improve the current density especially at high potentials we have tried to use metal complexes that have nitrogen and oxygen as starting materials. The ORR currents at 0.8 V vs. RHE were over 3 mA/cm² for Zr compounds. More than 100 times improvements have been achieved using these materials. Figure 1 shows the I-E curve of a single cell test using the Zr compound cathode and Pt anode. We got more than 0.3 A/cm² by this single cell test.

IV. CONCLUSION

Significant cost reduction might be possible using these materials. Although there is still some difference in the ORR activity from Pt/C catalyst, we should say these materials have great potential for a PEFC cathode.

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COMPARISON OF THE CATALYTIC PROPERTIES OF SOFC ANODE SUPPORTS UNDER DRY REFORMING OF METHANE


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Abstract - The work investigates the catalytic properties of different SOFC anode substrates towards the chemical conversion of methane and carbon dioxide into H2 and CO-rich mixtures. The analysis is carried out by means of experiments in micro-reactor configuration. A mass spectrometer is provided to analyze the composition of the gas mixture leaving the reactor and thus allowing the evaluation of methane conversion rate. Furthermore, Temperature Programmed Oxidation (TPO) experiments are performed on the anode samples aiming at the analysis of material activity towards the cracking reaction of methane.

Anode substrates based on different materials and microstructures are taken into account. The work features the effect of materials’ composition and microstructure on the methane conversion rate and carbon cracking.

Keywords - catalysis, SOFC anode, carbon deposition, microstructure.

I. INTRODUCTION

A promising application for solid oxide fuel cells could be the stationary generation of electricity and thermal energy through the utilization of biogas fuel [1]. In this framework, it is interesting to analyze the catalytic activity of typical fuel electrodes towards the chemical conversion of biogas mixtures based on methane and carbon dioxide. Those investigations have been carried out in previous studies [2,3,4,5]. The outline of this work is the evaluation of the impact of material composition and microstructure of SOFC anodes towards the catalytic conversion of methane and carbon dioxide mixtures.

II. EXPERIMENTAL

The analysis of catalytic properties has been carried out by an experimental approach coupling catalysis and microstructural characterizations.

First, different anode substrates based on Ni-YSZ were manufactured by means of tape casting and considering various sintering temperatures: 1200, 1400 and 1500 °C. Those anodes were compared with Ni-GDC substrates sintered at 1400 °C, being the gadolinium doped ceria oxide a better ionic conductor than yttrium stabilized zirconia oxide. Those materials has been compared than with a commercial Ni-based anode substrate.

Concerning the catalysis experiments, they were carried out in a micro-reactor chamber whose details has been reported elsewhere [2,3]. In particular, the TPO experiments were carried out after an exposure of 2 hours to a dry methane feed, increasing the temperature from ambient temperature to 800 °C at 10 °C/min, providing a mixture of 2% vol. O2 in Ar to the micro-reactor. The amount of solid carbon deposited on the catalyst surface during the exposure to methane was thus estimated through the signal of CO and CO2 production.

Figure 1. Comparison of methane conversion yield by different SOFC anode substrates at 800°C

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Specific surface area, mean size of pores and their distribution, which influenced the different responses of the chosen materials, have been estimated by means of BET measurements.

III. RESULTS AND DISCUSSION

In Figure 1, a comparison of methane conversion yield by different SOFC anode substrates at 800°C is shown as function of inlet CO2/CH4 molar ratio. The results suggest a significant effect of the anode sintering temperature on the catalytic conversion of methane; in particular, the higher is the sintering temperature and the lower is the methane conversion rate. For the investigated experimental conditions, the methane conversion yield was always higher than 70%. Moreover, results suggest that the maximum methane conversion is obtained by feeding the cell with an equimolar content of methane and carbon dioxide as explained in [2] with detail. The conversion rate of methane is directly related with the surface area of different materials as shown in Table 1. The results have been obtained by using BET analysis.

<table>
<thead>
<tr>
<th>Anode Typology</th>
<th>Surface area, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-YSZ sintered at 1200°C</td>
<td>1.86</td>
</tr>
<tr>
<td>Ni-YSZ sintered at 1400°C</td>
<td>0.75</td>
</tr>
<tr>
<td>Ni-YSZ sintered at 1500°C</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Ni-GDC sintered at 1400°C</td>
<td>0.9</td>
</tr>
<tr>
<td>Ni-YSZ commercial</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Table 1. Surface area of different anode substrates

In this paper, a catalytic analysis of different anode substrates was carried out aiming at investigating the methane conversion mechanisms in dry reforming conditions. The methane conversion yield has been demonstrated to be strictly related to the surface area of the anode substrate. Conversely, the tendency towards cracking is a more complicated phenomenon closely related to the anode microstructure and grain size. For instance, a proper microstructure design can be beneficial to improve the stability of Ni-YSZ cermet towards carbon formation in comparison with already proven Cu systems [6].

REFERENCES


Figure 2. Results from TPO experiment with Ni/YSZ, 1500°C sintered anode, Figure 2a; Results from TPO experiment with Ni/GDC, 1400°C sintered anode, Figure 2b; Results from TPO experiment with commercial Ni/YSZ, Figure 2c.

The methane conversion has to be coupled also with the activity of anodes towards its cracking into solid carbon. In Figure 2 the results obtained by the TPO are compared for three different anode substrates, namely Ni-YSZ sintered at 1500°C (Figure 2a), Ni/GDC sintered at 1400°C (Figure 2b) and commercial Ni-YSZ (Figure 2c). Results allow to estimate the amount of carbon removed in the course of the experiment; in particular, the minor amount of carbon was found with the Ni/YSZ anode sintered at 1500°C, in this case the amount of removed carbon was around 1.5 mg. In the other cases, the removed carbon was around 5.7 and 11.7 mg respectively for Ni/GDC and commercial Ni/YSZ anode.
THE EFFECT OF REGENERATION ON ADSORBENT MATERIALS FOR H$_2$S REMOVAL FROM BIOGAS FOR FUELING MCFCs

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Abstract - Biogas can be used as fuel for MCFCs, but a clean-up step is necessary to eliminate sulphur compounds and other impurities that can poison Ni electrodes catalysts with consequent decay of the cell performance. Removal of H$_2$S can be achieved by adsorption on suitable materials such as zeolites or active carbons. Nevertheless the choice of the best material should be linked to its regenerability that may reduce the overall costs of the entire clean-up process. In this work, we have studied the effect of regeneration on the adsorption capacity of 13X zeolite, 13X modified by ion exchange method (Cu$^{2+}$) and commercial activated carbon enhanced with Cu and Cr. Although activated carbon is commonly used for this purpose due to the high adsorption capacity, its efficiency drastically reduces after two adsorption/desorption cycles and becomes lower compared to that of 13X exchanged with Cu.

Index Terms - Biogas, MCFC, Regeneration.

I. INTRODUCTION

Besides various biogas applications the possibility of fuelling a Molten Carbonate Fuel Cells (MCFC) for the production of combined heat and power (co-generation) is showing interesting results. The combining of renewable energy sources and high efficiency devices with low environmental impact is certainly a most promising and interesting alternative to the use of fossil fuels [1]. Nevertheless, the biogas cannot be fed directly to the MCFC due to some poisoning compounds contained in the raw biogas, such as sulphur and chloride compounds, that react with Ni catalyst of the electrodes and with the electrolyte, leading to the degradation and short lifetime of the cell [2, 3]. H$_2$S is the most abundant poison compound contained in the raw biogas. Therefore, a clean-up step is necessary to lower the poisons concentration to the very low limits required by the MCFC ([H$_2$S] < 1ppm) [2, 4].

The research is mainly addressed to the removal of these compounds by adsorption on suitable materials that must guarantee low residual concentration, high selectivity and easy regenerability. Zeolites and activated carbons are commonly used for this purpose because of their high adsorption capacities [3, 5]. However, the choice of one or the other can depend strongly on their regenerability that reduces the overall costs of the clean-up plant.

In this work, we have studied the effect of regeneration on the adsorption capacity of some materials that appeared the most effective sorbent materials for H$_2$S removal from biogas.

II. EXPERIMENTAL

A. Materials and methods

Commercial 13X zeolite (Si/Al ratio = 1.5, spherical, d = 1.6 mm) was supplied by Union Carbide; activated carbon (AC) by Norit® (Norit RGM3) (cylindrical, d = 3 mm, l = 7 mm).

13X zeolite was modified with ion exchange technique using a 0.1M solution of Cu(NO$_3$)$_2$·2.5H$_2$O at 80 °C for 2h, under stirring condition. Afterwards the sample was separated from the solution and thermally treated in air flow at 250 °C for 2 h (13X Exchanged Cu) [5].

AC was modified by addition of Cu and Cr by Norit®. The samples were characterized by scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) for the elemental analysis using a Philips XL 30 apparatus.

Surface area measurements were carried out by N$_2$ adsorption at 77 K using a Micromeritics ASAP 2020 instrument.

B. Experimental apparatus

H$_2$S adsorption tests were carried out in an innovative laboratory apparatus, flowing a gaseous mixture (6 L h$^{-1}$) containing 10 ppm of H$_2$S through a fixed bed of the sample.
(0.02 g). The effluent from the adsorption cell was analyzed by a new potentiometric method in order to obtain the breakthrough curves. The details of this method were described in a previous work [5]. This technique allows a sensitivity as low as a fraction of 1 ppm H$_2$S in the gaseous phase.

C. Regeneration

The regeneration step was carried out in situ, under air flow (6 L h$^{-1}$) at 250°C for 6 h. Several adsorption/desorption cycles (from 0 to 4) were conducted to determine the degree of decay of H$_2$S adsorption efficiency of the materials studied.

III. RESULTS

The metal content and surface area of the samples are shown in Table I.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal content (mmoleq g$^{-1}$)</th>
<th>Surface area (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu$^{2+}$</td>
<td>Na$^+$</td>
</tr>
<tr>
<td>13X</td>
<td>3.65</td>
<td>1.92</td>
</tr>
<tr>
<td>13X Exchanged Cu</td>
<td>4.66</td>
<td>0.22</td>
</tr>
<tr>
<td>Norit RGM3</td>
<td>1.15</td>
<td>-</td>
</tr>
</tbody>
</table>

* K$^+$, Ca$^{2+}$, Mg$^{2+}$ for zeolites; Cr$^{3+}$ for AC.

The breakthrough curves were obtained for the starting samples and after each adsorption/desorption cycle. The quantity of H$_2$S adsorbed (mol g$^{-1}$) was measured at the breakthrough time corresponding an exiting concentration of 1 ppm: these values are reported in Fig. 1.

![Figure 1](image)

**Fig. 1.** Quantity adsorbed at [H$_2$S]$_{out}$ = 1 ppm as function of adsorption/desorption cycles

The results confirm that the presence of Cu into 13X zeolite increases the adsorption capacity, due to the high stability of Cu-S compounds. The performance of 13X Exchanged Cu sample decreases sharply with the first regeneration step, after which the adsorption capacity decays slowly. The unmodified zeolite does not show the initial marked decay and its adsorption capacity reduces with the adsorption/desorption cycles more slowly in comparison with the modified zeolite, even though the efficiency is still lower.

The sample Norit RGM3 shows better performance than the zeolites, due to the high surface area and the presence of Cu in the matrix that enhances the chemisorptions. The adsorption capacity of AC reduces drastically after two cycles and its performance becomes lower than that of 13X Exchanged Cu and comparable with that of the modified zeolite at the first cycle.

IV. CONCLUSION

A study on the regenerability of H$_2$S adsorbing materials has been carried out with a new laboratory apparatus that allows to evaluate H$_2$S concentrations of less than 1 ppm, the tolerance limit required for fueling MCFCs. The results show that the addition of Cu improves the H$_2$S adsorption capacity of 13X zeolite, even after several adsorption/desorption cycles. The activated carbon exhibits higher performance than zeolites in the first test, nevertheless its efficiency reduces drastically after few cycles and the adsorption capacity becomes lower compared with the modified and unmodified zeolites.

These data suggest that different regeneration procedures should be studied if the materials have to be used for several adsorption/desorption cycles. Moreover the study should be extended to other poisoning substances contained in the raw biogas, in view of designing a clean-up process for feeding MCFCs.

REFERENCES

HYDROGEN PRODUCTION BY METHANE ATR IN A COMPACT CATALYTIC REACTOR THERMALLY INTEGRATED: STRUCTURED CATALYSTS PERFORMANCES ANALYSIS

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Abstract – The present work focuses on the catalytic support influence on the performances of the methane auto-thermal reforming. The catalytic tests were carried out on an adiabatic reactor able to pre-heat reactants by exploiting sensible heat of exhaust stream. Activity tests were carried out on commercial honeycomb and foam noble metals based monolithic catalysts investigated. The honeycomb catalyst was used as one piece or sized in 5 bricks spaced between them, in order to understand the advantages of the different catalyst arrangement. As expected, the continuous reaction stream mixing occurred in 5 bricks arrangement led to a sensible improvement in system performances; on the other hand, the one piece arrangement promoted conductive heat transfer mechanism in the catalyst, resulting in a flatter thermal profile. The use of a foam catalyst combines the advantages of the one-piece and divided monolith, since a continuous stream mixing was obtained in a one-piece monolith.

Index Terms - Auto-thermal Reforming, Structured Catalyst,

I. INTRODUCTION

Nowadays, the combination hydrogen-fuel cell is seen as the most viable solution to counter the antithetic problems of energy growing demand and environmental pollution [1]. The high difficulties in H2 transport and storage make the distributed production a very interesting solution. Since very flexible production as well as quick start-up and shut-down procedure are fundamental features, H2 production by auto-thermal reforming of hydrocarbons results as the optimal solution for the coupling with a fuel cell system.

Auto-Thermal Reforming (ATR) is typically considered as the overlap of several chemical reactions, such as fuel partial and total oxidation, steam reforming. The different kinetics of the involved reactions suggest that the oxidation reactions occur as first; the heat developed by fuel oxidation is used to sustain the endothermic steam reforming reaction. Therefore, the choice of an appropriate catalytic system is a fundamental step in the reaction setup. It should show high selectivity towards reforming reactions (POX, SR), inhibit side reactions as cracking and coke formation, generate low pressure drop in operating conditions and, finally, it should be characterized by high resistance to mechanical shocks and thermal gradients. Previous studies confirmed the importance of a flat thermal profile along the catalytic bed: in this way, honeycomb and foam monolithic catalysts result as the favorite solutions.

Aim of this work is to analyze the influence of the catalytic supports in the performances of an ATR.

II. EXPERIMENTAL

Honeycomb and foam monoliths, with a similar chemical composition (noble metals based) were selected as support for methane ATR catalytic tests carried out in a thermally integrated reactor, designed and realized [2] to produce up to 5 Nm3/h of hydrogen. Air and water are also fed to the system; reactants flow rates are controlled by mass-flow controllers (Brooks) for gases and Quantum (Brooks) for liquid reactant.

The catalytic bed was designed with a rectangular section sized W60 x H80 x L75 mm that allows a quick access to the catalytic volume, so facilitating the maintenance procedures. Several catalyst arrangements as well as different support materials were used, in order to investigate the relevance of thermal properties and stream flux in the system performances.

In reactor design, great attention was paid to the thermal integration in order to obtain a total self-sustained process, without additional external heat sources, and so improving plant compactness. Downstream the reaction volume a specific heat exchanger was placed to pre-heat air and vaporize and over-heat water by recovering heat by products stream. The adopted configuration of heat exchange module maximizes the heat transfer to the reactants. Pre-heated reactants (steam and air)
and cold methane were sent to a mixing module placed just before the reactor. Its particular shape, realized with subsequent constrictions and expansions, assures a homogeneous reactants stream delivered to the reaction module. In the start-up phase, the reaction was triggered by an electrical resistance placed just before the catalyst volume.

Since the knowledge of temperature and composition profiles along the reactor allows to understand the trend of chemical reactions along the catalytic bed, the process monitoring was assured by a series of thermocouples and sampling lines placed along the reaction module as well as in the mixing module. Furthermore, the temperature was monitored also downstream the heat recovery module, in order to evaluate the heat exchange efficiency. Sampled streams were analyzed by means of a mass spectrometer. Compositions and temperatures were recorded by a Hiden Analytical system.

Activity tests were performed by feeding CH₄, air and H₂O at a space velocity of GHSV = 80,000 h⁻¹ and with a feed ratio H₂O/O₂/C = 0.49/0.56/1. In first tests, commercial noble metals based honeycomb monoliths (provided by BASF) were used. Two configurations were adopted: (i) the catalyst was placed as a singular structured unit inside the reactor volume or (ii) the catalyst was sized as 5 bricks, placed at 4 mm between them, in order to improve the mixing of streams. Moreover, a noble metals based alumina foam (AL92) catalyst (provided by Johnson Matthey) was tested: the catalyst was arranged as a continuous cylindrical shape. All tests were carried out at a pressure of 1.4 barg (0.1 barg for the one-piece honeycomb).

III. RESULTS AND DISCUSSION

Tests results are summarized in Figure 1 and Table 1:

![Figure 1 - Thermal profile along the catalytic bed for the different catalysts](image)

As the most evident result, the continuous structures show a flatter thermal profile along the catalyst: this result underlines the relevance of thermal conductivity phenomena for the catalyst performances. However, for the one-piece honeycomb catalyst, a not negligible heat loss along the catalytic volume was observed, that of course effected on thermal profile.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Test Tₜ</th>
<th>Test T_OUT</th>
<th>(Ad. React.) X₈CH₄</th>
<th>Test (Therm. Eq.) Y_H₂</th>
<th>Test (Therm. Eq.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>One Piece Monolith</td>
<td>730°C</td>
<td>693°C</td>
<td>851°C</td>
<td>89.2% (98.2%)</td>
<td>72.6% (82.0%)</td>
</tr>
<tr>
<td>5 Bricks Monolith</td>
<td>811°C</td>
<td>760°C</td>
<td>780°C</td>
<td>95.8% (98.7%)</td>
<td>77.0% (81.3%)</td>
</tr>
<tr>
<td>AL92</td>
<td>730°C</td>
<td>708°C</td>
<td>736°C</td>
<td>91.7% (92.7%)</td>
<td>72.0% (76.1%)</td>
</tr>
</tbody>
</table>

On the other hand, by comparing monoblock and 5 bricks honeycomb catalyst performances, a great influence of catalyst arrangement was observed. The stream mixing along the catalytic volume, assured by the 5 bricks arrangement, leads to an enhancement in the system performances, with an outlet composition very closer to thermodynamic values than in the case of one-piece catalyst. To confirm this feature, the AL92 foam catalyst approach very well as well as very quickly the thermodynamic equilibrium, however the AL92 catalytic formulation is quite different to the further.

IV. CONCLUSIONS

The catalyst structure and arrangement was studied. Experimental results underlined that the better thermal management in the catalytic volume allows a faster approach to thermodynamic equilibrium. On the other hand, the comparison between the one-piece and the 5 bricks monoliths performances remarked the relevance of a chaotic stream flux along the catalytic volume that assures a stream radial uniformity both in terms of gas composition and temperature. The process gas mixing obtained in the 5 bricks configuration and in the foam catalyst led to a very high hydrocarbon conversion and H₂ production just in the early zone of the catalytic bed, so resulting suitable to operate at higher operating conditions. To confirm that aspect, further studies will be carried out on foam and honeycomb catalyst with the same catalytic composition and loading.

V. ACKNOWLEDGEMENTS

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REFERENCES


ELECTROLYSIS STUDY OF CERIA-CARBONATE COMPOSITE FOR EFFECTIVE H2 PRODUCTION

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Abstract – The hybrid ionic conduction of ceria-carbonate composite is an interesting field that has attracted plenty attention in the past decade. However, it has not reached universal agreement among the researcher. Novel characterization method is still needed to reveal this complex system and benefit the future advanced materials design and development. In this work, the electrolysis operation is employed to investigate the possible ionic conduction behavior of ceria-carbonate. The other goal is to optimize the processing technology to maximum the kinetics rate for efficient hydrogen production. An impressive current density of 1.2 A cm$^{-2}$ has been achieved at 600 °C under voltage of 1.6 V at the absolute humidity of 3% and oxygen ionic operational mode.

Keyword: ceramic fuel cell, ceria-carbonate composite; Ni electrode, oxygen ion and proton conduction

I. INTRODUCTION

The ceria-carbonate composite has attracted considerable attention in the recent years because of its super-ionic conductivity and unique hybrid proton and oxygen ion conductive property for LT CFC and other advanced applications. The impressive electrolyte performances have been widely demonstrated by several research groups1-3. In parallel, the multi-ionic conductive properties and its related interface property, ionic conduction path and ionic interaction have also been extensively investigated. However, not like the approved excellent fuel cell performance, the studies of ionic conduction mechanism have not reached the universal agreement. Instead, some contrary conclusions were made4-6. Thus the investigation of ionic properties of ceria-carbonate is still an open question and a challenge.

Versatile techniques have been used to study the multi-ionic conduction behaviors of ceria-carbonate, such as the concentration cells, ac impedance spectroscopy, dc four-probe method even coupling with some advanced ex-situ instruments, like Fourier transform infrared spectroscopy. However, as suggested by B. Zhu, most of them can not suitable to determine the universal value of the conductivity and transport properties in composite electrolyte with multi-ions conduction7. Then fuel cell, i.e. in situ technique, was suggested to study the property. At a later time, high temperature electrolysis, a reverse process of fuel cell, is also adopted to study the ionic conductive behaviors in the composite electrolyte since it is more close the in-situ condition/atmosphere of fuel cell than other analysis8.

It should be noted that the high temperature electrolysis process is current the most high efficient process for hydrogen production. Especially, the electrolysis operation is the most closed situation to fuel cell condition. Thus it is very worthy to study the ionic conduction behavior of ceria-carbonate composite and simultaneously produce high valuable and green hydrogen fuel in the electrolysis process.

II. RESULTS AND DISCUSSION

Single cell with ceria-carbonate composite electrolyte and Ni-based electrode exhibits excellent performance both in fuel cell mode and electrolysis mode. A notable current density of 1.2 A cm$^{-2}$ has been obtained at 600 °C under applied voltage of 1.6 V and 3% humidity in cathode side, i.e. oxygen ionic conduction mode. The effect of temperature on the electrolysis cell is given in Figure 1. The ohmic resistance (the high frequency intercept of impedance spectroscopy) decreases with the incline of the temperature, while the electrode polarization resistance keeps almost unchanged, indicating the sufficient electrode catalytic activity of Ni-based electrode. The same phenomenon has also

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been observed in previous work\(^9\). Low total polarization resistance less than 0.6 Ωcm\(^2\) has been obtained at 500 °C.

The relative humidity also plays an important role on the electrolyze performance. Interesting, the increase of the humidity of anode chamber reduce the ohmic resistance and total polarization resistance, which can be ascribed to the suitable electrical conductivity and high catalytic activity of Ni-based electrode.

The performance of fuel cell under proton conducting mode, i.e. the water stream is provide from the anode side, is also investigated and the electrolysis rate is demonstrated to compared to the oxygen ionic conducting mode. The results presented here prove again that the ceria-carbonate composite is a hybrid proton and oxygen ionic conductor.

III. CONCLUSION

Ceria-carbonate composite and Ni-based electrode exhibited promising electrochemical properties in electrolysis mode, making it a alternative candidate for high efficient hydrogen production for future application.

ACKNOWLEDGMENT

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REFERENCES


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LOTUS: design and validation of a microCHP system and its components

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Abstract – In the LOTUS project a 1kWe micro-CHP is developed for residential applications. The system is based on SOFC technology operating at 650°C, lower than usual. The components of the system have been sourced as off the shelf products where possible. Some parts have been developed, built and tested at the partners facilities. Some of these data are described in this publication. The complete system has been assembled and tested.

Index Terms – burner, micro-CHP, SOFC, steam reformer

I. INTRODUCTION

In the, FCH-JU funded (GA256694), LOTUS project a micro-CHP system is designed, built and tested based on Low temperature SOFC technology combined with a natural gas steam reformer. Over the last three years the LOTUS project has resulted in the system prototype which has been operated to measure functionality, efficiency (based on a Natural gas consumption of 3.8 slm and 946.5 W electricity and 898 W heat out) and reliability. The technology is based on a 650°C – 700°C SOFC stack from SOFCpower (I), a natural gas steam reformer system from HyGear Fuel Cell Systems (NL) and blower technology from Domel (Sl). The presentation will show the entire cycle of the design and construction of the LOTUS system. From the early modelling, performed by IKTS (D) and component testing by the University of Perugia (I) and JRC (B), the component and system design, construction and finally the testing of the system, validating the modelling results.

During the previous Piero Lunghi Fuel cell conference in 2011 the first steps in the design and construction of the LOTUS system have been shown [1] describing the components which were to be delivered for a successful system. The components described in this contribution have been designed, constructed and some have been tested in separate testing environment prior to integration in the system. This paper shows results of the stand alone testing and show the final design of the system which will be tested.

II. BURNER TESTS

A. Experimental

Next to the SOFC stack and the reformer, the burner is one of the key-components of the system as it has the function to provide heat to the reformer, the air pre-heater and steam generator during start up and nominal operation. This means that the burner should have dual fuel capability, combusting natural gas and also anode tail gas from the SOFC stack. This functionality is checked in a separate burner test.

The burner is a swirl burner type and consists of a 4 cm diameter metal cup with 6 central holes for fuel inlet surrounded by 12 (4 primary and 8 secondary) air inlet holes. It has been tested in a test station which could provide the gas compositions supplied by the modelling of the LOTUS partner IKTS. The gas flows are given in table 1. The flow could be heated to the desired inlet temperature.

<table>
<thead>
<tr>
<th>Components</th>
<th>Start up (SLM)</th>
<th>Nominal operation (SLM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>330</td>
<td>242</td>
</tr>
<tr>
<td>CH₄</td>
<td>8.4</td>
<td>0.02</td>
</tr>
<tr>
<td>H₂</td>
<td></td>
<td>5.16</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td>14.74</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td>0.86</td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
<td>4.19</td>
</tr>
</tbody>
</table>

The critical parameter for the start up case is the combustion of the methane to avoid methane emissions during this phase. The critical parameter for the nominal operation is the combustion of hydrogen and carbon monoxide coming from a S/C ratio of 3 in the reformer. Both technical requirements are mainly determined out of certification and safety needs and mandatory for commercial future use.

B. Results

The methane destruction during start up simulation are shown in figure 1 below.
The left side of the plot shows that methane destruction is a function of the flow rate in general. Decreasing the methane and air flow increases the methane combustion. The middle section show that increasing the air fuel ratio decreases the methane combustion again, but if the air temperature is increased the methane is destroyed again at the start up conditions. Measured temperatures at various places in the burner tube showed around 1100°C close to the burner cup during an experiment. It has thus been shown that during the envisioned start-up procedure, with increasing air fuel ratios and increasing operation temperatures, methane combustion meets the targets. In the prototype testing it should be decided if these conditions lead to realistic start up times. These depend on the heating rates of the components in the system and is limited by the heating rate of the SOFC stack which should be not higher than 3°C/min.

In the SOFC system the air pre heater is the first component which will be heated to start up the stack. This means that using this burner set up controlling the fuel and air flow a zero emission start up of the system can be accomplished.

Experiments feeding the burner with simulated reformate show that all H₂, CO and CH₄ are combusted at temperatures of around 800°C in the burner.

III. THE LOTUS SYSTEM

The components (stack from SOFC Power and blower from Domel) for the LOTUS system have been collected at HyGear. All other components (Reformer, burner, heat exchangers and BOP) have been constructed or sourced at HyGear. The system has been assembled. In the prototype a lot of measurement equipment is installed like thermocouples, mass flow meters and pressure meters. These are needed to further develop and fine-tune the controls of the system.

The first phase of testing is to determine the control parameters (gas flows, temperatures) of the system to ensure safe and reliable operation. This requires special attention because the LOTUS system is equipped with only one blower, to reduce costs and increase reliability, which pulls the gas, steam and air through the system. The temperature of the stack will be controlled by the incoming air flow using the air preheater. A by-pass around this heat exchanger can be used to vary the inlet temperature and thus the stack temperature. The next testing phase will gather validation data for the dynamic system modelling performed by LOTUS partner IKTS.

Figure 2 shows a photograph of the LOTUS system without insulation to show the reactors and heat exchangers. In the back there is the stack box delivered by SOFC Power.

IV. CONCLUSIONS

The LOTUS system has been developed and constructed to meet the requirements of 45% electrical efficiency and 80% CHP efficiency.

Component testing of the burner showed that a combined start up and tail gas combustion has been successful showing that it is possible to operate the system without flammable or poisonous emissions.

ACKNOWLEDGMENT

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COMPATIBILITY STUDY OF La$_{1.5}$Sr$_{0.5}$Ga$_3$O$_{7.25}$ ELECTROLYTE WITH LANTHANUM FERRITE-BASED CATHODE


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Abstract - Melilite-type gallate, La$_{1.5}$Sr$_{0.5}$Ga$_3$O$_{7.25}$ (LSG) appears to be promising as electrolyte material for intermediate temperature solid oxide fuel cells (IT-SOFCs). To achieve good cell performances, the cathode material must be chemically stable at high temperature, the reactivity among adjacent components must be at minimum and the thermal expansion must match. In this study, the compatibility between LSG and doped lanthanum ferrite, La$_{0.8}$Sr$_{0.2}$Fe$_{0.9}$Cu$_{0.1}$O$_{3-d}$ (LSF9C1) as cathode material was investigated. A 50:50 mixture of the two as-prepared materials was pressed in the form of pellet and thermally treated in the range 773-1573 K. After each thermal treatment, X-ray diffraction patterns of the mixtures were recorded to check for formation of new phases resulting from reaction between the two phases. This study shows the high stability and compatibility of the LSG-LSF9C1 system to be used for IT-SOFC applications.

Index Terms – Melilite-type gallate, solid oxide fuel cells, electrode-electrolyte chemical compatibility, doped lanthanum ferrite

I. INTRODUCTION

Recently, melilite-type gallate La$_{1.5}$Sr$_{0.5}$Ga$_3$O$_{7.25}$ has attracted interest as electrolyte for intermediate temperature solid oxide fuel cells (IT-SOFCs) [1] due to its good oxide ion conductivity (0.02-0.1 S cm$^{-1}$ for $x=0.54$) between 873 K and 1173 K. However, the electrolyte must also show a good chemical compatibility with the other components of the fuel cell assembly. The formation of low conductive phases at the electrolyte-electrode interface due to high temperature reaction of the components can be detrimental to the fuel cell performance. At present, one of the most used cathodes for SOFCs is the perovskite oxide La$_{1-x}$Sr$_x$MnO$_3$ (LSM). However, it is known that manganese is a mobile species at high temperature, thus to minimise its migration the fabrication temperature has to be below 1473 K. An alternative cathode material is the series La$_{1-x}$Sr$_x$Fe$_{1-y}$Cu$_y$O$_{3-d}$, which was first proposed for IT-SOFCs applications by Coffey et al. [2]. In this work the perovskite-type L$_{0.8}$Sr$_{0.2}$Fe$_{0.9}$Cu$_{0.1}$O$_{3-d}$ (LSF9C1) is proposed as cathode material in combination with La$_{1.50}$Sr$_{0.50}$Ga$_3$O$_{7.25}$ (LSG) as electrolyte. The chemical stability of LSG-LSF9C1 system is extensively studied as a function of increasing temperature (up to 1573 K) in order to test the feasibility of this novel system for IT-SOFC applications.

II. EXPERIMENTAL PROCEDURE

A. Synthesis of La$_{1.50}$Sr$_{0.50}$Ga$_3$O$_{7.25}$ (LSG)

La$_{1.50}$Sr$_{0.50}$Ga$_3$O$_{7.25}$ melilite powder was prepared by solid state reaction. La$_2$O$_3$, SrCO$_3$ and Ga$_2$O$_3$ were used as starting materials. All precursors were weighed in the stoichiometric amounts and ground together in an agate mortar. Ga$_2$O$_3$ was weighed with a 3.0%wt excess in order to prevent the gallium evaporation at high temperature. The precursor mixture was pelletized in an isostatic oil press (2000 bars for 5 min) and treated twice at 1473 K for 20 h and 15 h respectively, and finally at 1673 K for 8 h. Each step was accompanied by an intermediate grinding and repelletization.

B. Synthesis of La$_{0.80}$Sr$_{0.20}$Fe$_{0.9}$Cu$_{0.1}$O$_{3-d}$ (LSF9C1)

La$_{0.80}$Sr$_{0.20}$Fe$_{0.9}$Cu$_{0.1}$O$_{3-d}$ (LSF9C1) was prepared by sol-gel method using citric acid as chelating agent. La$_2$O$_3$, Fe(NO$_3$)$_3$•9H$_2$O, Cu(NO$_3$)$_2$•2.5H$_2$O and Sr(NO$_3$)$_2$, (C$_6$H$_8$O$_7$•H$_2$O),HNO$_3$, (65%), and NH$_3$ were supplied by Sigma-Aldrich. La$_2$O$_3$ was dissolved in HNO$_3$ solution to prepare the corresponding nitrate salt. The solution of metal nitrates in water was poured in citric acid solution, with the molar ratio of metal ions to citric acid being set at 1:1. After
adjusting the pH to about 7 by NH₃ addition, the solution was evaporated and the obtained dry gel was heated in air to 523 K to start ignition and at 873 K for 3 h to remove any organic residue.

C. Compatibility Tests
A 50:50 wt% powder mixture was prepared by blending the melilite powder with LSF9C1. The obtained powder was pressed isostatically at 2000 bars for 5 min to enhance the contact between the two phases. The obtained dense pellets were then treated for 12 h at selected increasing temperature of 773 K, 973 K, 1173 K, 1373 K and 1573 K.

D. Materials Characterization
X-ray powder diffraction data were collected using a Bruker D8 diffractometer with Cu Kα₁ radiation and 1D scintillator detector. Each measurement was performed in Bragg-Brentano geometry, with flat aluminum sample holder, 0.02° increment size and acquisition time of 15 sec/step over the 20 angular range 10-90°. X-ray diffraction was used to verify the purity, crystallite size and structure of the synthesized compounds, and to investigate the presence of impurity phases after the thermal treatment of the mixture.

III. RESULTS AND DISCUSSION
Structural characterization confirmed that the prepared materials are single phases. Rietveld refinements were performed with FullProf package to obtain the lattice parameters. The obtained results are in agreement with the literature data [1,3]. Figure 1 shows the diffraction analysis progression for the mixture. As shown in the figure, no evidences of variation in composition, such as new diffraction peaks or other significant profile modifications, can be detected up to 1573 K for the mixture. A detailed analysis of the diffraction peaks shows that the broad peaks of the nanometric LSF9C1 powder get progressively narrower increasing the temperature. A slight shift of the peaks to higher angles is also observed, due to the increasing treatment temperature. Despite these minor changes, the materials show a high thermal stability and a very good compatibility with no evidence of chemical reaction, confirming a feasible application of this system in intermediate and high temperature fuel cell devices.

IV. CONCLUSION
The chemical reaction at high temperatures between La₁.50Sr₀.50Ga₃O₇.25 and La₀.8Sr₀.2Fe₀.9Cu₀.1O₃₋₋ was investigated in order to test the suitability of these materials as electrolyte and cathode materials for IT-SOFCs, respectively. The thermal stability and chemical reactivity between the two phases was studied by XRD analysis. No significant reactions between the two materials was observed in the investigated temperature range (773-1573 K), which proves the feasibility of this novel electrolyte-electrode system for IT-SOFC applications.

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REFERENCES
A REVIEW OF THE MOST EFFICIENT LOW-PT AND PT-FREE ELECTROCATALYSTS FOR HYDROGEN PEMFCs

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Abstract – The main target of the PEMFC’s scientific community is to reduce the total Pt loading to ca. 150 g cm\(^{-2}\) MEA, maintaining simultaneously high PEMFCs performances. The last years, promising results have also been reported concerning the design, fabrication, characterization and testing of novel Pt-free anodes and cathodes for H\(_2\)-PEMFCs applications. The present work aims at providing the state-of-the-art of the most efficient low-Pt and Pt-free electrocatalysts for H\(_2\)-PEMFC.

Keywords: Low Pt loading electrocatalysts, Pt-free electrocatalysts, H\(_2\)-PEMFC’s.

I. INTRODUCTION

The higher energy efficiencies for both anode and cathode reactions in polymer electrolyte membrane fuel cells (PEMFCs) fed with hydrogen have been achieved over Platinum-based electrocatalysts. The scarce world reserves of Pt and its high price significantly contribute to the total cost of PEMFCs hindering a feasible commercialization of them. Many studies have been devoted to the reduction of Pt loading and development of electrodes high performance. Taking into account all the previous studies with different conditions that were tested, in order to obtain electrodes with high performances for HOR and the ORR, we present here the most efficient low Pt and Pt-free electrocatalysts for Hydrogen PEMFC reported in the International literature.

Low platinum Anode for Hydrogen PEMFC

In order to reduce Pt loading in PEMFCs the techniques of: sputter deposition [1], hydrothermal method [2], electrospinning and chemical Dealloying [3, 4], thin film [5, 6], ion beam assisted deposition method [7] etc are used. The maximum power density (1200 mW cm\(^{-2}\), Fig. 1), was reached by Manthiram et al. [6] over uncatalyzed gas diffusion electrodes. The anode and the cathode were loaded each one with 100 µg cm\(^{-2}\) of Pt supported on carbon black. Pintauro et al. [4] obtained 906 mW cm\(^{-2}\) (59 µgPt cm\(^{-2}\)), with long-term durability. Sung et al. achieved 750 mW cm\(^{-2}\) (32 µgPt cm\(^{-2}\)) [8]. Brault et al.[9] fabricated electrodes with ultralow content (10 µg/cm\(^{2}\) for the anode and 10 µg/cm\(^{2}\) for the cathode) by the aid of magnetron co-sputtering of carbon and platinum on commercial E-Tek uncatalyzed gas diffusion layer which presented high power density of 400 mWcm\(^{-2}\) corresponding to a specific power of 20 mW/µgPt\(^{1}\).

Fig. 1. Maximum Power Density (mW cm\(^{-2}\)) dependency over different low platinum anodes and cathodes. In the brackets is reported the total platinum amount (µg cm\(^{-2}\)) contained.

As is observed, despite the very low Pt loading, this electrocatalyst presented the highest power density values. Erlebacher et al. [10] fabricated platinum-plated nanoporous gold leaf (Pt-NPGL) MEA (carbon-free electrocatalyst) exhibiting maximum power density 250 mW cm\(^{-2}\).

Low platinum Cathode for Hydrogen PEMFC

As it can be distinguished in Fig. 1, ultra-low pure Pt-based electrodes were prepared by dual ion-beam assisted deposition method by Mukerjee et al. [11] which exhibited a performance of 922 mW cm\(^{-2}\) with cathode platinum loading of 50 µg cm\(^{-2}\). Due to this significant improvement, Mukerjee et al. [7] used the same method with cathode platinum loading of 80 µg cm\(^{-2}\) and H\(_2\)-PEMFCs performance value at 788 mW cm\(^{-2}\). Ultra-low platinum loading cathode electrocatalyst of 12 µgPt cm\(^{-2}\) was fabricated using thin films of multivall carbon nanotube supported Pt catalysts (Pt/MWNTs) [12]. As it can be seen (Fig.1) the peak power density, for a membrane electrode assembly with 12 µgPt cm\(^{-2}\) tested at 70°C, is 613 mW cm\(^{-2}\).

Non platinum Anodes and Cathodes for Hydrogen PEMFC

Many investigations have been devoted to the study of Pt-free anodes or Pt-free cathodes for H\(_2\)PEMFCs. Fig.2 demonstrates the potential for expensive and scarce Pt to be replaced by non-Pt electrocatalysts in PEMFC anodes. The highest performance...
Recently, Chang et al. [14] over Pd/Au/WC catalyst achieved a performance of 238 mW cm\(^{-2}\). In case of PdNi/WC anode, the strong interaction between PdNi alloys and WC caused a performance of 230 mW cm\(^{-2}\).[15]. Jacobson et al. [16] measured maximum power density value of 100 mW cm\(^{-2}\), which is the third better fuel cell performance on non-Pt anodes.

The highest performance reported in the literature for non-platinum cathode in H\(_2\)-PEMFC, obtained by Proietti et al.[17]. They achieved 910 mW cm\(^{-2}\), for Fe-based cathode catalysts.

II. CONCLUSION

In the present work are illustrated the most efficient low and non-Pt anode catalysts reported in the international literature. The highest performance for Pt-free anodes reported in literature was 560 mW cm\(^{-2}\) and obtained by a carbon supported 40%Ir-10%V/C, while the highest maximum power density reached 1200 mW cm\(^{-2}\) during H\(_2\)-PEMFC operation over thin film Pt/C anodes.

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REFERENCES


Pd$_x$Ru$_y$/C binary catalysts for glucose electrooxidation

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Abstract - Pd$_x$Ru$_y$/C (x:y=1:2, 1:3, 2:1 and 3:1) electrocatalysts are prepared by a modified pulse microwave assisted polyol method and are studied for glucose electrooxidation in alkaline media. The effects of glucose’s concentrations as well as of temperature on the activity of electrocatalysts are also investigated. According to the CV results, the electro-catalytic activity towards glucose electrooxidation of the investigated catalysts has the following order: Pd$_2$Ru/C > Pd$_3$Ru/C > PdRu/C > PdRu$_2$/C > PdRu$_3$/C. It was found that increasing glucose’s concentration from 0.02 M to 0.5 M the current increases. Additionally, the increment of temperature enhances glucose electrooxidation until 40°C.

Keywords: glucose electrooxidation, alkaline media, Pd$_x$Ru$_y$/C electrocatalysts, direct glucose fuel cells.

I. INTRODUCTION

The electrooxidation of glucose has been studied extensively principally because of the interest in the development of glucose sensors [1]. An implantable, miniature, accurate and reliable sensor to monitor the glucose concentration in the body is desirable for treatment of diabetes mellitus. An implantable glucose-oxygen fuel cell has been proposed for artificial hearts using glucose and oxygen in the blood as the reactants [1]. Glucose oxidation reaction has been studied in acid, neutral [2] and alkaline solutions. In acid solutions, the oxidation of glucose has been studied on the Pt electrode mostly in H$_2$SO$_4$ and HClO$_4$. While usually the neutral electrolyte is phosphate buffer and the alkaline electrolyte is sodium or potassium hydroxide. In literature has been proved that alkaline environment enhances electrooxidation of liquid fuels [3]. However, platinum is not a suitable electrode for the sensor application in the blood and psychological condition due to itself poisoning in glucose oxidation and chemisorption of chloride ion and other blood components. Moreover, it lacks long term stability, it is rare and expensive metal [4]. In the present work we report for first time in literature, the study of glucose electrooxidation on Pd$_x$Ru$_y$ (20 wt%)/C (x:y=1:1, 1:2, 1:3, 2:1, 3:1). More precisely, the effect of glucose’s, electrolyte’s concentration and temperature were studied, extracting important kinetic parameters for glucose’s reaction.

II. EXPERIMENTAL

A. Catalysts’ Preparation

The Pd$_x$Ru$_y$/C electrocatalysts were fast and easily prepared by a modified pulse-microwave assisted polyol synthesis method [5].

B. Physicochemical Characterization

The X-ray Diffraction (XRD) measurements were carried out by the aid of a D/Max-IIIA (Rigaku Co., Japan) employing Cu K$_\alpha$ ($\lambda=0.15406$ nm) as the radiation source. The samples were scanned over the range 10° ≤ 2θ ≤ 86°. The peak at 68° (Pd 220) was used for the calculation of crystallites size. Transmission electron microscopy (TEM) was used to determine the surface morphology and size of the particles.

C. Electrochemical Characterization

The as-prepared electrocatalysts were evaluated for glucose electrooxidation in a three-electrode cell assembly connected to electrochemical station (AMEL 5000). As reference electrode was used a mercury/mercury oxide (Hg/HgO) (in 1.0 mol L$^{-1}$ KOH) and as a counter electrode was used a platinum wire one. The catalyst layer was prepared dispersing 5.0 mg of the as-prepared electrocatalyst powder in 1.8 mL ethanol and 0.2 mL Nafion® ionomer for 40 min. The catalyst ink was then quantitatively (10 µL) transferred onto the surface of the glassy carbon disk electrode by using a micropipette and dried under infrared lamp to obtain a catalyst thin film.
III. RESULTS AND DISCUSSION

A. Physicochemical Characterization

From the Scherrer’s equation [6] and the TEM images the nanoparticles sizes were calculated for all the samples 2.0 - 4.0 nm. Moreover, from the TEM images the nanoparticles were homogenously distributed on Vulcan-XC-72.

B. Electrochemical Characterization

In Fig. 1 are depicted the cyclic voltammograms of the Pd_{x}Ru_{y}/C electrocatalysts in 0.5 M KOH containing 0.5 M glucose. As it is observed (Fig. 1) two anodic broad peaks (united in one) are formed.

The observed two peaks during the forward scan can be attributed to the oxidation of glucose and resulting intermediates. During the cathodic potential scan, the oxidation of glucose is suppressed in the high potential range because of the presence of surface oxide [7].

As it is observed from Fig. 2, increasing the temperature, the electrocatalytic activity is enhanced and peak potentials shift to more positive values. Moreover, increasing glucose’s concentration, current density increases (Fig. 3).

IV. CONCLUSION

In this study binary Pd_{x}Ru_{y}/C electrocatalysts were studied for the glucose electrooxidation reaction. The increase of ruthenium’s content in PdRu/C electrocatalyst suppresses current density, while on the other hand the addition of palladium (until Pd:Ru=2:1) enhances catalytic activity to glucose electrooxidation, with Pd_{2}Ru/C to exhibit the highest catalytic activity. According to cyclic voltammetry results, many intermediates are formed on Pd_{x}Ru_{y}/C electrocatalysts, whose effect is reduced when electrolyte’s concentration increases to 2 M KOH. Moreover, increasing temperature from 25°C to 40°C current density increases.

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REFERENCES

Development of Non-coated Stainless Steel Bipolar Plate for PEMFC

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Abstract - The super-ferritic stainless steel (POS470FC) having both of high corrosion resistance and low interfacial contact resistance under the PEMFC operating conditions has been developed. A good contact resistance can be obtained by surface modification process instead of coating process. The corrosion resistance and interfacial contact resistance (ICR) of POS470FC alloy are satisfied with the DOE ’15 commercial targets. The long-term stability of the cell equipped with POS470FC bipolar plate is confirmed in the constant current and simulated automotive drive cyclic mode during 15,000 hrs and 34,000 cycles, respectively. After the long-term evaluation of the cell, there is no increase of electrical resistance and membrane electrode assembly (MEA) contamination by dissolved metal ions as well as no sign of corrosion on the bipolar plate surface.

The 1kW stack is successfully fabricated and operated with stamped POS470FC bipolar plate for application of residential 1kW combined heat and power (CHP) system.

Index Terms – PEMFC, stainless steel, bipolar plate

I. INTRODUCTION

POS470FC is a super ferritic stainless steel designed specially at POSCO for non-coated bipolar plate of polymer electrolyte membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC)

II. TEST RESULTS

The contact resistance and corrosion resistance of POS470FC was evaluated under simulated PEMFC operating condition. Both of the physical properties satisfied with DOE ’15 target. Fig.1 shows the contact resistance, it is comparable to graphite's one.
evidence of metal ion contamination on the MEA. Fig. 3 shows the single cell performance during the 5,000 hours with graphite and POS470FC bipolar plate.

![Graph showing single cell performance](image)

**Fig. 3** long term stability of graphite and POS470FC

Finally, the 1kw CHP residential system with stamped POS470FC bipolar plate is fabricated and the system officially certified by KEMCO. For this, the research on the stamping process including spring back also performed. Fig. 4 shows the shape of 1kW stack and Fig. 5 shows the initial performance data.

![Image of 1kW stack for CHP system](image)

**Fig. 4** 1kW class stack for CHP system

![Image of 1kW class stack initial I-V curve](image)

**Fig. 5** 1kW class stack initial I-V curve

**III. CONCLUSION**

1) POSCO has developed the new super-ferritic stainless steel (POS470FC) for non-coated PEMFC bipolar plate.
2) The corrosion resistance and interfacial contact resistance of POS470FC are satisfied with the DOE '15 commercial targets.
3) The long-term stability of the cell equipped with POS470FC bipolar plate is confirmed in the constant current and simulated automotive drive cyclic mode.
4) The 1kW CHP system is successfully fabricated with stamped POS470FC bipolar plate and officially certified by Korea Energy Management Corporation (KEMCO).
MODIFIED NAFION/TIO2 MEMBRANES FOR PROTON EXCHANGE MEMBRANE FUEL CELLS


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Abstract - Nafion/oxide composite membranes were produced by pulsed laser ablation method using UV laser pulses generated by a COMPEXPro 205 KrF* excimer laser source. TiO2 material was uniformly distributed over the surface of Nafion 112 membrane using 100, 250 and 500 laser pulses and an incident laser fluence set at 5 J cm−2 were applied to improve the water retention property and corresponding proton conductivity under high temperature operating conditions. UV-Vis spectroscopy, scanning electron microscopy and EDS Spectroscopy tests indicated the oxides distribution in the composite membranes. Proton conductivity characterization was carried out in the temperature range of 40-120 °C, and water uptake was measured at 25 and 80 °C. The results proved an increased proton conductivity of the composite membranes compared with Nafion at 120 °C, and higher water uptake at 25 and 80 °C. Finally, the composite membranes functionality was tested by current-voltage measurements using a home-made fuel cell.

Index Terms – Nafion, Laser Ablation, PEM Fuel Cells

I. INTRODUCTION

In proton exchange membranes fuel cells (PEMFCs), a proton-conducting polymer membrane, separates the anode and cathode sides. Several issues such as water, thermal, and air management for the PEMFCs with typical operating temperature between 60 and 80 °C. Nafion, is widely used as the polymer electrolyte membrane in low-temperature hydrogen/oxygen fuel cells because of its excellent chemical, mechanical, and thermal stability, as well as its relatively high proton conductivity when fully hydrated. The proton conductivity of a Nafion membrane depends strongly upon the relative humidity (RH) of the reactant gases and the membrane needs to be kept humidified for good ionic conductivity. Development of nanocomposite proton exchange membranes (NCPEM) by addition of an inorganic material like TiO2, SiO2 or other metal oxide and may provide solution can improve the water uptake of Nafion and enable high temperature and low relative humidity PEMFC operation [1]. In this paper we report the synthesis and characterisation of modified Nafion/TiO2 composite membranes by TiO2 uniformly distribution over the surface of Nafion 112 substrate using pulsed laser ablation (PLA) method in order to improve the water retention property.
and the corresponding proton conductivity under high temperature operating conditions.

II. RESULTS AND DISCUSSIONS

Membranes preparation was carried out by applying pulsed laser ablation (PLA) of pure targets for nanoparticles transfer to Nafion membrane. The deposition of the metal oxide nanoparticles was performed inside a stainless steel vacuum chamber (Fig. 1).

![Fig 1. PLA experimental set-up](image)

The ablation was performed in 10 Pa oxygen atmosphere. The ablated material was collected on 127 µm thickness Nafion 112 membrane positioned at 50 mm from the targets and kept at room temperature. The incident laser fluence was set at 5 J cm⁻². We prepared three types of Nafion/TiO₂ composite membranes corresponding to the applied 100, 250 and 500 subsequent laser pulses, respectively.

The uniform distribution of TiO₂ nanoparticles with the Nafion membrane has been confirmed by SEM images (Fig. 2). The elemental composition of the hybrid membranes was put in evidence by EDS method. From the EDS spectra it was calculated that the highest value of 1.44 At% was obtained for Nafion/TiO₂ 500.

![Fig 2- SEM images of Nafion 112 and Nafion/TiO₂ composite membrane](image)

EDS data together with SEM analysis proved the increasing of Ti concentration once the number of laser pulses increased, and the nanoparticles uniform distribution within the membrane surface.

The incorporation of TiO₂ nanoparticles into hybrid membranes produced by PLD method was determined qualitatively by UV–Vis technique. From the UV–Vis spectra for Nafion 112 and Nafion/TiO₂ composite membranes is observed a decay of transmittance value with the increase of the number of laser pulses was evidenced. This might be associated with the absorption of light due to the excitation of electrons from the valence band to the conduction band of TiO₂, indicating an effective insertion of TiO₂ particles into Nafion matrix.

The water uptake measurements of the Nafion/TiO₂ 500 sample, showed at 80 °C a value equal to 29%, useful for expecting great proton conductivity values. Conductivity of Nafion 112 nanocomposite membranes was tested in a temperature range of 40 - 120 °C using a home-made cell geometry. From the values of the conductivity measurements we could notice a decreasing of the real value of impedance (Zre) associated with slightly increased the conductivity value of the composite membranes in comparison with simple Nafion membrane over 80 °C. Nevertheless, the proton conductivity measurements proved that the sample Nafion/TiO₂ 500 sample achieved the best value of 3.59·10⁻¹ S cm⁻¹ at 120 °C (Fig. 3).

![3. EIS spectra of Nafion 112 and Nafion/TiO₂ composite membranes at 120 °C](image)

The composite membranes functionality was tested by current-voltage measurements using a home-made 11.3 cm² active area. The fuel cells measurements for all Nafion/TiO₂ samples proved and increasing of the limiting current density with the number of inorganic filler, that is in accordance with the proton conductivity data. The experimental results suggest that Nafion/TiO₂ composite membranes are suitable for potential application in high temperature fuel cells.

References

HYPERWIND; FACILITATING THE PENETRATION OF RENEWABLE ENERGIES AND HYDROGEN MOBILITY BY MSMP’S

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Abstract - The penetration of renewable energies such as wind and solar into the energy market on a large scale introduces periods of electricity surpluses and shortages of supply caused by the intermittent nature of these sources, leading to uncertainty and sometimes instability in the operation of the grid. This paper proposes HyperWind; a solid oxide cell used for flexible power and high quality hydrogen co-production. It is an alternative solution to mitigate power surplus or periods of low power production with high demand in the operation of the renewable energy sources, using the multisource-multiproduct feature of the solid oxide cell that can both produce electricity or consume electricity combined with high quality hydrogen production in a flexible way with the option of upgrading hydrogen mixtures (biogas) into pure hydrogen.

Index Terms - Hydrogen and power coproduction, flexibility, MSMP

I. NOMENCLATURE
MSMP = Multi Source Multi Product energy system
SOFC = Solid Oxide Fuel Cell
SOEC = Solid Oxide Electrolyser
SOFEC = Solid Oxide Fuel assisted Electrolyser
Hyperwind = MSMP concept based on an IR-SOFC/SOEC

II. INTRODUCTION
In the superwind concept published before an internal reforming high temperature fuel cell is used to compensate for fluctuations in wind energy (or solar energy for that matter) [1]. It was found that by reducing the electric output of the fuel cell by electric control, while keeping the input of fuel (natural gas, biogas or a mixture of the two) constant the anode off gas contains a larger amount of hydrogen. In other words, fuel utilization is decreasing. Therefore, it appears that a peak in wind energy, that is compensated by a decrease in electric output from the fuel-cell is converted into three or four times more hydrogen in energy units. This is not a violation of the first law of thermodynamics, but a more efficient operation of the fuel cell, whereby less heat is produced. In normal operation of the fuel cell unspent fuel is unwanted because one wants to convert as much fuel as possible. However, if one can find an application for the hydrogen it is a meaningful way of operating the fuel cell, thereby compensating for fluctuations in wind energy and at the same time producing hydrogen in a very flexible way. Hereby one can circumvent the chicken and egg problem encountered in developing fuel-cell vehicles and a hydrogen infrastructure. In this study we use a solid oxide fuel cell and will examine a wider range of operation possibilities that exist, at least in principle. We understand that there will be materials issues in the solid oxide fuel cell, when operated in different modes, for example as an electrolyzer in reverse mode, but for the moment, we assumed that these problems can be resolved by materials scientists. The various operation modes led to the concept of ‘HyperWind’, as an extension of the superwind concept. The SOFC can operate as electrolyzer (SOEC), Fuel assisted electrolyzer (SOFEC), standard SOFC and hydrogen producing SOFC either in high efficiency or in high power mode.

The methodology consists in the identification of the operation characteristics of HyperWind, developing an electrochemical model in Matlab and then simulating a complete SOFC power/hydrogen plant using the flowsheet software Cycle-Tempo. Secondly, the energy market is explored. Thirdly, different operation strategies for HyperWind are defined in response to the electricity market. Fourthly, an analysis of the integration of HyperWind in the society was performed, examining the technical and economic feasibility of the technology. During the research, it was identified that a SOEC can reach efficiencies up to 93% (not taking into account the efficiency of the energy source) and 85% operating as SOFEC. With the results obtained from the simulations and the energy market characteristics, different operation strategies for HyperWind were suggested. The ‘optimum’ strategy proposed for HyperWind in a practical market situation was found to be operating 4% of the time in SOEC mode, 20% in SOFEC, 73% in SOFC high efficiency and the rest of the time in SOFC in high power mode. Besides the operation description, the technology was compared with other hydrogen production technologies such as steam methane reforming (SMR) and coal gasification. With the analysis it was identified that HyperWind is an excellent alternative to develop the required infrastructure to foster the penetration of battery electric and hydrogen...
vehicles as well as facilitate implementation of fluctuating renewable energy sources.

III. HYPERWIND

A. SOEC

The Solid Oxide Electrolyzer Cell is a high temperature electrolyzer that can operate in the same temperature range as the standard SOFC. The main characteristic of the high temperature electrolyzer is that it requires electrical energy as well as heat for its operation. Increasing the temperature reduces the amount of electrical energy needed for the electrolysis due to the entropy production in the overall reaction. Therefore, its efficiency is high.

B. SOFEC

The Solid Oxide Fuel-assisted Electrolyzer Cell is a SOEC that uses methane (natural gas/biogas) at the inlet of the anode to develop steam reforming and water shift reactions that produce hydrogen that can react with the oxide ions produced at the cathode side by the electrolysis reaction. These reactions reduce the electrical energy required split water in hydrogen and oxygen. Instead of oxygen, now steam and CO2 are formed at the anode. It depends on the circumstances whether or not this is meaningful to do. In case one wants to convert a surplus of wind energy (peak shaving), it is more logical to operate as a standard electrolyzer (SOEC), since the price of electricity’s very low. In other cases, one can take advantage of the fact that effectively a mix of (fuel) gases, For example, biogas is converted into very pure hydrogen (electrolyzer quality) released at the other electrode. One could say that one is converging dirty hydrogen into pure hydrogen as a side effect of operating as an electrolyzer. The conventional conversion of biogas into pure hydrogen is very cumbersome and expensive requiring steam reforming, shift reactions and hydrogen separation. Also the conversion of biomass via gasification into electricity, is characterized by a low efficiency of 25 to 35% even with fuel cells. Upgrading in high quality hydrogen using the SOFEC might be a good alternative.

IV. HYPERWIND SIMULATIONS

After characterize the electrochemical operation of the SOEC using MatLab, it was necessary to understand the operation of the system in a broader scenario, identifying other elements required for the operation of the system and at the same time to have a general picture of the order of magnitude of the auxiliaries, including the balance of plant (BOP) and possible additional utilities for the plant. To characterize the system, the software used was Cycle-Tempo, that was developed at TUDelft. It is used to characterize energy systems, plant operations, energy efficiencies in power plants. The main scope of modeling the system was to evaluate the cell operating together with the auxiliaries in order to obtain the most appropriate operations modes and at the same time, to obtain a general estimation of the inputs and outputs of the utilities in order to identify scenarios were the system can be implemented.

V. CONCLUSIONS

1. HyperWind is a system designed to operate 24/7 with production of hydrogen and either consumption or production of electricity.
2. HyperWind can mitigate the peak demands and energy surplus that can be present in the electricity market using its operation flexibility.
3. SOEC and SOFEC modes are useful during energy surplus in the energy market.
4. SOEC can increase the electricity demand during surplus periods reducing the possible negative prices that can exist in the energy market.
5. The SOFEC mode was suggested to be implemented when the electricity price is lower than the marginal cost of energy production operating in SOFC high efficiency - high fuel utilization mode.
6. Reserve capacity is another alternative for the operation of HyperWind, however, it is necessary to explore the limitations and transient operation between the modes before entering this market.
7. HyperWind is definitely an important tool to facilitate the penetration of intermittent renewable energies into the energy market, covering the inflexibility of the operation of the must-run generators presented in a normal electricity network.
8. It is recommended to explore deeply the hydrogen market to find operation alternatives for HyperWind.
9. A cost analysis is still required to determine the real operation market points and the levelized electricity and hydrogen cost when they are produced in the HyperWind system.

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2R-CELL™: A REDOX ANODE SUPPORTED CELL FOR SOFC APPLICATIONS.

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Abstract - Fiaxell Sàrl developed an anode supported half-cell, the 2R-Cell™, that can survive multiple thermo- and redox-cycles. In this paper we compare 2R-Cell™ to standard non-redox cells in order to highlight their performances. Furthermore we discuss the improvements that can be obtained operating on the buffer layer that protects the electrolyte from the cathode material.

Index Terms – Cell testing, Gadolinia-doped Ceria, Redox cell, SOFC

I. INTRODUCTION

2R-Cell™ half-cell has been developed in the aim of combining the performances of anode supported cells (ASE) and the robustness of electrolyte supported cell (ESC). The main feature of 2R-Cell™ is their mechanical robustness under redox-cycles (fig.1).

Fig. 1. A standard ASE (left) and 2R-Cell™ based (right) cell after a redox cycle.

Electrochemical stability has been tested over 1800h using a standard LSM cathode [1] as illustrated in fig.2.

In order to obtain a performing cell, it is necessary to optimize the cathode material. A popular choice is the use of mixed ionic and electronic conductors as La$_0.6$Sr$_0.4$CoO$_3$ (LSC) or La$_0.6$Sr$_0.4$Co$_0.2$Fe$_0.8$O$_3$ (LSCF), however these materials induce the formation of a highly resistive Sr-doped-Zirconia phase in the YSZ. A protective layer of GaCeO (ceria layer in the following) is therefore used to separate the cathode from the electrolyte. In this paper we discuss the effect of the ceria buffer layer on the performances of 2R-Cell™ based cells and we show how its deposition and densification are crucial for optimal cell operation.

Fig. 2. Voltage and Current Density vs. Time of a 2R-Cell™ tested with a LSM cathode.

II. EXPERIMENTAL

A. Cell Preparation

2R-Cell™ are prepared via tape casting and screen printing using standard row materials as NiO and 8YSZ in water dispersion and water soluble polymer paste [1,2]. The result of the process are half-cells, with surface area of 10 to 120 (cm$^2$) and thickness of 0.3 to 1.2 (mm), on top of which the cathode can be post-sintered in air at temperatures up to 1300°C with no degradation of the substrate. In this paper we present results obtained with a LSC in situ cathode (La$_0.5$Sr$_0.5$CoO$_3$ is printed and left to dry without any sintering). In order to protect the electrolyte form the cathode, a 2%Co doped Ceria buffer layer (Co-GDC) is screen printed on the half cell and sintered at 1200°C for 3h. Dense GDC layers, deposited via reactive magnetron sputtering [4], has been therefore tested on 2R-Cell™ and compared with previous results.
B. Testing Set-Up

All electrochemical measurements have been carried out in the Open Flanges Set-Up that has been developed and commercialized by Fiaxell Sàrl. This test rig allows for a simple and rapid mounting of cells of different sizes, ranging from 20 (mm) to 80 (mm) in diameter and gives highly reproducible results. The distinctiveness of the Open Flanges Set-Up is that no sealing is required: the SOFC cell is simply squeezed between two alumina felts, and current collection is provided by a nickel foam on the anode side and a grid on the cathode side. A fuel flow rate of 120 to 200 (ml/min), depending on the cell size, is enough to ensure OCV values close to the theoretical ones. Furthermore, the set-up can be adapted, by adding a specific in situ steamer, to perform experiments with carbon or liquid fuel.

Fig. 3. Overview of the Open Flange set-up (top) and of other products offered by Fiaxell Sarl

In addition to the Open Flange set-up, Fiaxell is offering a wide range of products for SOFC testing including Gold and Crofer grids and Hydrogen Generators.

III. RESULTS AND DISCUSSION

Polarization curves of three different cells equipped with a LSC in situ cathode are reported in fig.4. Operating conditions are: \(T=760(˚C)\), \(H_2=180\) (ml/min), \(Air=390\) (ml/min).

Fig. 4. I-V curves of standard cell (green), 2R-Cell™ with sintered ceria (blue) and 2R -Cell™ with PVD ceria (red).

The green curve represents a 2R-Cell™ cell while the blue one is a standard non-redox cell and it can be observed that they show a similar behavior. The red curve presents, on the other hand, enhanced electrochemical performances. This result has been obtained for the 2R-Cell™ based cell on which a dense ceria layer has been deposited.

In order to understand the origin of such amelioration, the two layers have been observed at a scanning electron microscope (SEM). Sintered ceria reveals a porous structure that could be responsible for a reduction in electrical conductivity of the cell. This assumption has been confirmed by electrochemical impedance spectroscopy (EIS) measurements (reported in fig.5). The red curve refers again to the cell equipped of PVD deposited ceria, while the blue belongs to sintered ceria; both spectra were taken at a polarization current of 400 (mA/cm²); operating conditions are: \(T=760(˚C)\), \(H_2=180\) (ml/min), \(Air=390\) (ml/min).

Fig. 5. Electrochemical spectra of two cells with different GDC layers. An increase in ohmic resistance can be observed for sintered (non dense) GDC.

It can be observed that, while the polarization resistance is comparable for the two cells, the ohmic contribution is strongly lower in the case of dense ceria. A qualitative estimation can be obtained as the high frequency intercept with the real axis: this reads 320 (mΩ cm²) for the sintered layer and only 150 (mΩ cm²) for the PVD deposited one.

This result confirms the importance of the quality of the ceria buffer layer on the performances of SOFC cell equipped with Sr-based cathode.

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HYDROGEN PRESSURE SWING RECIRCULATION SYSTEM

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Abstract – Proton Exchange Membrane Fuel Cells are electrical generators that use oxygen and hydrogen to produce electricity. To minimize the wastage of hydrogen, recirculation systems are used to prevent the flooding of the fuel cell and to limit the reactant losses. Those systems impact the efficiency of the fuel cell due to their electrical consumption. A new system of hydrogen recirculation is presented using the hydrogen consumption as the driving force of the system instead of a pump. This recirculation device was successfully tested on a 70 cells 5 kW stack.

Index Terms – hydrogen recirculation, suction pressure, fuel cell, reactant losses.

I. INTRODUCTION

PEMFC are energy power generators that are considered in more and more application thanks to their high power density, environment friendly aspects, low operation temperature and quick start-up capacity [1].

PEMFC use a chemical reaction between oxygen and hydrogen to create electricity, water and heat. The electricity is injected in the electrical circuit while the heat is, most of the time, evacuated by the cooling system. The water produced may create plugs that will prevent the reaction to occur. It must be evacuated. One of the solutions is to discharge the reactant in the atmosphere; this will drag the water out of the fuel cell. This solution creates reactant losses that impact the efficiency and the safety of the system. Another solution is to use a recirculation device which will create a reactant flow to drag the water out and inject the remaining reactant back in the fuel cell. Such a solution also impacts the efficiency due to the electrical consumption of the device. We present here a recirculation device we have designed and tested on a 70 cells stack, the pressure swing recirculation system.

II. PRINCIPLE

This pressure swing recirculation system evacuates the water from the fuel cell without using a pump or an ejector. The driving force of this device is the hydrogen consumption during the fuel cell operation.

A. Design

The following figure shows the design of the recirculation device.

Fig1 : Schematic diagram of the pressure swing recirculation system.

Only the anodic side of the fuel cell is shown. This device is composed of several elements: a pressure regulator, the anodic compartment where the hydrogen consumption occurs, a gas tank, also used as a water trap, 2 check valves and a solenoid valve commanded by a pressure measurement on the anodic compartment. It is the only device that consumes electricity. The next section will explain the driving force of the device.

B. Driving force of the system

PEM Fuel cells use the chemical reaction between H2 and O2, often from air, to generate electricity. The hydrogen is oxidized on the anode; the electrons are injected in an external electrical circuit whereas the ions go through the membrane. Then both of them react with oxygen on the cathode to create water and heat. The hydrogen consumption in the anodic compartment creates a pressure drop which is used as the driving force of the pressure swing recirculation system. The following section will explain the functioning of the pressure swing recirculation device.

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C. Functioning principle

The functioning of this system is based on a four steps cycle shown in the following figure.

1. The solenoid valve and the two check valves being closed, the hydrogen is consumed by the fuel cell. The pressure thus decreases in the anodic compartment of the stack.
2. The pressure decrease causes the opening of the check valve CV2. This leads to a discharge of the gas from the tank to the stack due to the pressure difference (higher pressure in the tank). The pressure in the anodic compartment and the stack still decreases due to the continued consumption of hydrogen.
3. When the pressure reaches the low pressure limit, the solenoid valve opens. The pressure rises in the anodic compartment leading to the shutdown of the check valve CV2.
4. The difference of pressure between the anodic compartment and the tank causes the opening of the check valve CV1 (higher pressure in the anodic compartment). Then the anodic compartment discharges itself in the tank creating an overflow through the anodic compartment which expels water and inert gas out of the stack. When the anodic compartment pressure reaches the high pressure limit, the solenoid valve closes along with CV1. The cycle can start again.

This system was already tested on a single cell [2]. We have tested it on a 5kW 70 cells fuel cell stack.

III. EXPERIMENTS

A 70 cells fuel cell stack with an active area of 200 cm² using hydrogen and air as reactant is used in the experiment. The membrane electrode assemblies (MEA) are constituted of Nafion, Pt/C electrodes with a Pt catalyst loading of 0.1 mg/cm² on the anode and 0.4 mg/cm² on the cathode, and GDLs (24 BC). The pressure of air in the cathodic compartment is 1200 hPa(abs). The pressure of hydrogen swings between 1450 and 1400 hPa. The temperature of the fuel cell is 60°C. The air stoichiometry is set to \( \lambda_c = 2.5 \). This system is made of two check valves with a pressure crack of 30 hPa. A solenoid valve was added to the hydrogen line. The volume of the gas tank and the pipes between the two check valves is 4 l. The water trap is made up of a condenser and a bucket trap.

IV. RESULTS

The fuel cell system was tested at a current density of 0.5 A/cm² during one hour with and without the pressure swing recirculation device. The mean voltages of the stack during the two tests are presented in the following figure.

The performance of the fuel cell stays almost steady with the pressure swing recirculation system whereas the performance decreases rapidly without it due to the water stagnation in the anodic compartment. The slope of the mean voltage when the recirculation device is used can be explained by the nitrogen accumulation in the anodic compartment.

V. CONCLUSION

We tested a new reactant recirculation system on a 5 kW PEMFC stack. The system only requires two check valves and a solenoid valve. The driving force is the suction of hydrogen consumed on the anode. Experimental stability performance tests were performed. The stack performance in the hydrogen recirculation mode was stable for over 1h, whereas the stack “crashed” in less than 20 min without any recirculation device. In the end, this system has a lower impact on the fuel cell efficiency (~0.5%) than pump recirculation system (5%).

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POSSIBILITY OF HYDROGEN UNDERGROUND STORAGE IN ROMANIA

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Abstract - The present work features an analysis of the current state of Romania’s potential in the context of hydrogen economy. In the transition to the hydrogen economy is not so important who took the start first also how to use own potential and resources optimally and to turn them into advantages. Large scale underground gas storage is a relatively mature solution from an economic and technical perspective. In close connection with this hydrogen underground storage can becoming a potentially attractive solution. Currently, main uses of salt caverns include storage of hydrocarbons or wastes disposal. Recently, salt caverns have stirred the interest of the scientific community regarding the potential applications in hydrogen economy. Romania has a long tradition of salt extractions. In our days, Romania has active mines or caverns and others closed, many of them have the potential to be used from hydrogen storage. These facts represent an interesting situation in order to initiate studies or assessments of the potential hydrogen underground storage. The salt mines, hydrogen producers, renewable energy sources and research centers with high qualified scientists, represent essentially elements for new type of studies regarding hydrogen economy. In the context of scientific community's efforts from Eastern Europe to active assert in the area of hydrogen technologies, this approach can certainly constitutes an attractive example for pan-European cooperation.

I. INTRODUCTION

Large scale underground gas storage is a relatively inciting solution from an economic and technical perspective. In close connection with this, hydrogen underground storage can be a potentially attractive solution. Currently, main uses of salt caverns include storage of hydrocarbons or wastes disposal. Recently, salt caverns have stirred the interest of the scientific community regarding the potential applications in hydrogen economy. Romania has a long tradition of salt extractions and in our days there are active or closed mines and caverns, many of them have the potential to be used for hydrogen storage. These facts represent an interesting situation in order to initiate studies or assessments of the hydrogen underground storage potential. The salt mines, hydrogen producers, renewable energy sources and research centres with high qualified scientists, represent essentially elements for new type of studies regarding hydrogen economy. In the context of scientific community's efforts from Eastern Europe to active assert in the area of hydrogen technologies, this approach can certainly constitutes an attractive example for pan-European cooperation.

Regarding results presented in, hydrogen underground storage in salt caverns is presented as a really promising technology due to its high volumetric energy storage density. Even the most ambitious case of Renewable Energy Sources integration (100%) seems to be feasible by the implementation of a huge but not unrealistic amount of hydrogen energy storage. Taking into account that the penetration of Renewable Energy Sources in the energy mix by 2050 would be less than estimated, and taking also into account that other technologies like Pumped Hydro Energy Storage will contribute to the energy management, and other solutions such as high voltage transmission lines are defined as a priority, with a plan to develop energy storage capacity in medium and long term, the objectives established in the Energy Roadmap 2050 could be fulfilled without major problems.

The methodology of the project planned foresees that group
of researchers carries out the information and data compilation and their assessment as well as the formulation of the Romanian Case Studies, which is sustained by a wider group of supporters.

II. RESULTS AND DISCUSSIONS

As a result of participating in the project HyUnder, Romania team began to identify the possibilities of the hydrogen underground storage. As part of the entire project, the case study for Romania has been divided in two parallel directions. The first direction aims to acquire information about underground storage of hydrogen and second, to achieve data about the potential of the renewable energy and energy infrastructure.

HyUnder project (Grant no. 303417) is supported by the FCH JU (Fuel Cell and Hydrogen Joint Undertaking) and is directly within the scope of the Annual Implementation Plan 2012. The HyUnder consortium comprises 12 leading organizations from 7 different European countries including large companies, small medium enterprises and research institutes. This variety ensures that all fundamental competencies are available to carry out the project, including: geology of underground formations suitable for gas storage and below ground technology, underground storage engineering along with above ground process technology. Other important competencies with a specific focus on hydrogen are also included, such as electrolysis, hydrogen use for wind energy load balancing, hydrogen rich gas mixtures and hydrogen use in transport. In addition workshops are planned to stimulate the discussion in Europe at three levels, a public, a topical stakeholder and a hydrogen expert level.

Broadly in Romania have been identified next three hydrogen storage options: mines, depleted gas fields and salt mines and caverns. The first option theoretically it is possible, but is difficult to take into account due to many disadvantages to do it practically usable. For the second it is useful to note that currently in Romania are 8 depleted gas fields with 2684 million of m³ working gas capacity, used for seasonal storage of natural gas. The last option, salt mines and caverns, has been studied extensively, being the subject of study HyUnder project. Because some activities are still on-going it is possible that some of the results may undergo further changes. In our days, Romania has 7 active sites, including both mines and caverns, and other closed. Many of these sites have the potential to be used from hydrogen storage. At this moment in Romania was identified 38 old salt mines closed, collapsed, flooded, embanked, closed, landfills or touristic activity; 33 active mines and 93 brine wells, active or closed. At this moment the situation of underground voids is: old mines – 22 793 865 m³; active mines – 14 387 708 m³ and caverns –27 536 263 m³. Possibilities for exploitation and utilization of underground voids are still the subject of study, requiring an additional analysis for identification.

III. NEXT STEP

Based on the achieved results a quantitative approach for salt formations will be attempted. The goal is (1) to estimate the amount of hydrogen which can be stored in salt caverns and (2) to approximate it technical-economic effect. All actual progresses are available on www.hyunder.eu.

IV. CONCLUSION

At this point the project is too early to indicate some conclusions. However, the manuscript shows the collective efforts of researchers from National Research and Development Institute for Cryogenics and Isotopic Technologies - ICSI Rm.Valcea (National Hydrogen and Fuel Cell Center) to highlight potential in Romania in terms of hydrogen storage. At the time we obtained encouraging results, but they are still too rough to make accurate predictions.

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EXPERIMENTAL INVESTIGATION OF DIRECT METHANOL FUEL CELL DEGRADATION IN REAL OPERATION REPRESENTATIVE CONDITIONS AND DURING ACCELERATED STRESS TESTS (AST)

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Performance degradation is one of the most critical issues of Direct Methanol Fuel Cells (DMFC). The experimental investigations of DMFC degradation found in literature show that degradation has both permanent and temporary contributions; the last one can be recovered after an operation interruption for diagnostic. This work aims to investigate the DMFC degradation during real operation representative conditions and to provide a comparison with the degradation that occurs during accelerated stress tests (AST). The degradation rate in the first case is found to be comparable with manufacturer data; anode degradation is very low and it confirms that cathode is mainly responsible for permanent degradation. During Accelerated Stress Tests, degradation rate highly increase despite the highest part of the degradation is recoverable; the behaviour of methanol crossover in the tests is also investigated. Methanol concentration is found to be a critical parameter for the anode side stable operation and low degradation.

Index Terms - AST, degradation, DMFC, EIS, methanol crossover, performance recover.

I. NOMENCLATURE

AST: Accelerated Stress Test
CV: Cyclic Voltammetry
DMFC: Direct Methanol Fuel Cell
EIS: Electrochemical Impedance Spectra
OCV: Open Circuit Voltage

II. INTRODUCTION

Direct Methanol Fuel Cells (DMFC) is a promising power source mainly due to high power density and liquid fuel. However, performance degradation and methanol crossover from the anode to the cathode are the most critical issues that hinder the commercialization of Direct Methanol Fuel Cells. The experimental investigations of DMFC degradation found in literature show that degradation has both permanent and temporary contributions [1]; the last one can be recovered after an operation interruption for diagnostic or due to some opposite operation procedures [2-3]. However literature does not present experimental investigations of DMFC degradation with methanol crossover measurement. Furthermore electrochemical impedance spectra (EIS) is a diagnostic technique that can be performed without interrupting the degradation test and it allows investigating temporary degradation.

The majority of the works in literature investigate DMFC degradation by means of catalyst ex-situ characterization and they identify the main degradation mechanisms such as platinum agglomeration and ruthenium loss that determines Electro-Chemical Surface Area (ECSA) reduction. However they usually perform non-systematic experimental tests in order to analyse operating parameters influence.

This work aims to improve DMFC degradation understanding by means of:

- Performing of sensitivity analysis on operating parameters effect on DMFC degradation;
- Measuring methanol crossover and EIS during experimental tests;
- Developing preliminary AST.

III. EXPERIMENTAL

Two experimental setups are used in this work and they are described in references [3-4]; one in typical fuel cell operation (galvanic operation) and one in anode polarization with cathode set as a hydrogen reference electrode. The same tests are performed on both the experimental setup in order to investigate the anode degradation and to separate the different degradation effects.

Performances, mass transport analysis such as methanol crossover and water transport and Electrochemical Impedance Spectra (EIS) are performed during the degradation tests; polarization curves and Cyclic Voltammetry (CV) act as
IV. TEMPORARY DEGRADATION CHARACTERIZATION

In a previous work [4] the authors identified a temporary degradation at the anode working in anode polarization due to CO₂ accumulation effect on GDL and electrode mass transport properties resulting in a lowering of water and methanol concentration. They also found that the operation strategies [3] are a key aspect to minimize temporary degradation of a DMFC.

New aspects of the DMFC temporary degradation are highlighted in this work: the effect of cathode dehydration is investigated as showed in figure 1 where the reduction of cathode air leads to a significant membrane ohmic resistance reduction, the hydrogen production at the anode due to electrolytic operation when the air feeding is interrupted. However the main effect determining cathode DMFC temporary degradation is the mechanism of formation and reduction of platinum oxides/hydroxides [5] that can be minimized by means of proper operating strategies that involve cathode air feeding interruption and OCV.

V. PERMANENT DEGRADATION CHARACTERIZATION

The experimental investigation of DMFC degradation confirms that the main part of the permanent degradation is due to cathode electrode efficiency loss. Indeed, experimental tests reports that the permanent degradation that occurs at the anode is very low if compared with the overall measured degradation. Furthermore, during the tests, the membrane internal resistance slightly increases with time coherently with a slight reduction of methanol crossover measured during the diagnostic polarization curves. However water content in cathode exhaust remains about constant during all the degradation tests and, from this result, it is possible to exclude a strong GDL degradation.

Cyclic voltammetries, that can be used only at the cathode while at the anode of a DMFC are not reliable, demonstrates that the cathode surface area loss is very important. The summary of the diagnostic performed during the degradation tests is reported in figure 2. It is possible to suppose that the permanent degradation of a DMFC is mainly attributable to the cathode electrode deactivation due to degradation mechanisms already highlighted in literature.

Taking into account this consideration, a preliminary AST for the cathode of a DMFC has been developed and tested.

VI. CONCLUSION

The following conclusion can be drawn from this work:
- The main part of the DMFC performance loss is temporary and, so, recoverable with proper operating strategies;
- Temporary degradation occurs both at anode and cathode electrode and the main component is due to platinum oxides formation and reduction mechanism;
- Permanent degradation of a DMFC is mainly attributable to the cathode electrode performance loss.

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EFFECTS OF ANODE MPL ON DMFC MASS TRANSPORT PHENOMENA AND ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY: EXPERIMENTAL AND MODELING ANALYSES

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Abstract - Direct Methanol Fuel Cells (DMFCs) are a promising energy source for portable and automotive applications, mainly due to the direct use of a liquid fuel and low emissions. However the widely use of the DMFC technology is still hindered by some technological issues, among which water management is one of the most important. High water crossover through the membrane may cause cathode flooding and enhance methanol crossover. Moreover water management can affect DMFC lifetime, that is limited by several interconnected degradation phenomena. The most common technique to monitor system internal losses during real operation is the Electrochemical Impedance Spectroscopy (EIS). Despite the potentiality of this in-situ measurement technique, the interpretation of impedance data is still object of discussion in the literature.

This work aims to characterize the effects of anode MPL on water transport, methanol cross-over and EIS by means of a combined experimental and modeling approach.

Index Terms – DMFC, EIS, mass transport, model.

I. INTRODUCTION

DMFC anode gas diffusion layer (GDL) is often composed by an additional micro porous layer (MPL), characterized by a reduced porosity and a high hydrophobicity. The presence of MPL plays a significant role in reducing water and methanol cross-over through the membrane. However a detailed comprehension of mass transport phenomena through anode GDL is required to further optimize DMFC components and operation strategies.

In this work a combined experimental and modeling approach is proposed to provide an insight into the understanding of the basic principles regulating mass transport phenomena and electrochemical behavior of DMFC anode.

II. EXPERIMENTAL

The DMFC has a maximum cross-sectional area of 25 cm²; two anode GDL configurations have been considered: the first one with the MPL (MEA MM), the second one without the MPL (MEA GM).

The mass transport measurements are coherent with those reported in the literature [1]: the presence of anode MPL lowers water and methanol crossover.

Moreover, in order to elucidate the main physical phenomena governing impedance behavior, a systematic experimental analysis of anode EIS has been performed. Methanol concentration turns out to strongly affect the low frequency region: low methanol concentration enhances mass transport effects, while high methanol concentration enlarges inductive behavior. These considerations provide an insight into the development of interpretation models, that should take into account a detailed description of mass transport phenomena through anode side.

III. MODELING

The previously developed 1D+1D DMFC model [2] has been firstly integrated with a detailed description of mass transport phenomena through anode GDL and a catalyst layer with a finite thickness. In particular the water flux through the GDL is governed by liquid permeation, while the methanol flux is regulated by gas and liquid diffusion and liquid permeation.

Subsequently, considering the same mathematical approach presented in [3], a physically based DMFC anode impedance model has been developed [4]. In this dynamic model the GDL is not assumed to be always flooded with fully liquid pathways, but liquid permeation is considered as process of capillary

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pressure buildup and breakthrough at the interface of GDL intersecting fibers.

IV. RESULTS

The developed model has been firstly validated on three different typologies of measure at the same time: performance, methanol cross-over and water flow at cathode outlet. Model simulations reproduce experimental data with good accuracy, as reported in Fig.1.

Model results show that the presence of anode MPL cause an inversion of water liquid diffusion through the membrane at high current density, lowering methanol cross-over and cathode flooding. Instead without anode MPL the liquid diffusion is always directed from anode to cathode.

Moreover model predictions highlight that with anode MPL methanol liquid diffusion is the main transport mechanism for current densities lower than 0.05 A cm\(^{-2}\), but it becomes negligible for current densities higher than 0.15 A cm\(^{-2}\). Instead without anode MPL liquid diffusion is always a relevant influence, due to the higher liquid saturation in the porous media. However, in order to correctly reproduce both performance and methanol crossover all the above mentioned methanol transport mechanisms have to be considered.

Anode impedance model qualitatively reproduces the magnitude of resistances and the relaxation frequencies and therefore all the main physical phenomena are correctly described. Impedance simulations confirm that liquid permeation through the GDL is an intermittent phenomenon; this implies a superimposition between the arches peculiar of kinetic and mass transport losses.

Furthermore model predictions without the effects of mass transport phenomena through the GDL evidence that their contribution is relevant even at low current density. From the comparison between model results with and without the implementation of GDL effects along channel length, Fig.2, it is evident that at the end of channel the mass transport losses due to the presence of a diffusion layer are more pronounced, as expected.

V. CONCLUSIONS

From this work the following conclusions can be drawn:

- the presence of anode MPL causes an inversion of water liquid diffusion through the membrane;
- methanol transport through anode GDL is regulated by three transport mechanisms, whose magnitude is strongly affected by the presence of MPL;
- the intermittent description of liquid permeation through anode GDL is of fundamental importance to correctly simulate anode impedance features;
- the contribution of GDL to the impedance is relevant even at low current density and increases along channel length.

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A NEW CARBON-BASED PAINT FOR LOW-COST CATHODES AND ANODES IN MICROBIAL FUEL CELLS

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Abstract – Production of cost-effective Microbial Fuelcells is here demonstrated by the concomitant utilization of metallic anodes (AISI304 SS) and of commercial conductive carbon-based paints. Electrochemical and physico-chemical analyses demonstrate the potentialities and the drawbacks. Corrosion is prevented by the anaerobic conditions and the paint. Power production is increased by the bacterial affinity for the carbonious surface. Although great attention must still be devoted to the electrode lifetime and real surface extension, the promising answer of these SCMFCs is here demonstrated.

Index Terms – Single Chamber Microbial Fuelcell, electrodic binder, AISI 304SS anode, corrosion

I. INTRODUCTION

A Microbial Fuelcell (MFC) represents a flexible technology with manifold fields of application. Laboratory-scale electrodes are usually equipped with carbon-based materials (graphite, or more complex and expensive carbon cloths). Previous studies in our laboratories proved the effectiveness of developing a biocathode, without any expensive electrocatalyst for the activation of the cathodic reactions. The key-point in the development of a practical cathode is the substitution of expensive binders with cheaper ones. In this work, commercial water-based graphite paint is applied on standard lab-scale Single Chamber Microbial Fuel Cells (SCMFCs).

II. EXPERIMENTAL

A. Microbial Fuel Cell Construction

Single chamber microbial fuelcells (SCMFC) are in this work employed, with an open-air cathode and an anode, exposed to the anaerobic conditions of the chamber.

Anaerobicity is ensured by the medium, urban wastewater (from Milan wastewater plant). Endogeneous bacterial community was fed by the addition of acetate, as needed. A resistance of 100Ω connected the electrodes. Different electrodes were produced: a set of cells were equipped with a standard Teflon-based carbon cloth cathode and painted metallic (AISI 304SS) anode; another set is equipped with standard carbon cloth anode and painted carbon cloth cathode. Paint is a commercial water-based graphitic conductive paint (TIMCAL Q®).

B. Analytical Techniques

SCMFCs were tested by electrochemical (cyclic voltammetry, polarization curves, power production, polarization resistance, conductivity) and non-electrochemical techniques (Scanning Electron Microscopy). Physico-chemical parameters (pH, conductivity, redox potential, sulphide concentration) were recorded in the bulk solution and near the electrode by means of microelectrodes.

III. RESULTS AND DISCUSSION

A. Conductive Paint Coated Cathode

The first type of SCMFC, equipped with standard anode and painted cathode, showed a current production (potential at the heads of the 100Ω resistance) depicted in Fig. 1.

After two days, the cell starts to grow a biofilm on both electrodes, and both anodic and cathodic reactions take place, producing up to 60mV. The exhibited potential then decreases quickly within two days, demonstrating problems in the
cathodic reaction.

**Fig. 1. Potential development of a SCMFC equipped with a painted carbon cloth cathode.**

**B. Conductive Paint Coated Anode**

SCMFCs equipped with painted-metallic anode show a completely different behavior. In Fig. 2, three selected types of SCMFCs are shown:

- pure 304SS anode (naked, in Fig. 2) shows a delayed startup of the cell, and a low conversion of the acetate.
- A monolayer of paint (1 layer, in Fig. 2) increases voltage output and ensures a more monotonic and prompt startup.
- Two consecutive layers of paint (2 layers, in Fig. 2) induce a further increase in the voltage output.
- The productivity and coulombic efficiency is greatly increased with the application of conductive paint.

**Fig. 2. Potential development of a SCMFC equipped with a painted carbon cloth Anode.**

The determination of the polarization resistance (RP) partly explains the behavior shown in Fig. 2.

**Fig. 3. Polarization Resistance (RP) calculated at different days on the metallic-painted anodes.**

The productivity and coulombic efficiency is greatly increased with the application of conductive paint.

**IV. CONCLUSION**

Water-based carbon conductive paint demonstrated the possibility of obtaining SCMFCs with competitive power outputs. The effect of the conductive painted anode is connected with its corrosion protection behavior and the decrease of the metallic natural passivation.

Painted cathodes show a more unstable behavior, probably connected with oxygen diffusion problems.

Microelectrode measurements, SEM images, polarization curves and cyclic voltammetries point to a complex microenvironment establishing inside the SCMFC. Cell geometry and materials contribute to the effective production of current, avoiding corrosion and diffusion problems.

**ACKNOWLEDGMENT**

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Abstract - This review focuses on: (a) describing the physico-electrochemical transport phenomena in alkaline Anion Exchange Membrane Fuel Cells (AEMFCs) and acidic Proton Exchange Membrane Fuel Cells (PEMFCs) fed with hydrogen or hydrogen-rich alcohols, such as e.g. ethanol, methanol, and (b) reporting alkaline AEMFC vs. acidic PEMFC polarisation performance characteristics such as, maximum area-specific and mass-specific power densities.

Index Terms – PEMFCs, AEMFCs, hydrogen-fed polymer electrolyte fuel cells, direct alcohol fuel cells

I. INTRODUCTION

Much research attention has focused on proton exchange membrane (PEM) fuel cells [1] and, more recently, on anion exchange membrane (AEM) fuel cells [2-4] fed with hydrogen, or hydrogen-rich alcohols such as e.g. methanol or ethanol.

Table I provides with electrochemical oxidation reactions and characteristics of various hydrogen-rich alcohols in alkaline media.

Alkaline AEMs conduct hydroxyl ions (OH-) and represent the high pH equivalent to PEMs employed in the acidic-type PEMFCs. AEM-based polymer electrolyte fuel cells (PEFCS) have been attracting attention worldwide, mainly due to the prospect of using Pt-free electrocatalysts.

However, both PEM- and AEM-based PEFCS continue to be limited by difficulties with water management, particularly the issue of electrode flooding, as well as fuel crossover mainly in the case of direct alcohols fuel cells (DAFCs).

II. PEM-TYPE VS. AEM-TYPE FUEL CELLS

AEM-based PEFCs exhibit several advantages over the PEM-based ones, such as: (i) faster oxygen reduction reaction (ORR), thus introducing lower activation overpotentials; (ii) non-precious metal catalysts can be used effectively; (iii) a potentially simplified water management, which is necessary to avoid either cathode flooding (high water crossover) or a high cathode activation loss (too low water crossover) is the case in AEM-based FCs (water is produced at the anode and consumed at the cathode); and (iv) fuel crossover within the membrane (mainly for direct liquid fuel cells) is less severe in AEM-based PEFCs, because it takes place in the opposite way to the OH- transport.
Fig. 1. Schematic of the PEM-based (left) and AEM-based (right) fuel cells

III. TRANSPORT PHENOMENA, ELECTROCHEMICAL KINETICS AND CELL OPERATION

One of the mass transport issues in acidic PEMFCs is water management, aiming at maintaining a delicate balance between membrane dehydration and cathode flooding. Flooding occurs when excess liquid water nucleates at the cathode (PEMFCs) or anode (AEMFCs), inhibiting the fuel cell reactions (mostly ORR).

In AEM D AFCs, however, a common conception is that cathode flooding is unlikely due to the fact that water is consumed as a reactant at the cathode and the electro-osmotic drag moves water from the cathode to anode.

Recently, it was shown [5] that cathode flooding also occurs in an AEM DAFC, primarily because the diffusion flux from the anode to the cathode outweighs the total water flux due to the both ORR and electro-osmotic drag. Therefore, avoiding cathode flooding is a water management issue in AEM DAFCs as well.

In case of a hydrogen-rich alcohol fuel, alcohol crossover through the membrane (either PEM, or AEM) is a significant drawback as well; crossover, adversely affects fuel efficiency (i.e., energy density) due to the wasteful oxidation on the cathode side leading to a mixed potential formation [6, 7].

However, in an AEM-type DAFC the direction of the electro-osmotic drag is from the cathode to the anode, which can reduce the rate of fuel crossover from the anode to cathode, improving the cell performance.

IV. CONCLUSION

Hydrogen-rich alcohols are considered as ideal fuel sources for direct oxidation fuel cells. Compared to hydrogen, they possess features such as higher energy densities, as well as easier transportation, storage and handling.

These features make DAFCs a promising device for portable and mobile applications. Conventional DAFCs that are based on PEM such as e.g. Nafion membranes and Pt-based catalysts exhibit substantially lower performance than the one of hydrogen fed PEMFCs.

Alcohol crossover via the membrane (either PEM, or AEM) is a significant drawback in this respect. Enhancing the anode alcohol electrooxidation rate, it is an important target towards reduction of the alcohol crossover rate.

Although the power densities of AEM-based DAFCs are lower than the ones of direct methanol fuel cells (DMFCs) with conventional PEMs, the further development of novel non-Pt catalysts and AEMs with improved stability and ionic conductivity would provide with a basis for performance and durability improvements of AEM DAFCs.

Furthermore, the higher reactivity of polycarbon alcohols, such as ethanol, ethylene glycol, glycerol and isopropanol, in alkaline media as compared to acidic media, renders them potential candidates for fuelling AEM-based DAFCs for portable devices, yet breaking of the C-C bonds present in polycarbon alcohols is still an active research objective.

ACKNOWLEDGMENT

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REFERENCES


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Abstract - A degradation and destruction mechanism of solid oxide fuel cell by redox cycles have been reported. Some redox cycles causes micro-cracks at the interface between Ni particles and YSZ particles in the anode. Then, accumulation of the micro-cracks leads to destruction of YSZ network in the anode and at the interface between the anode and the electrolyte. Finally, a delamination of the anode from the electrolyte occurs. According to the degradation mechanism, an enhancement of YSZ network possibly improves the redox tolerance. Some anode samples with various YSZ network were prepared depending on sintering temperature or particle diameter of raw material. Their redox tolerance was evaluated using cumulative redox strains (CRSs). As a result, micro-cracks at YSZ network caused large CRS by redox cycling, which indicates that enhancement of YSZ network has effect on the improvement of redox tolerance.

Index Terms – Solid oxide fuel cell, anode, redox, oxidation.

I. INTRODUCTION

Degradation and destruction mechanism of solid oxide fuel cell by partial redox cycles to the anode have been studied. In our previous studies, an electrochemical oxidation with oxide ions like fuel shortage and a chemical reduction with hydrogen were used as redox cycles [1-3]. The partial redox cycles causes an expansion of Ni particles in the anode, which generates micro-cracks at the interface of YSZ particles in the anode and subsequently at the interface between the anode and the electrolyte. An accumulation of micro-cracks by increasing the number of redox cycles finally leads to cell failure such as a crack in the electrolyte.

The destruction mechanism suggests that higher tolerance for the redox cycle is obtained by enhancement of YSZ network in the anode. In the presentation we will show some results that enhancement of the YSZ network suppresses an expansion of the anode during a redox cycle.

II. EXPERIMENTAL

Some anode samples were prepared depending on sintering temperature or particle diameter of raw material. A mixed powder of 8YSZ (TOSO Co. Ltd.), NiO (Seido Chemical Industry Co., Ltd), and pore former were pressed and sintered to form rectangular bars. Porosities of the samples were also measured using a gas pycnometer. The properties of the samples are listed in Table 1. These samples were heated in a furnace to 800 °C and exposed to 4% H2 – N2 gas and air alternately as shown in Fig.1. During one redox cycle cumulative redox strains (CRSs) were measured in order to evaluate the tolerance for the redox cycle [4]. Microstructures of the anodes were observed using a scanning electron microscopy (SEM).

Table 1. Properties and CRSs at reduced state of Ni-YSZ samples.

<table>
<thead>
<tr>
<th>No.</th>
<th>Ratio (wt%)</th>
<th>Sintering temperature(°C)</th>
<th>Porosity (%)</th>
<th>other</th>
<th>CRS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni : YSZ = 6 : 4</td>
<td>1500</td>
<td>30.4</td>
<td>-</td>
<td>0.53</td>
</tr>
<tr>
<td>2</td>
<td>Ni : YSZ = 6 : 4</td>
<td>1400</td>
<td>38.5</td>
<td>-</td>
<td>1.08</td>
</tr>
<tr>
<td>3</td>
<td>Ni : YSZ = 6 : 4</td>
<td>1500</td>
<td>44.1</td>
<td>-</td>
<td>0.34</td>
</tr>
<tr>
<td>4</td>
<td>Ni : YSZ = 6 : 4</td>
<td>1500</td>
<td>15.9</td>
<td>-</td>
<td>1.14</td>
</tr>
<tr>
<td>5</td>
<td>Ni : YSZ = 5 : 5</td>
<td>1500</td>
<td>29.0</td>
<td>-</td>
<td>0.50</td>
</tr>
<tr>
<td>6</td>
<td>Ni : YSZ = 4 : 6</td>
<td>1500</td>
<td>27.8</td>
<td>-</td>
<td>0.36</td>
</tr>
<tr>
<td>7</td>
<td>Ni : YSZ = 6 : 4</td>
<td>1500</td>
<td>31.5</td>
<td>CeO2 1wt%</td>
<td>0.15</td>
</tr>
<tr>
<td>8</td>
<td>Ni : YSZ = 6 : 4</td>
<td>1500</td>
<td>32.9</td>
<td>CeO2 10wt%</td>
<td>0.27</td>
</tr>
</tbody>
</table>

III. RESULTS AND DISCUSSION

The CRSs of the anodes prepared at 1400 °C (No. 2 in Table 1) and 1500 °C (No. 1 in Table 1) are shown in Fig.2. Both
CRSs show large strain by oxidation compared with small shrinkage by re-reduction. The irreversible strain means the microstructure of the anodes were destructed by oxidation and the strain was cumulated after the re-reduction.

Compared with both anodes, lower CRS were shown in the anodes sintered at 1500 °C than that at 1400 °C, which means the anode prepared at 1500 °C has higher tolerance for the redox cycle. It was known that the porosity has much effect on the redox tolerance [4]. As to our samples, an anode with higher porosity also showed lower CRS among the samples prepared under the same condition. On the other hand, the porosity of the anode prepared at 1400 °C is higher than that at 1500 °C. Therefore, the lower CRS of the anode prepared at 1500 °C than that at 1400 °C cannot be explained by their porosities.

Microstructure of the anode sintered at 1400 °C after the redox cycling is shown in Fig.3. Some cracks at the interface between the YSZ particles were observed in the anode. These cracks were not observed before the redox cycling. This result indicates the cracks were caused by redox cycling. Klemensø et al. reported redox cycling decreased an ionic conductivity of YSZ network in the anode because of fractures of YSZ network [5]. These results indicate the higher tolerance for the redox cycling is achieved by enhancement of YSZ network in the anode.

Fewer cracks were observed in the anode sintered at 1500 °C after the redox cycling than that at 1400 °C. It was suggested that the micro-cracks at the YSZ network in the anode lead to large CRS by redox cycling. This result indicates that sintering at higher temperature is one of the meanings of the enhancement of YSZ network in the anode. Today’s presentation will show other meanings.

IV. CONCLUSION

The anodes sintered at 1400 °C and 1500 °C were prepared. The CRSs by redox cycling and microstructure observation was evaluated. As a result, micro-cracks at YSZ network caused large CRS by redox cycling, which indicates that enhancement of YSZ network has effect on the improvement of redox tolerance.

REFERENCES


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CO₂ IN MOLTEN CARBONATES: A KEY CHALLENGE

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Abstract – This work is dedicated to the feasibility of CO₂ dissolution and electroreduction into CO. It is based on a predictive thermodynamic study, through a potential-oxoacidity diagram relative to Li₂CO₃-K₂CO₃ (62-38 mol%) eutectic. An experimental analysis by cyclic voltammetry at a gold electrode in the same electrolyte at 575°C shows CO₂ reduction wave at around -1.2 V vs. Ag/Ag.

Index Terms: carbon dioxide reduction, Li₂CO₃-K₂CO₃ electrolyte, potential-oxoacidity diagram, cyclic voltammetry.

I. INTRODUCTION

European Union aims at decarbonizing its electricity supply by 2050. One of the most promising routes to decrease the emission of greenhouse gas effects would be to capture CO₂ and re-use it. Molten carbonates, successfully used as electrolytes in molten carbonate fuel cells (MCFC), with good dissolving properties towards CO₂, could be interesting media for the electrolysis of this gas and its transformation into valuable fuels [1-4]. The goal here is to estimate the feasibility of CO₂ electroreduction from predictive thermodynamic data and an experimental work based on cyclic voltammetry at Au electrode in Li₂CO₃-K₂CO₃.

II. CO₂ TRANSFORMATIONS IN MOLTEN CARBONATES

A. Molten carbonates

Molten alkali carbonates are well-known MCFC electrolytes. Their physico-chemical properties are very interesting for carbon dioxide capture and electrolysis. In Li₂CO₃-K₂CO₃ eutectic (Li-K), the limits of the oxoacidity domain are given by molten salt saturated with Li₂O (most basic medium) and CO₂ vapor pressure at a given partial pressure: P(CO₂). This range is characterized by the self-ionization equilibrium [5]:

Li₂CO₃ ↔ CO₂gas + Li₂O (1)

Equilibrium constant K* is associated to this reaction:

\[ K^* = \frac{a(Li_2O)P(CO_2)}{a(Li_2CO_3)} \] (2)

a is the activity of each species. K* is deduced from the standard formation values of all species involved are required:

\[ K^* = \exp\left(\frac{\Delta_f\mu(Li_2CO_3(1)) - \Delta_f\mu(Li_2O(0)) - \Delta_f\mu(CO_2(0))}{RT}\right) \] (3)

As a(Li₂CO₃) is not equal to 1 in the selected eutectic, an apparent constant is defined as follow:

\[ K_d = P_{CO_2}a(Li_2O_{sat}) \] (4)

K₆ defines the limits of the oxoacidity domain in the molten carbonate electrolyte. Thus, the pK₆ is expressed from (4):

\[ pK_d = -\log(K^*) - \log(a(Li_2CO_3)) \] (5)

B. Predictive thermodynamic analysis

Electrochemical stability domain of molten carbonates can be deduced from thermodynamics data [7,8]. The behavior of different electrolytes can be predicted from potential-oxoacidity diagrams: E=f(P(CO₂), as largely described [6]. Fig. 1 provides data on the stability of different reactants in Li₂CO₃-K₂CO₃ melt at 575°C: C(0), CO (+II), CO₂(IV) and oxygen in its different oxidation states (O₂²⁻, O₂⁻, O₂). The reduction ranges of CO₂ into CO and CO₂ into Cgr can be observed in the lower left part of the diagram. Under high CO₂ vapor pressure (used in MCFC cathode conditions), CO₂ reduction into CO occurs at slightly higher potentials than CO₂ reduction into Cgr. The production of CO depends on its partial pressure, for instance P(CO) 10⁻¹ or 10⁻² atm.; in effect, reduction in oxoacidic media is predominantly limited by CO₂ reduction into CO: \[ -\log(P(CO_2)<1.2 \text{ for } P(CO)=10^{-2} \text{ atm. and } -\log(P(CO_2)<0.9 \text{ for } P(CO)=10^{-1} \text{ atm. However, reduction of CO₂ into } C_{gr}, \text{ even if less favorable thermodynamically, may occur because its potential is close to that of } CO_2/CO. \] K* reduction into K occurs at lower P(CO₂). In brief, it is compulsory optimizing the experimental conditions for producing CO and not Cgr.
C. Experimental work

This work is a preliminary approach to the reduction of carbon dioxide at Au electrode by cyclic voltammetry in MCFC cathode conditions. The electrochemical cell is a single-compartment crucible of 70x50 mm² contained in an alumina Al₂O₃ reactor of 250x 60 mm² hermetically sealed by a stainless steel cover with a Viton O-ring. Au working electrode is a 2 cm² plate. Auxiliary electrode is a 6 cm² Au spiral wire. Ag wire and anhydrous silver sulfate constitute the reference electrode. The electrolyte is a mixture of Li₂CO₃ and K₂CO₃ at a molar ratio of 62-38 mol. %. Under pure CO₂ (1 atm.), the mixture is heated up to 650°C to form the melt and lowered to 575°C. Temperature is controlled by a calibrated chromel/alumel thermocouple.

D. Results and Discussion

The thermodynamic study showed that CO₂ in Li-K electrolyte can be reduced either into CO or C⁰ at 575°C, but the first reaction is predominant in oxoacidic media. It should be stated that the potential shift between the O₂/Li₂O reference used for thermodynamic calculations and the experimental Ag+/Ag reference is around 50 mV at 650°C. Cyclic voltammetry performed at different scan rates, for example at 50 mV s⁻¹, indicates that the reduction of CO₂ into CO occurs at around -1.2 V vs. Ag+/Ag in Li₂CO₃-K₂CO₃ (62-38 mol. %) at 575°C on a gold electrode at 50 mV s⁻¹. Nevertheless, it appears necessary to optimize the surface treatment of the Au working electrode and the nature and properties of the carbonate electrolyte to enhance the electrochemical reactivity of CO₂.

III. CONCLUSIONS

Electrochemical stability of molten Li₂CO₃-K₂CO₃ was determined through its acidity-potential diagram at 575°C. According to the acidity level and the potential, the reduction limit corresponds to the formation of CO, C⁰ or K. CO₂ reduction into CO occurs at around -1.2 V vs. Ag+/Ag in Li₂CO₃-K₂CO₃ (62-38 mol. %) at 575°C on a gold electrode at 50 mV s⁻¹. Nevertheless, it appears necessary to optimize the surface treatment of the Au working electrode and the nature and properties of the carbonate electrolyte to enhance the electrochemical reactivity of CO₂.

REFERENCES

THE THROUGH-PLANE THERMAL CONDUCTIVITY AND THE CONTACT RESISTANCE OF THE COMPONENTS OF THE MEMBRANE ELECTRODE ASSEMBLY IN PROTON EXCHANGE MEMBRANE FUEL CELLS

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Abstract - The thermal conductivity of the components of the membrane electrode assembly (MEA) must be accurately estimated in order to better understand the heat transfer processes in proton exchange membrane (PEM) fuel cells. In this study, an experimental investigation has been performed to measure the through-plane thermal conductivity and the contact resistance for a number of gas diffusion layer (GDL) materials. The sensitivity of these quantities to the temperature, PTFE content and micro-porous layer (MPL) coating has been undertaken. In addition, the through-plane thermal conductivity of the membrane has been measured and reported as a function of temperature and water content. Further, the through-plane thermal conductivity of the catalyst layer has been determined as a function of temperature and platinum loading. It has been found that the through-plane thermal conductivity of the components of the MEA decreases when the temperature increases, and the through-plane thermal conductivity of the GDL is significantly lower than its in-plane thermal conductivity.

Index Terms – catalyst layer, gas diffusion layer, membrane, through-plane thermal conductivity.

I. NOMENCLATURE

\( A_s \) Cross-sectional area of the sample (m²)
\( k_s \) Thermal conductivity of the sample (W m⁻¹ K⁻¹)
\( L_s \) Length of the sample (m)
\( q_s \) Heat transfer through the sample (W)
\( \Delta T \) Temperature drop across the sample (K)

Abbreviations:
GDL Gas Diffusion Layer
MEA Membrane Electrode Assembly
MPL Micro-porous Layer
PEM Proton Exchange Membrane
PTFE Polytetrafluoroethylene

II. INTRODUCTION

The knowledge of the thermal properties of the components in PEM fuel cells is essential for the heat and water management in PEM fuel cells. Many studies have focused on the thermal conductivity of the gas diffusion layer (GDL). In particular, Khandelwal and Mench [1] measured the through-plane thermal conductivity of Toray and SIGRACET® carbon papers under 20 bar compression pressure. Ramousse et al. [2] estimated the thermal conductivity of a typical GDL to be lower than the thermal conductivity of pure carbon. In this study, an experimental technique is developed to measure the through-plane thermal conductivity of the GDL as a function of PTFE loading, temperature and compression pressure. In addition, for the present study to be comprehensive, the through-plane thermal conductivities of Nafion membranes and catalyst layers are measured and reported as a function of temperature.

III. EXPERIMENTAL SETUP

A. Test apparatus

An experimental apparatus has been developed to measure the thermal conductivity of the various components of the MEA. The formula employed to achieve this is the Fourier law:

\[
q_s = k_s A_s \frac{\Delta T}{L_s}
\]

The test apparatus is shown in Figure 1. It consists of, from top to bottom, (i) a dial gauge indicator to measure the reduction in the thickness of the sample under compression, (ii) a load cell which records the compression pressure on the sample, (iii) the upper steel flux meter, which contains 3 thermocouples, (iv) the tested sample, and (v) the lower steel flux meter which also contains 3 thermocouples and its temperatures are maintained low and constant using a cooling system.

Fig. 1. Configuration of the experimental set-up to measure the through-plane thermal conductivity of the MEA components.
B. Materials

The through-plane thermal conductivity of the GDL is determined for five different SGL samples (10AA, 10BA, 10CA, 10DA, 10EA) whose PTFE loading are 0, 5, 10, 20 and 30%, respectively. The through-plane thermal conductivity of a 115 Nafion® membrane and typical catalyst layers is determined and reported as a function of temperature spanning between 35 and to 80 °C, which is most likely the temperature at which the PEM fuel cell is operated.

C. Conditions

All measurements were made under vacuum conditions to eliminate heat transfer by convection. Moreover, the fixtures and the samples were well insulated to minimise the heat loss in the radial direction.

IV. RESULTS AND DISCUSSION

As illustrated in Figure 2, the thermal resistance of the treated GDL was higher than that of the untreated GDL. This is due to the increase in the contact resistance between the samples and the GDL after adding the PTFE.

![Fig. 2. Measured thermal resistance of the GDLs at different compression loads.](image1)

It was found that the through-plane thermal conductivity of GDL decreases when the temperature increases. This is due to the fact that the GDL contains a polymeric resin whose thermal conductivity decreases with increasing temperature. Also, the through-plane thermal conductivity of the GDL was found to increase with compression pressure, as shown in Figure 3.

![Fig. 3. Measured thermal conductivity of the GDLs at different compression loads.](image2)

Furthermore, the through-plane thermal conductivities of the membrane and catalyst layer decrease slightly with increasing temperature as shown in figure 4, and they were found to be comparable with their in-plane thermal conductivities [3].

![Fig. 4. Measured thermal conductivities of the membrane and the catalyst layers.](image3)

V. CONCLUSION

An experimental technique has been developed in this study to determine the through-plane thermal conductivity and the contact resistance of the components in the MEA. The results show that the through-plane thermal conductivity of the GDL decreases with increasing temperature and increases with increasing compression pressure. Further, the through-plane thermal conductivity of the membrane and catalyst layer decrease when the temperature increases and it is comparable to that of the in-plane direction. The through-plane thermal conductivity of the MEA components provide some of the necessary parameters which will enhance the future prediction of the temperature and water saturation in PEM fuel cells and accurately predict the performance of PEM fuel cell.

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ENERGY FLOW DIAGRAM ANALYSIS OF FUEL CELL PLUG-IN HYBRID ELECTRIC BUS DEMONSTRATION IN SINGAPORE

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Abstract - During the 2010 Singapore Youth Olympic Games, the 4th generation of hydrogen fuel cell buses, developed by Tsinghua University, were demonstrated for 3 months in Singapore. With the function of electric grid charging, the capacity of the lithium ion battery is larger than those of previous generations which were demonstrated in 2008 Beijing Olympic Games and 2010 Shanghai World Expo. In this paper, an internal energy flow was investigated and analyzed based on statistical method by utilizing Matlab/Simulink tool and Sankey diagram. The calculation results show that the fuel cell system provides 45%-47% energy converting efficiency from hydrogen to electricity in the whole demonstration period; mid- high speeds contribute the most of total trip distance, while the low-speed and idling operations consume the most hydrogen energy to maintain the auxiliary power and charge the battery. As the larger capacity battery and brake energy regeneration installed, the hydrogen consumption decreases to 6-8kg/100km.

Index Terms - demonstration, energy flow diagram, plug-in fuel cell bus, platform

I. INTRODUCTION

With the rapid development of clean vehicle technology, there is increasing attention to hydrogen fuel cell buses. In order to improve performance and realize commercialization, a number of demonstration projects which focused on fuel cell vehicles and hydrogen stations were carried out worldwide. They in total drove 248,200 miles and fueled 136 tons of hydrogen respectively [1]-[2]. In 2006, there were also some demonstrations supported by GEF/UNDP and Chinese Government deploying fuel cell buses in Chinese cities. The most representative projects were tested in 2008 Beijing Olympic Games and 2010 Shanghai World Expo which used the domestically manufactured fuel cell systems to support daily operation. This paper utilizes the 4th generation fuel cell plug-in hybrid electric bus which was developed and optimized by Tsinghua University, and adds larger capacity lithium ion battery (175Ah) to improve the driving mileage and fuel cell durability.

II. REAPPEARANCE PLATFORM OF ENERGY FLOW

In order to deal with the massive data, which was collected from the sensors effectively and clearly, we designed and built a reappearance platform of energy flow for the fuel cell bus (Fig.1). It includes two parts: the batch processing platform of massive data and the energy flow diagram model. Based on programming in Matlab, the batch processing platform could handle automatically all raw data collected within a month, which saved by a data acquisition unit. The characteristic data covers the expected calculated results which include mileage, components power, and hydrogen or electricity consumption. The energy flow diagram model is a schematic diagram which describes the internal components orientation and structure clearly. Combined with the output results and the tool Sankey diagram, a completed internal energy flow is drawn simply. It depicts the efficiency from the hydrogen tank to the transmission to show the internal variation of energy and illustrates auxiliary consumption to indicate opportunities for optimization of components.

III. ENERGY FLOW DIAGRAM ANALYSIS

Fig2 shows the energy flow Sankey diagram which was calculated by the reappearance platform.
To assume hydrogen tank output energy ratio equals 100%. The fuel cell efficiency is 45.26%. DC/DC output has 39.23% energy ratio, and approximately to 50% charges the battery (19.34%). The rest of the energy (19.89%) combines with the discharging electric energy (36.65%) to maintain the auxiliary power (24.08%) and electric motor (38.00%). Because of 5.55% braking electric energy regenerated, the drive efficiency of the electric motor reaches up to 90.54%; the braking efficiency is 92.99%. Therefore, electric motor output is 34.41% energy ratio to the transmission. The final output energy is 32.69%. The powertrain efficiency is 29.33%.

Fig. 3 describes the results in six speed ranges. It shows that the fuel cell bus consumed about 33% of total time to maintain auxiliary consumption and only drove 5% of total mileage during the idling and low speed range.

### Table I

<table>
<thead>
<tr>
<th>Date</th>
<th>Total mileage/km</th>
<th>Average speed/(km/h)</th>
<th>Hydrogen consumption/(kg/100km)</th>
<th>Final output energy/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>07/31/2010</td>
<td>106.43</td>
<td>26.28</td>
<td>8.03</td>
<td>27.15</td>
</tr>
<tr>
<td>08/26/2010</td>
<td>183.31</td>
<td>27.08</td>
<td>6.64</td>
<td>32.69</td>
</tr>
<tr>
<td>09/11/2010</td>
<td>124.24</td>
<td>22.07</td>
<td>7.82</td>
<td>36.38</td>
</tr>
</tbody>
</table>

### IV. CONCLUSION

During the 3 months demonstration, the calculated results with the platform show that the fuel cell bus consumed long time and most of the total fuel energy to maintain auxiliary power and charge the battery during the idling and low speed range; when the battery worked without fuel cell system and brake energy existed, the final output energy is increased by 10%.

### ACKNOWLEDGMENT

This research is funded by the Ministry of Science and Technology of China under the contracts of No. 2011AA11A269, 2011AA11A288, 2010DFAF72760, 2011DFA60650, 2012DFA81190, 2011BAG02B12; thanks the support of the Beijing Municipal Science & Technology Commission (Z121100007912001).

### REFERENCES


DESIGN AND ANALYSIS OF AN INTEGRATED AUTOTHERMAL REFORMING AND HT-PEMFC SYSTEM FOR AUTOMOTIVE APPLICATION

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** Computational Process Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

Abstract - The aim of this study is to investigate the performance and efficiency of an integrated autothermal reforming and HT-PEMFC system fuelled by methane for automotive applications. The autothermal reforming (ATR), which has higher reaction rate at an initial period than a steam reforming and can be operated without external heat unit to supply heat for the reforming process, is chosen as a fuel processor. The HT-PEMFC and methane autothermal reformer systems with and without a CO removal process are considered. The operating parameters, such as reformer temperature, inlet temperature and steam to carbon ratio (S/C), are key factors to achieve a high system efficiency. The results indicate that the HT-PEMFC system without a CO removal process should be operated under low reformer temperatures and high S/C ratio. The optimal operating conditions of the autothermal reformer and the system efficiency for different system designs are reported.

Index Terms – HT-PEMFC, Autothermal reforming, System design, Automotive application

I. INTRODUCTION

High-temperature proton exchange membrane fuel cell (HT-PEMFC) is one of the promising technologies developed to handle with the CO poisoning problem found in a conventional PEMFC. At a high-temperature operation, the amount of CO that is adsorbed on Pt catalyst in HT-PEMFC reduces. Thus, it could be possible to directly use the reformate gas from a fuel processor with a simplified purification process of hydrogen for HT-PEMFC process. In addition, a flooding problem is solved because water is present only in the vapor phase and the transport of water is easily balanced. These factors make the design of HT-PEMFC system be less complicated than the conventional PEMFC. For automotive applications, the low weight and size of an overall fuel cell system is required and the fast starting up is also preferred. Thus, an autothermal reforming is more suitable for this application than a steam reforming [1]. The aim of this study is to design and investigate the performance and efficiency of an integrated autothermal reforming and HT-PEMFC system fuelled by methane for the automotive application. The effect of operating parameters, such as reformer temperature, inlet temperature, and S/C ratio, on the reformer efficiency, hydrogen yield and CO content is analyzed. The optimal operating conditions of the autothermal reformer providing the suitable product gas for HT-PEMFC is given. The efficiency and performance of the HT-PEMFC systems are analyzed by considering the complexity of each designed HT-PEMFC system.

II. SYSTEM DESCRIPTION

Two HT-PEMFC systems are considered in this study. The first system consists of the HT-PEMFC and methane autothermal reformer without a CO removal process. The second one involves the HT-PEMFC with the fuel processor consisting of the methane autothermal reformer and a water gas shift reactor (WGS). The autothermal reforming (ATR) is chosen as a hydrogen production process for automotive application because it provides higher reaction rate at an initial period than a steam reforming. In addition, it is possible to operate the autothermal reformer without the requirement of an external heat unit to supply heat for the reforming process. In this study, the methane autothermal reforming is operated under an adiabatic condition by controlling the oxygen feed ratio.

III. MATHEMATICAL MODEL

An equilibrium composition of the reformate gas obtained from the methane autothermal reforming is calculated from the direct minimization of Gibbs free energy. The WGS reactor is
also modelled as an equilibrium reactor and its operating temperature is specified at 473.15 K. For HT-PEMFC, the basic relation of voltage and current density, which represents its electrical performance, is described by Eq. (1). The cell voltage \( E_{\text{cell}} \) can be calculated by subtracting the reversible cell potential \( E_r \) by various voltage losses \([2]\).

\[
E_{\text{cell}} = E_r - \eta_{\text{act,a}} - \eta_{\text{act,c}} - \eta_{\text{ohmic}}
\]  

(1)

where \( \eta_{\text{act,a}} \) is the activation loss at the anode, \( \eta_{\text{act,c}} \) is the activation loss at the cathode and \( \eta_{\text{ohmic}} \) is the ohmic loss.

Because the fuel fed into the anode is not pure hydrogen and have some CO contamination, the CO poisoning effect is also considered in this work.

The efficiency of a fuel processing process \( (\eta_{FP}) \) can be determined by the following expression:

\[
\eta_{FP} = \frac{n_{H_2} \cdot LHV_{H_2}}{n_{CH_4} \cdot LHV_{CH_4} + Q_p}
\]

(2)

where \( n \) is the molar flow rate, \( LHV \) is the lower heating value and \( Q_p \) is the heat requirement for preheating the reactant.

The fuel cell stack efficiency \( (\eta_{\text{FC}}) \) and system efficiency \( (\eta_{\text{sys}}) \) can be defined as follows:

\[
\eta_{\text{FC}} = \frac{P_{\text{FC}}}{n_{H_2} \cdot LHV_{H_2}}
\]

(3)

\[
\eta_{\text{sys}} = \eta_{FP} \cdot \eta_{\text{FC}}
\]

(4)

The mathematical models of the HT-PEMFC system integrated with the methane autothermal reforming process are programmed using Matlab.

IV. RESULT AND DISCUSSIONS

The methane autothermal reforming and HT-PEMFC integrated systems with and without a water gas shift reactor are considered. Firstly, the effects of reformer temperature, inlet reformer temperature and S/C on the hydrogen fraction, CO fraction, fuel processor efficiency are studied. The inlet temperature has significant effect on system efficiency because the required oxygen flow rate to sustain the autothermal reforming operation decreases with increasing the inlet reformer temperature. Therefore, the hydrogen loss due to oxidation reaction reduces at high inlet reformer temperature. In addition, increases in operating temperature and S/C enhance the hydrogen fraction and reduce the CO fraction (dry basis).

Compared to the HT-PEMFC system with WGS reactor, higher S/C ratio and lower temperature are preferred for HT-PEMFC system without WGS reactor. Table 1 shows the optimal operating conditions of methane autothermal reforming with and without WGS reactor for HT-PEMFC. At these conditions, the highest hydrogen fraction and fuel processor efficiency at the acceptable CO level for HT-PEMFC are obtained.

The target power output of the HT-PEMFC systems for automotive application is 50 kW at specified active area and number of cell. The comparison of methane autothermal reforming efficiency, fuel cell stack efficiency and system efficiency at different system designs is shown in Table 2. It is observed that the HT-PEMFC system with WGS reactor where \( T_{in} = T_R \) shows the highest system efficiency but this system has larger size than another system.

Table 2 Efficiency of methane autothermal reforming, fuel cell stack and system at the optimal operating conditions

<table>
<thead>
<tr>
<th>Case</th>
<th>( P_{in} ) (K)</th>
<th>S/C</th>
<th>( \eta_{FP} )</th>
<th>( \eta_{\text{FC}} )</th>
<th>( \eta_{\text{sys}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-PEMFC system without WGS reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 1: ( T_{in} = 25^\circ \text{C} )</td>
<td>873</td>
<td>3</td>
<td>0.38</td>
<td>4.09</td>
<td></td>
</tr>
<tr>
<td>Case 2: ( T_{in} = T_R )</td>
<td>873</td>
<td>3</td>
<td>0.52</td>
<td>5.81</td>
<td></td>
</tr>
<tr>
<td>HT-PEMFC system with WGS reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 1: ( T_{in} = 25^\circ \text{C} )</td>
<td>873</td>
<td>3</td>
<td>0.42</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>Case 2: ( T_{in} = T_R )</td>
<td>973</td>
<td>2</td>
<td>0.41</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>

The efficiency of a fuel processing process \( (\eta_{FP}) \) can

\[
\eta_{FP} = \frac{n_{H_2} \cdot LHV_{H_2}}{n_{CH_4} \cdot LHV_{CH_4} + Q_p}
\]  

(2)

where \( n \) is the molar flow rate, \( LHV \) is the lower heating value and \( Q_p \) is the heat requirement for preheating the reactant.

The fuel cell stack efficiency \( (\eta_{\text{FC}}) \) and system efficiency \( (\eta_{\text{sys}}) \) can be defined as follows:

\[
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\]

(3)

\[
\eta_{\text{sys}} = \eta_{FP} \cdot \eta_{\text{FC}}
\]

(4)

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<table>
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<tr>
<th>Case</th>
<th>( P_{in} ) (K)</th>
<th>S/C</th>
<th>( \eta_{FP} )</th>
<th>( \eta_{\text{FC}} )</th>
<th>( \eta_{\text{sys}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-PEMFC system without WGS reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 1: ( T_{in} = 25^\circ \text{C} )</td>
<td>67.8</td>
<td>31.4</td>
<td>21.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 2: ( T_{in} = T_R )</td>
<td>69.5</td>
<td>32.1</td>
<td>22.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HT-PEMFC system with WGS reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 1: ( T_{in} = 25^\circ \text{C} )</td>
<td>74.9</td>
<td>32.5</td>
<td>24.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 2: ( T_{in} = T_R )</td>
<td>87.8</td>
<td>32.9</td>
<td>28.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

V. CONCLUSIONS

The methane autothermal reforming integrated with HT-PEMFC for automotive applications is designed and analyzed in this work. The inlet reformer temperature has a crucial effect on efficiency because it is a key factor for controlling the energy usages of autothermal reformer. To provide suitable product gas for HT-PEMFC, HT-PEMFC system without WGS reactor should be operated at higher S/C ratio and lower reformer temperature compared to the HT-PEMFC system with WGS reactor. In addition, it is found that WGS reactor is necessary for the fuel processor of HT-PEMFC system when the system efficiency is a key factor for system design.

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REFERENCES


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DRY REFORMING OF MODEL BIOGAS USING A HIGHLY STABLE LA-PROMOTED NI CATALYST: INFLUENCE OF REDUCTION TEMPERATURE

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Abstract – A La-promoted Ni-based catalyst was evaluated in dry reforming of methane reaction. Two reduction temperatures (650 and 750 °C) were tested during 300 h catalytic tests. They were performed at 750 °C and a CH₄:CO₂ molar ratio of 1:1. Used catalysts were characterized by Temperature Programmed Oxidation (TPO) and Transmission Electron Microscopy (TEM). Good stability was observed in both tests. When the catalyst was reduced at 750 °C a higher activity and a lower carbon deposition rate was obtained.

Index Terms – Biogas, dry reforming, hydrogen, reduction treatment.

I. INTRODUCTION

There is a growing interest in the development of power sources that use renewable fuels and reduce emission of pollutants, i.e. fuel cells. One example of renewable fuel is biogas, which typically refers to a gas produced by the biological breakdown of organic matter in an oxygen-free environment. Biogas is a readily available but underexploited energy source, because its high levels of carbon dioxide hinders its use in conventional power-generation systems, resulting in relatively low electrical conversion efficiency. An interesting alternative is H₂ production from biogas reforming. Since CH₄ and CO₂ are their main constituents, CO₂ reforming of methane seems to be an appealing process. The major drawback of this reaction is coke deposition [1]. Consequently, highly stable catalysts have to be developed in order to achieve that this technology become feasible. Catalysts obtained from calcination of hydrotalcite-like precursor show very interesting properties such as high surface area, basic properties and high dispersion [2]. However, they do not provide a sufficient degree of stability which is required by an industrial process. Previous works [3] reported the addition of lanthanum as a way to enhance catalytic stability in dry reforming of methane when calcined at 750 °C. The aim of this work is to study the influence of reduction temperature over catalytic activity and stability in dry reforming of methane.

II. EXPERIMENTAL

A hydrotalcite precursor was synthesized by the co-precipitation method under low supersaturation conditions and the catalyst was prepared after calcination of the precursor at 750 °C. Its composition was: Mg/Al molar ratio of 2.2, 2.8% Ni and 1.9% La. The preparation method and the characterization of this catalyst was reported elsewhere [3,4].

Catalytic tests were carried out in a tubular fixed-bed reactor at 750 °C and CH₄:CO₂ 1:1. Reaction products were analyzed by gas chromatography. In order to evaluate the influence of reduction temperature, the catalyst was reduced at two different temperatures: i) 650 °C and ii) 750 °C. The tests were performed at the highest space velocity which allowed a maximum conversion and thus deactivation would not be hidden as a consequence of an excess of active sites. Then, space velocity was 4,800 cm³·gcat⁻¹·h⁻¹ for the catalyst reduced at 650 °C and 18,000 cm³·gcat⁻¹·h⁻¹ when it was reduced at 750 °C. Used catalysts were characterized by TPO and TEM analysis.

III. RESULTS AND DISCUSSION

A. Catalytic tests

Since the test of the catalyst being reduced at 650 °C was reported elsewhere [5], and the conversions were the same as the obtained when the catalyst was reduced at 750 °C, Fig. 1 only shows the evolution of conversions and H₂/CO ratio versus time when catalyst was reduced at 750 °C. In this test, the catalyst was stable during the whole experiment (300 h), detecting only a 1% decrease of CH₄ and CO₂ conversions after 250 h. Nevertheless, when the catalyst was reduced at 650 °C no sign of deactivation was observed (figure not shown) but, it
was necessary to operate at lower space velocity in order to achieve the same conversions. The catalytic activity of the catalyst being reduced at 650 °C was 0.093 mol CH\textsubscript{4}·h\textsuperscript{-1}·g\textsubscript{cat}\textsuperscript{-1}, while it was 0.3mol CH\textsubscript{4}·h\textsuperscript{-1}·g\textsubscript{cat}\textsuperscript{-1} when the catalyst was reduced at 750 °C. This increase on the activity when the reduction temperature is raised may be explained by a higher amount of Ni\textsuperscript{0}.

Carbon dioxide conversion (XCO\textsubscript{2}) was higher than methane conversion (XCH\textsubscript{4}) what must be attributed to the reverse water-gas-shift reaction (RWGS), confirmed by water presence in product stream (1%) and the H\textsubscript{2}/CO ratio below 1 (0.9). Moreover, the conversions (XCH\textsubscript{4} = 89% and XCO\textsubscript{2} = 92% - taken after 230 h on reaction-) were higher than thermodynamic equilibrium estimation (86%), what suggests that other reactions were taking place. These reactions could be methane decomposition or methane steam reforming which will consume water formed by means of RWGS [8].

Moreover, the conversions (XCH\textsubscript{4} = 89% and XCO\textsubscript{2} = 92% - taken after 230 h on reaction-) were higher than thermodynamic equilibrium estimation (86%), what suggests that other reactions were taking place. These reactions could be methane decomposition or methane steam reforming which will consume water formed by means of RWGS [8].

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Higher space velocity (18,000 cm\textsuperscript{3}·h\textsuperscript{-1}) was necessary to operate at lower space velocity in order to achieve the same conversions. The catalytic activity of the catalyst being reduced at 650 °C was 0.093 mol CH\textsubscript{4}·h\textsuperscript{-1}·g\textsubscript{cat}\textsuperscript{-1}, while it was 0.3mol CH\textsubscript{4}·h\textsuperscript{-1}·g\textsubscript{cat}\textsuperscript{-1} when the catalyst was reduced at 750 °C. This increase on the activity when the reduction temperature is raised may be explained by a higher amount of Ni\textsuperscript{0}.

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B. Post-reaction characterization

TPO characterization showed that carbon deposited during the tests. The coke deposition rate when the catalyst was reduced at 750 °C was 0.18 mg\textsubscript{C}·g\textsubscript{cat}·h\textsuperscript{-1} while it was 2.3 mg\textsubscript{C}·g\textsubscript{cat}·h\textsuperscript{-1} when it was reduced at 650 °C. Then, the increase in reduction temperature produces a lower carbon deposition rate with values closer to other author’s results. Xu et al. [7] reported a coking rate of 0.0946 mg\textsubscript{C}·g\textsubscript{cat}·h\textsuperscript{-1} when he operated at 800 °C, a CH\textsubscript{4}:CO\textsubscript{2} ratio of 1:1 and at 6,000 cm\textsuperscript{3}·g\textsubscript{cat}·h\textsuperscript{-1} during 290 h. Al-Fatesh [8] reported a coking rate of 0.12 mg\textsubscript{C}·g\textsubscript{cat}·h\textsuperscript{-1} when he operated at 850 °C, a CH\textsubscript{4}:CO\textsubscript{2}:N\textsubscript{2} ratio of 5:5:1 and at 2,640 cm\textsuperscript{3}·g\textsubscript{cat}·h\textsuperscript{-1} during 130 h. It is noteworthy that we were operating at lower temperature and higher space velocity (18,000 cm\textsuperscript{3}·g\textsubscript{cat}·h\textsuperscript{-1}), which indicates a higher activity of our catalyst besides a good stability and low carbon deposition rate.

TEM micrographs of the used catalysts (not shown) showed a higher average Ni particle size (17 nm) when the reduction temperature was 750 °C. When the catalyst was reduced at 650 °C (two maximums were observed, one at 8 nm and another at 14 nm). This may indicate that partial sintering occurred during the test, which may explain the slight deactivation after 250 h on reaction.

IV. Conclusion

The influence of reduction temperature in dry reforming of methane reaction has been studied using a La-promoted Ni-based catalyst. In both tests the stability was good, only detecting a decrease of conversion of 1% when the catalyst was reduced at 750 °C. Better results (higher activity and lower carbon deposition rate) were obtained when the catalyst was reduced at 750 °C. This higher activity will mean a higher hydrogen production. Moreover, the costs would be also lower because a lower amount of catalyst would be necessary and then the reactor could be smaller.

ACKNOWLEDGMENT

Financial support from Comunidad de Madrid (DIVERCELCM, S2009/ENE-1475) is gratefully acknowledged.

REFERENCES


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THE IMPLEMENTATION OF THE EUROPEAN BUILDINGS DIRECTIVE (EPBD): OPPORTUNITIES OR THREATS FOR THE MARKET INTRODUCTION OF THE FUEL CELL SYSTEM

M. Mitterndorfer*, G. Simader*

*Austrian Energy Agency, Vienna (Austria)

The buildings sector represents 40% of the European Union’s total energy consumption (around 30% in Austria). Buildings will play a major role in achieving the European Union’s goals regarding energy efficiency till 2020. The EPBD contributes to achieve the 20% efficiency goal by proposing guiding principles for Member States (MS) regarding the energy performance of buildings. It aims to promote the energy performance of buildings and building units within the MS.

Index Terms – energy performance of buildings, European Buildings Directive, market introduction of fuel cell systems

The general objective of the EPBD is to increase the overall energy efficiency of buildings. Before the implementation of the EPBD in Austria, there have only been upper limits for the heating demand relating to the thermal building envelope. In addition to the needs concerning the thermal building envelope, primary energy consumption and CO₂ emissions, there are now requirements concerning the energy efficiency of the HVAC (heating, ventilation and air conditioning) system. Moreover, the demands regarding the thermal building envelope depend on the efficiency of the HVAC system. Through the new directive, energy efficiencies of HVAC systems will have to be considered when issuing an energy performance certificate. Furthermore, CO₂ emissions and the primary energy demand of the building have to be calculated. The new situation in the construction environment provides new opportunities for fuel cells and micro-CHP systems in buildings. In the study, those parts of the Buildings Directive (like Art. 9 - nearly zero energy buildings) which will have a significant impact on fuel cells or micro CHP systems are introduced and analyzed.

Through the implementation of the EPBD a new set of cost optimum energy efficiency requirements have to be implemented in the future. In the study, the impact of the EPBD implementation in Austria on the market uptake of fuel cell and micro CHP systems has been analyzed. Micro CHPs and/or fuel cells are neither considered in the legislation for energy performance certificates (EPC’s) nor in the calculation methodologies for this legislation. The launch of the EPBD in the MS requires - among other things - the creation of national plans of each MS regarding future building standards. On the basis of the national plan for Austria (see Table I), representative example buildings were developed in a first step. In particular, the required thermal building standard for 2020 (“nearly zero energy buildings”, “major renovations”) were considered.

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>NATIONAL PLAN FOR AUSTRIA: MINIMUM ENERGY PERFORMANCE REQUIREMENTS FOR NEW RESIDENTIAL BUILDINGS.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HWBmax, sk [kWh/m²a]</td>
</tr>
<tr>
<td>2014</td>
<td>16 x (1+3.0/lc) using default HTEBRef</td>
</tr>
<tr>
<td>2016</td>
<td>14 x (1+3.0/lc) using default HTEBRef</td>
</tr>
<tr>
<td>2018</td>
<td>12 x (1+3.0/lc) using default HTEBRef</td>
</tr>
<tr>
<td>2020</td>
<td>10 x (1+3.0/lc) using default HTEBRef</td>
</tr>
</tbody>
</table>

Abbreviations: lc...characteristical length of a building, which is the reciprocal value of the form factor A/V [m]
HWB...space heating demand [kWh/m²a]
EEB...energy performance factor [-]
PEB...primary energy demand [kWh/m²a]
CO2...CO₂ emissions [kg/m²a]
HTEB...heating system energy demand
In the future, buildings must have a high thermal standard and an efficient heating system. Due to the high thermal building standard, the heat demand is largely determined by the demand for hot water. The hot water demand is relatively constant over the year. This leads to flatter load curves which favors the use of monovalent systems. The use of monovalent systems could lead to a cost leap and contribute to the economic competitiveness of micro CHP systems. In the present calculations only bivalent systems consisting of micro CHP and peak load boiler equipped with puffer and hot water storage systems were investigated. The reference building and the heating system were defined as follows (see Table II):

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space heating demand [kWh/m²a]</td>
<td>32</td>
</tr>
<tr>
<td>Peak load boiler [kW]</td>
<td>15</td>
</tr>
<tr>
<td>Fuel cell - electrical power [kW]</td>
<td>1</td>
</tr>
<tr>
<td>Fuel cell - thermal power [kW]</td>
<td>2</td>
</tr>
<tr>
<td>Buffer storage volume [l]</td>
<td>500</td>
</tr>
</tbody>
</table>

The design of the system (see Fig.1) leads to a thermal cover ratio of 90% through the fuel cell. The remaining 10% of the heat demand are covered through the peak load boiler. The fuel cell provides 75% of the electricity demand with a direct utilization of almost 50%.

The fuel cell has been economically compared with a conventional gas condensing boiler system and a grid based electrical supply. The input parameters for the economic calculation are based on commercialization strategies of leading European boiler manufacturers and on Austrian/European standards and guidelines. The following three different scenarios for feed-in tariffs and investment costs were considered and analyzed (see Table III):

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Investment costs gas boiler system [€]</th>
<th>Investment costs fuel cell system [€]</th>
<th>Feed-in tariff [€/kWh]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario 1</td>
<td>11,186</td>
<td>15,000</td>
<td>0.037</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>11,186</td>
<td>15,000</td>
<td>0.215</td>
</tr>
<tr>
<td>Scenario 3</td>
<td>11,186</td>
<td>15,000</td>
<td>0.144</td>
</tr>
</tbody>
</table>

The performed calculations (see Fig.2) show that the analyzed fuel cell system cannot achieve an economic competitiveness to the conventional gas condensing boiler based on the present frame conditions (scenario 1).

Fig. 2. Different scenarios of the economic comparison between fuel cell system and gas condensing boiler system

In conclusion, it should be noted that subsidies for market uptake, regarding feed-in tariffs and investment costs, are necessary (scenario 2 & 3) in order to achieve economic competitiveness for the analyzed fuel cell system to conventional gas condensing boilers. The comparison of CO₂ emissions and primary energy demand show advantages for the fuel cell system. Further detailed analyses are necessary for a detailed quantification of the benefits of a decentralized supply.

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HYDROGEN PRODUCTION AND CO CLEANING BY SINGLE STAGE WATER-GAS-SHIFT REACTION

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Abstract – In this work a water-gas-shift catalyst designed and patented by our group was tested in order to examine the influence of the operation parameters when the feed consists on the typical output of a biogas dry reformer. It was observed that it was necessary to operate at 350 ºC, GHSV ≥ 15,000 h⁻¹ and S/CO ≥ 7.3. Since the output of the biogas dry reformer contains a higher CO₂ content, the formation of monodentate superficial carbonates is favored. The catalyst was also tested during 100 h at 350 ºC, GHSV = 15,000 h⁻¹ and X/CO = 7.3 and it didn’t show any sign of deactivation. This high stability together with the possibility of working at high space velocities allows the use of smaller reactors.

Index Terms – Water-gas-shift, hydrogen, biogas, operating parameters.

I. INTRODUCTION

Hydrogen is a perspective energy carrier that can be used in fuel cells, avoiding CO₂ emissions. Some of the technologies that produce hydrogen (steam reforming, partial oxidation, and autothermal reforming of hydrocarbons) also generate CO, which should be eliminated to ppm level in order to avoid PEMFC poisoning [1]. Water gas shift reaction (WGS: CO + H₂O ⇌ H₂ + CO₂) is a well-established process which reduces CO concentrations. However, this reaction is a critical step in a compact fuel processor for on-board hydrogen production integrated with a fuel cell because its reactor volume occupies ca. 70% of the total volume in a fuel processing system. Thus, a robust single-stage WGS reactor is desirable for a compact fuel processing system. Therefore, novel catalysts with high activity and stability need to be developed in order to reduce reactor volume.

The aim of this work is to study the influence of several operating parameters.

II. EXPERIMENTAL

The tested catalyst was developed and patented by our group [2]. For the experiments, the catalyst was diluted with CSi and was reduced in situ at 350 ºC during 1 h with 100 mL·min⁻¹ of H₂. Catalytic tests were carried out in a tubular fixed-bed reactor and reaction products were analyzed by chromatography. Three experiments were performed: 1) a study of S/CO ratio influence at 300 and 350 ºC; 2) a test of GHSV influence and 3) a stability test. Feeding composition was in all cases the typical output of a dry biogas processor (39% H₂, 42 % CO, 7 % CO₂ y 12% CH₄). This composition is the most demanding since when other reforming processes are involved lower CO concentrations at the output are obtained.

III. RESULTS AND DISCUSSION

A. S/CO influence

S/CO influence depends to a large extent on reaction temperature (Fig. 1).

FIG. 1. CO CONVERSION VS. S/CO.
At 300 ºC, the increase on CO conversion (XCO) is greater than at 350 ºC and it may be due to an equilibrium shift according to L’Chatelier laws because at 300 ºC conversion is far from thermodynamic equilibrium. Optimal temperature range of this catalyst was estimated to be between 250-300 ºC [2], when the feeding had low CO₂ content. CO₂ presence is supposed to favor the formation of monodentate superficial carbonates which can block active centers [3, 4]. It is likely that at 350 ºC thermal decomposition of this intermediates occurs, active sites are released and CO can adsorb on them.

B. GHSV influence

In order to design a compact fuel cell processor, it is necessary to be able to operate at high GHSV. Fig. 2 shows the evolution of XCO versus GHSV. This test was performed at 350 ºC and a S/CO ratio of 7.3.

![Fig. 2. CO conversion vs. GHSV.](image)

It can be observed that conversion decreases from GHSV > 15,000 h⁻¹, so the catalyst should not be operated beyond that limit. This space velocity is higher than that necessary for commercial catalysts (6,000 h⁻¹) [5], what indicates a great improvement.

C. Stability test

Catalyst stability was evaluated at 350 ºC, a S/CO ratio of 7.3 and a GHSV = 15,000 h⁻¹ during 100 h (Fig.3). The catalyst showed no sign of deactivation during the whole experiment, showing a XCO of 99%. These results may permit a compact processor design since it will not be necessary to put an excess of catalyst in order to counteract deactivation phenomena. H₂ and CO₂ selectivity were 61 and 31%, respectively while the amount of CO in the outlet was 0.6% and no changes in CH₄ concentration were detected.

![Fig. 3. CO conversion vs. time.](image)

IV. Conclusion

The catalyst synthesized and patented by our group is able to operate in a single stage water-gas-shift reactor. When the water gas shift catalyst was operated with a CO₂-rich feed, it was necessary to increase the temperature to 350 ºC. It may be due to CO₂ favoring the formation of monodentate superficial carbonates which cannot decompose at 300 ºC. An increase in S/CO ratio leads to an increase in XCO, being less evident at 350 ºC. The catalyst showed the highest conversion at GHSV ≥ 15,000 h⁻¹. This fact together with the good stability observed during 100 h may allow us to build a lower reactor and then a more compact processor.

ACKNOWLEDGMENT

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COVAPORS INFLUENCE ON ACTIVATED CARBON FILTER PERFORMANCE REMOVAL FROM A BIOGENOUS FUEL SUITABLE FOR SOFC APPLICATION USING A RAPID AND ONLINE TOOL.

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Abstract - One of the main advantages for SOFCs is fuel flexibility. Biogas derived from anaerobic digestion of the organic fraction of municipal solid waste (OFMSW) has great potential. In this work, the removal efficiency of commercial activated carbon filters for biogas cleaning were investigated through an innovative mass spectrometry technique (PTR-ToF-MS). In particular, we consider sulfur compounds adsorption and the co-vapor influence of aromatic, carbonyl and chloro-compounds. By looking at the breakthrough time as the performance indicator of the selected adsorbent material, we estimated the impact of co-vapor adsorption on the overall filter lifetime. Post-mortem SEM images on spent adsorbents were also conducted; (images for an R8 sample from Sulfatraps TDA inc. are presented). The presence of co-vapors in the as-received biogas stream causes a strong sulfur adsorption on the carbon surface as could be seen from the map of element respect to sulfur adsorption only, this implying that the sorbent material achieves faster deactivation.

Keywords – SOFC, OFMSW, biogas, gas cleaning.

I. NOMENCLATURE

II. INTRODUCTION
Fuel cells directly and efficiently transform fuel into electrical energy by electro-chemical reactions. Amongst fuel cells, SOFCs achieve the highest electrical conversion efficiencies [1]. Extensive research has been performed on fuel cells, even if real world applications are still too expensive to become a widespread commodity [2]. One of the challenges is that SOFCs have a low tolerability for contaminants (e.g., VOCs): in presence of fuel impurities the cell voltage decreases and thus electrical power drops. Hence, main sources of anode degradation (or de-activation) are fuel impurities [3] as well as carbon deposition phenomena. Concerning contaminants, either are selected electrode materials that are more robust and thus tolerant against VOCs [4], or the amount of VOCs must be drastically reduced in the fuels [5]. The most relevant volatile contaminants are sulfur, aromatic, carbonyl, chlorine [6][7] and siloxanes compounds. The latter two groups are derived from the starting biomass loaded into the digester [6]. Hence, it is necessary to implement a cleaning section which effectively removes VOCs from the as produced biogas in order to feed SOFC generators. In this work, we focused our efforts on the impact of co-vapors (aromatic, carbonyl and chloro-compounds) on the sulfur removal of a commercial activated carbon filter. We used a novel gas analysis technique (PTR-MS) for VOC trace detection before and after the filter.

III. MATERIALS AND METHODS
For the removal capacity of those several VOCs contained in biogas, commercial activated carbons, Sulfatraps R8 (TDA Research Inc., USA) and Norit RGM3 (Norit, USA) were adopted and grounded to grain dimensions of about 0.5 – 1 mm. Humidity conditions and starting VOC concentrations were kept constant. The biogas pollutants are simulated by using two prepared gas cylinders mixtures (Rivoira S.p.a., Italy), see Table 1. PFA tubes (1/4 inch diameter, length ~3m) and fittings (Swagelok Ltd, USA) were used for the experimental set-up. Carbon cartridges consisted of Teflon tubes (4 cm length and 6 mm diameter) by positioning ca. 0.04 g of activated carbon each.

<p>| TABLE 1 |</p>
<table>
<thead>
<tr>
<th>VOCS concentration contained in cylinder gas B1 and B2</th>
<th>Compound in N₂</th>
<th>Concentration (ppmv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>H₂S</td>
<td>5.51</td>
</tr>
<tr>
<td></td>
<td>CH₃SH</td>
<td>4.75</td>
</tr>
<tr>
<td></td>
<td>CH₃SCH₃</td>
<td>5.84</td>
</tr>
<tr>
<td></td>
<td>CS₂</td>
<td>5.98</td>
</tr>
<tr>
<td></td>
<td>C₃H₇SH</td>
<td>6.01</td>
</tr>
<tr>
<td></td>
<td>C₄H₇SH</td>
<td>5.98</td>
</tr>
<tr>
<td>B2</td>
<td>C₂H₅Cl</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>C₃H₇O</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>4.83</td>
</tr>
<tr>
<td></td>
<td>C₆H₆</td>
<td>5.29</td>
</tr>
</tbody>
</table>

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Fig 1 depicts the experimental set up. A PTR-ToF-MS 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria) in V-mode configuration was adopted for VOCs detection.

Gas after the filter is directly injected into the drift tube of the instrument via a heated (110°C) PEEK tube and a heated multi-port valve for the simultaneous measurements of two samples and a blank. Additional details can be found elsewhere [8].

IV. RESULTS AND DISCUSSION

Fig. 2 shows the breakthrough time for 4 different sulfur compounds. The relative breakthrough time for H2S, CH3SH, CH3SCH3 and CS2 are shown. In particular, when the filter section is doubled, there is an increase in the removal performance, that is almost twice. R8+RGM3 represents the best option for the sulfur removal from the biogas stream.

The simultaneous presence of sulfur and aromatic compounds decrease the filter performance. Looking at the H2S profile in double filter configuration, by adding aromatic compounds performance 70% performance decrease is observed (Fig. 2). This result was achieved when the outlet concentration achieved 1% of the inlet concentration. Fig. 3 shows an elemental map (SEM images) for the R8 sample. Carbon samples operated with only sulfur compounds (1), no VOCs (2) or co-vapors (3) are shown respectively. Co-vapors concentration caused a strong sulfur adsorption on the carbon surface as could be seen in the lower part of Fig. 3 with respect to sulfur adsorption only, see also table 2.

V. CONCLUSION

It was demonstrated that even only 1 ppmv of aromatic, carbonyl and chloro-compounds can drastically reduce the removal efficiency of a sulfur filter. R8 could be sufficient to achieve a clean biogas suitable for SOFC applications in case of sulfur compounds only. However, taking into account the simultaneous presence of other biogas contaminants, the best option is the double filter configuration ‘R8+RGM3’.

REFERENCES


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DIRECT BIOGAS STEAM REFORMING ON NICKEL ANODE SUPPORTED CELL: EFFECT OF HIGHER HYDROCARBONS AND SULFUR IMPURITIES ON THE CELL PERFORMANCE

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Abstract - A sustainable fuel for SOFCs, since it comes from waste derived biomass – is biogas produced from the dry anaerobic digestion (AD) of organic waste or from waste water treatment plants (WWTs). A simulated biogas mixture pre-mixed with steam was entirely (100%) or partly fed (70%-50%) to an anode-supported fuel cell in order to check directly the steam reforming on a Nickel based fuel cell (SOFCpower S.p.a, Italy and H.C. Starck ceramics, Germany). Different steam to carbon ratio (S/C) were also tested. A stable voltage condition for the direct steam reforming of biogas at 50% and 750°C was achieved. The effect of pollutant compounds, such as sulfur (H2S) at higher and lower concentration was investigated. Higher hydrocarbons influence as toluene (C7H8) was checked at two different concentration values. Breakthrough concentration values were identified using impedance analysis and V-t curves for the entire test session that works for more than 1000 h.

Keywords – SOFC, biogas contaminants, toluene, hydrogen sulfide

I. INTRODUCTION

One of the main positive aspects of SOFCs is represented by the fuel flexibility of hydrocarbons even at lower concentrations. A possible and sustainable fuel is biogas coming from waste derived biomass, in which carbon dioxide ranges from 40 to 50%vol. This kind of fuel in classical generators is not exploitable due to the higher carbon dioxide content. A fuel mixture with 5%vol. of CH4 is an available fuel for SOFCs. The main problem related to this kind of fuel is the tolerability to VOCs concentration content, especially sulfur, chlorine and in some way higher hydrocarbons or tars. Literature studies [1], [2] show the impact and the mechanisms of higher H2S concentration on anode Ni-based fuel cell. A lack at the ultra-low concentration level of H2S needs investigation. In this work we tried to asses on these aspects. Lower masses of tars as toluene, a possible VOC contained in the biogas [3], could be detrimental for SOFC generators. In this work it was assessed the impact of lower and higher concentrations of such compound.

II. EXPERIMENTAL

A planar SOFC (47 cm² surface area) was used to test the electrochemical oxidation of a simulated conventional biogas mixture (CH4/CO2 = 1.5). Direct internal reforming with steam was studied varying the ratio of water vapor added to the main fuel stream using a liquid mass flow controller coupled with a controlled evaporator mixer (Bronkhorst, The Netherlands). The oxidant flow at the cathode side was fixed to 1.5 Nl min⁻¹. The anode feed gas was obtained by mixing pure gases contained in certified gas bottles (Siad Spa, Italy), fed to the anode and regulated by means of mass flow controllers (Bronkhorst, The Netherlands). Fuel utilization adopted was fixed to 30% with a current density around 0.32 Acm⁻² at 750 °C adopting a commercial Ni-based fuel cell made from SOFCpower S.p.a, (Italy) and H.C. Starck ceramics, (Germany). The H2S concentration varied for the lower levels from 78 ppbv to 174 ppbv. For the higher levels the concentration varied from 801 ppbv to 6683 ppbv. The C7H8 concentration varied from 3 to 24.2 ppmv.

III. RESULTS

Figure 1 shows the cell voltage at different direct internal reforming ratio (DIR) of biogas from 50 to 100%. Stable cell voltage were achieved at DIR 50% and for the entire test (1000 h) was selected this value.
IV. CONCLUSION

DIR ratio affects the fuel cell behavior and stable performance are achieved at 50% value. The steam to carbon ratio that allows to achieve a stable behavior is selected between 0.4 or 2. The influence of toluene, as tar model compound was investigated, as reported also for H₂S for sulfur compounds. Lower concentrations of this biogas contaminants doesn’t affect the cell behavior. Whereas higher concentrations start to be detrimental for the cell performance up to be irreversible.

REFERENCES


Determination of the impedance contributions in Anode Supported Solid Oxide Fuel Cells with \((\text{La, Sr})(\text{Co, Fe})\text{O}_{3-\delta}\) cathode

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Abstract - In this study, Anode Supported Fuel Cells have been electrochemically tested by varying testing conditions (gas partial pressure, occurrence of \(\text{H}_2\text{S}\) impurities, temperature), as well as cells materials and microstructure (current collecting layer, diffusion barrier layer). The comparison of the different Nyquist plots, Bode plots and fitting results obtained allowed us to separate the different contributions and attribute them to the anode or the cathode.

Index Terms – solid oxide fuel cells, impedance spectroscopy, LSCF cathode

I. INTRODUCTION

Understanding the reactions mechanisms associated to Solid Oxide Fuel Cells (SOFC) operation is essential in order to improve the electrochemical performances by optimizing materials and production processes as well as to prevent degradation.

Electrochemical Impedance Spectroscopy (EIS) is a very powerful technique to investigate the reaction mechanisms which contribute to the total impedance. A general method to investigate the resistances associated to electrode reactions comprises EIS measurements on symmetrical cells, consisting of the same electrode material (anode or cathode) applied on a supporting electrolyte. This method allows to obtain EIS spectra associated to only one electrode. By this way, it is possible to distinguish the resistances associated to the anode side with respect to those related to the cathode.

However, the fabrication process for symmetrical cells can be very different with respect of commercial fuel cells, especially in the case of anode supported fuel cells. For this reason, the EIS information obtained on symmetrical cells could not be really representative of the electrochemical phenomena occurring on real SOFCs. Conversely, due to the overlapping of the electrodes contributions, it is difficult to interpret the processes occurring respectively at the anode and the cathode. To better understand the processes occurring at the electrodes, it is necessary to separate the different contributions.

In order to discriminate the impedance contributions to the total SOFC impedance, several approaches have been proposed. A general methods comprises a selective changes of testing conditions (gas atmosphere, temperature, addition of poisoning species) and changes of electrode materials or microstructure.

In this study, Anode Supported Fuel Cells with LSCF cathode have been electrochemically tested by varying testing conditions (e.g. gas partial pressure, occurrence of \(\text{H}_2\text{S}\) impurities, temperature), as well as cells materials and microstructure (e.g. current collecting layer, diffusion barrier layer). The comparison of the different Nyquist plots, Bode plots and fitting results obtained allowed us to separate the different contributions and attribute them to the anode or the cathode.

II. EXPERIMENTAL

Reference Cells consist of a thin (ca. 10 \(\mu\text{m}\)) 8mol\% \(\text{Y}_2\text{O}_3\) stabilized Zirconia (YSZ) electrolyte supported by a porous Ni/YSZ fuel-electrode (ca. 250 \(\mu\text{m}\)). The Oxygen electrode is based on \((\text{La, Sr})(\text{Co, Fe})\text{O}_{3-\delta}\) (LSCF) perovskite and doped-Ceria barrier layer. A \((\text{La, Sr})\text{CoO}_{1.4}\) (LSC) layer is applied on top of the cathode to provide efficient current collection.

Electrochemical measurements were performed by using Autolab PGSTAT302N potentiostat/galvanostat. EIS spectra were collected in the range of frequency 20kHz-0.01Hz and using 20mV perturbation amplitude. Where not differently specified, measurements were performed under 3vol\%\(\text{H}_2\text{O}/\text{H}_2\) atmosphere at the anode and compressed air at the cathode. The active area, corresponding to the cathode, is 3.14 \(\text{cm}^2\).
III. RESULTS AND DISCUSSION

A. Setting of the method

Before starting to study the impedance contributions associated to different mechanisms, a preliminary work has been addressed to investigate the reliability of the technique and the testing equipment. With this aim, EIS measurements were performed on 6 reference cells produced in different batches and mounted on different test benches. Results demonstrated a very good reliability. The data deviation from the average value increases by reducing the temperature.

B. Anode

Anode impedance was determined by comparing the results obtained on the reference cells with respect to cells produced by using different anode raw materials, where a different resulting microstructure has to be expected. Results are given in Fig. 1. It was clearly observed that the cell produced with different raw materials results in a significant increase of the high frequency (500-600Hz) resistance, which can be associated to anode charge transfer reaction. This different becomes more pronounced reducing the temperature at 650°C.

An additional evidence of the importance of the anode impedance at ca. 600Hz was obtained by using H2S (20ppm) containing H2 atmosphere. In this case the test was performed under dry atmosphere. As shown in Fig. 2, the peak at ca. 600 Hz significantly increases after H2S poisoning.

Fig. 1. Comparison between reference cells (green) and a cell produced with different anode raw materials (red). Measurement performed at OCV at 700°C.

Fig. 2. Effect of H2S poisoning on the anode. Orange: before H2S addition; Red: after H2S addition. Measurement performed at 700mV at 750°C.

Cathode

The effect of H2 partial pressure on the anode impedance was investigated by diluting H2 by N2, maintaining a constant flow rate. Results demonstrated that reducing the H2 concentration leads to an increase of the impedance at ca. 0.1 Hz.

C. Cathode

The effect of O2 concentration on the cathode impedance was studied by working under static air and different voltages. Results (Fig. 3) demonstrate that oxygen gas conversion affects the impedance at ca. 0.02Hz.

Fig. 3. Effect of O2 gas conversion at the cathode, at different voltages.

The effect of the diffusion barrier layer (DBL) on the impedance was investigated by comparing a reference cell with a cell comprising a DBL with increased porosity. It was observed that the different microstructure affects the Ohmic resistance and the at low frequency impedance contribution (1Hz).

The effect of the current collecting layer on the cathode performances was investigated by considering LSC with different Sr doping concentrations. It was observed that increasing the concentration of Sr from 30 to 50% (with respect to La) significantly decreases the impedance at ca. 2Hz, while the Ohmic resistance remains unaffected.

IV. CONCLUSION

This work discriminate the different EIS contributions to the total impedance observed in SOFC with LSCF cathode. Anode Impedance was associated to Hydrogen partial pressure at 0.1Hz and anode charge transfer reaction at ca. 600Hz. An anode contribution at ca. 10 Hz was not easily discriminated from a similar mechanism occurring at the cathode and normally observed at slightly lower frequency (2-4 Hz). Cathode Impedance was associated to H2 gas conversion at ca. 0.02Hz and oxygen surface diffusion at 2-4Hz. The microstructure of the Ceria diffusion barrier layer was observed to affect the peak at medium frequency (1 Hz) and the Ohmic resistance. The composition of the current collector only affects the impedance at ca. 2Hz, without modifying to the Ohmic resistance.
Application of the triode concept to anode supported solid oxide fuel cells

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Abstract - In this work, we present the preliminary results of electrochemical measurements performed on a prototype anode supported SOFC triode cell. The experiments investigate cell performances under hydrogen and steam reforming conditions. The electrochemical measurements performed on the cathode and auxiliary circuits were compared.

Index Terms – triode, solid oxide fuel cells, internal steam reforming

I. INTRODUCTION

The Triode Concept, consists of a cell with a three-electrode design: anode, cathode and auxiliary circuit. While the anode and the cathode work in conventional SOFC-mode, the auxiliary circuit runs in electrolytic mode. In this way the anode or cathode of the cell can be forced to operate at controlled potential differences that are inaccessible under standard operation. Triode operation is especially advantageous when a significant anodic overpotential is present, as is expected to be the case with natural gas and gasoline-fuelled SOFCs. Others key features offered by triode approach is that of inducing potential modulations that allow to work under potential difference conditions that are inaccessible in conventional operation. Moreover, the auxiliary circuit, working in SOE-mode force oxygen anion migration to the catalyst surface allowing to control the rate of carbon deposition and poisoning by fuel impurities.

In this work, we present the preliminary electrochemical results obtained on a Solid Oxide Fuel Cell based on the cathode triode design. Cells performances were initially tested under humidified hydrogen conditions, and then the electrochemical behavior was also studied under internal steam reforming with natural gas.

II. EXPERIMENTAL

Reference Cells consist of a thin (ca. 10 µm) 8mol% Y₂O₃ stabilized Zirconia (8YSZ) electrolyte supported by a porous Ni/YSZ fuel-electrode (ca. 250 µm). The Cathode and the Auxiliary electrode are based on a mixture of (La₀.₆₅Sr₀.₃₅)MnO₃₋δ (LSM) perovskite and 8YSZ. A pure phase LSM layer is applied on top of the cathode to provide current collection.

Electrochemical measurements were performed by using Autolab PGSTAT302N potentiostat/galvanostat. EIS spectra were collected in the range of frequency 20kHz-0.01Hz and using 20mV perturbation amplitude.

Fig. 1. Anode supported solid oxide fuel cell with triode cathode design

Fig. 2. Electrochemical setup per triode measurements including the cathode (circuit 1) and Auxiliary electrode (circuit 2).

Measurements under steam reforming conditions were performed by using Natural Gas (NG) diluted by Nitrogen.
Before feeding the cell, the gas mixture pass through a bubbler filled by distilled water at controlled temperature, which determine the water partial pressure allowing the regulation of the steam to carbon ratio (S/C).

The cell used for triode operation was an anode supported solid oxide fuel cells, with a two electrode air side design (Fig. 1). the auxiliary electrode consists of an internal disk with diameter 0.3 cm² area. The Cathode consists of a ring with 0.9 cm² area. Hereafter we use the notation circuit 1 for the cathode and circuit 2 for the anode. Each electrode is connected to 4 wires (2 for the circuit 1 and 2 for the circuit 2) for electrochemical measurements (Fig. 2).

III. RESULTS AND DISCUSSION

Preliminary results of cell characterization under different conditions, at 800°C, are given in Fig. 3. A measurement under H₂ atmosphere was performed for reference. Measurements under internal steam reforming were performed in the 0.5-2.0 S/C range. The concentration of the fuel mixture was 10vol%NG/N₂. The electrochemical performances increase by increasing S/C. Electrochemical Impedance Spectroscopy analyses demonstrated, as expected, an increase of the polarization resistance with decreasing S/C. This resistance can be likely associated to carbon deposition, obstructing the pores of the anode and resulting an impedance of the increase at 0.1 Hz (Fig. 5). Moreover, S/C reduction also lead to an increase of the impedance at medium frequency (200-500Hz) (Fig. 5), probably related to a reduction of the extent of triple phase boundaries due to carbon deposition.

In order to check the effect of geometrical issues on the electrochemical behavior of the cathode and the auxiliary electrodes, a preliminary characterization was performed under H₂ atmosphere. The IV curves obtained on the two circuit were compared and no significant differences where observed (Fig 6). Since this test was performed under excess of H₂, this result allow to demonstrate that, at low fuel utilization, despite the different geometry, the two circuits are completely equivalent from the electrochemical point of view. By reducing the H₂ concentration, a small difference between the two circuits was observed, being the polarization resistance of the circuit 2 slightly higher with respect to the circuit 1. This resistance is related to an increase of the impedance at ca. 10 and 200 Hz.

IV. CONCLUSION

In this work we reported the preliminary results of the electrochemical characterization performed on SOFC with a triode cathode design. It was observed that under internal steam reforming conditions the cell demonstrates slight degradation due to carbon deposition but this does not lead to failure. This measurements have been repeated under triode operation (applying reverse current on the circuit 2 while working in SOFC-mode on the circuit 1) and results will be presented in the full paper.

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BIO-GAS STEAM REFORMING TO PRODUCE HIGH GRADE HYDROGEN FOR PEM FUEL CELLS VIA PD-BASED MEMBRANE REACTOR TECHNOLOGY

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Abstract - Hydrogen, as clean energy carrier, is considered to be one of the main energy sources of the future.

Today, hydrogen is a large-scale production via reforming process of light hydrocarbons such as natural gas. Nevertheless, the reforming technologies at moment show a number of technical/scientific challenges, which depend on various needs among the quality of raw materials, the conversion efficiency and safety for the integration of the hydrogen production with its purification and further utilization. Biogas is a high-potential versatile raw material for reforming processes, which can be exploited as an alternative and renewable feedstock instead of derived of fossil fuels. This could favor a large reduction of greenhouse gas emissions. In this context, the integration of biogas reforming processes and the activation of fuel cell using high grade hydrogen represent a viable opportunity for generating clean energy with added high-energy efficiency.

In particular, the use of Pd-based membrane reactors for producing high grade hydrogen from bio-gas steam reforming could constitute an alternative process to the conventional systems, because able to combine in a single device the chemical reaction for producing hydrogen and its separation/purification for further applications. In this study, porous Al$_2$O$_3$ supported Pd-thin layer membrane is studied in membrane reactor to carry out the bio-gas steam reforming reaction to produce high-grade hydrogen.

Index Terms - hydrogen, palladium membrane, PEM fuel cell, membrane reactor.

I. INTRODUCTION

In the last decades, the depletion of the emission of greenhouse gases (GHG) as well as the development of technologies showing benefits from bio-feedstocks exploitation have attracted a great attention [1]. Alternative technologies to conventional power generation systems are proton exchange membrane fuel cells (PEMFCs), which are zero-GHG emission devices useful to convert the chemical energy of the electrochemical reaction within hydrogen and oxygen into clean electrical power [2]. Unfortunately, as a main drawback, PEMFCs are supplied by high-grade hydrogen (CO < 10 ppm) in order to avoid the anodic Pt-based catalyst poisoning at T < 100 °C caused by the presence of CO. At industrial level, hydrogen production is realized by steam reforming of natural gas carried out in conventional reactors (CRs). In particular, a reformed stream coming from a CR contains mainly hydrogen needing further separation/purification stages to reach the required purity for PEMFC supplying (high and low temperature water gas shift (WGS) reaction stages, preferential oxidation (PROX) and pressure swing adsorption). Therefore, a growing interest has attracted the utilization of membrane reactor (MR) technology to produce high-grade hydrogen from reforming reactions of bio-feedstocks, for example, for PEMFCs supplying [3]. Hydrogen selective Pd-based MRs make possible the economic advantage of combining the hydrogen production process with the hydrogen separation stage in a single device. This is due to the particular behavior of Pd-based membranes in terms of high hydrogen perm-selectivity with respect to all other gases [4].

Among various feedstocks, the exploitation of bio-gas in reforming reaction could be useful for hydrogen generation via membrane reactors. According to the literature, the following reactions are the prevailing reaction routes [5]:

R1 : CH$_4$ + H$_2$O = CO + 3H$_2$  $\Delta$H$^{\text{298K}}$ = 206.2 kJ/mol
R2 : CH$_4$ + 2H$_2$O = CO$_2$ + 4H$_2$  $\Delta$H$^{\text{298K}}$ = 164.9 kJ/mol
R3 : CO + H$_2$O = CO$_2$ + H$_2$  $\Delta$H$^{\text{298K}}$ = - 41.2 kJ/mol

As the first two reactions R1 and R2 are highly endothermic,
EXCESSIVE AMOUNTS OF HEAT SHOULD BE PROVIDED TO THE REACTOR IN ORDER TO MAINTAIN THE DESIRED HIGH TEMPERATURE. THIS SITUATION CAN BE IMPROVED IF EXOTHERMIC REACTIONS SUCH AS WGS (R3) ARE INCLUDED IN THE CATALYTIC REACTION SCHEME. Indeed, THIS APPROACH SHOWS ALSO THE ADVANTAGE TO CONTROL COKE FORMATION, RESPONSIBLE OF CATALYST DEACTIVATION. HowEVERT, TO THE BEST OF OUR KNOWLEDGE, THERE IS NOT AN EXTENSIVE LITERATURE ADDRESSED TO HYDROGEN PRODUCTION FROM BIOGAS STEAM REFORMING REACTION IN MEMBRANE REACTORS, BUT ONLY IN CONVENTIONAL REACTORS [6-10].

This manuscript deals with bio-gas steam reforming reaction performed in a MR housing a composite membrane, constituted by a thinner dense Pd-layer (~ 7 µm) deposited via electroless plating onto an Al2O3 support.

II. EXPERIMENTAL

The MR houses a porous Al2O3 supported Pd-based membrane, which has been produced at Nanjing University of Technology (the porous Al2O3 support is given by Gao Q Funct. Mat. Co.). It is 75 mm length, 13 mm o.d., 9 mm i.d. and possesses an effective membrane area around 17 cm². The composite membrane is constituted by a thin dense Pd-layer (~ 7 µm) deposited via electroless plating onto a porous Al2O3 support. The base of the substrate material is a conventional porous α-Al2O₃ with a symmetric structure, modified with γ-Al2O₃ coating. The plating bath has been composed by PdCl₂ (5 g/L), Na₂EDTA (70 g/L) and NH₃·H₂O (28%, 250 mL/L), and a 0.5 M hydrazine solution has been utilized as a reducing agent. The MR annulus has been packed with 0.5 g of a CuO/ZnO/Al₂O₃ (CuO 51wt%, ZnO 31wt%, Al₂O₃ 18wt%) commercial catalyst (ICI83-3), provided by Synetix. A P680 HPLC pump (Dionex) has been used for supplying liquid methanol and two mass-flow controllers (Brooks Instrument) have been used for feeding CH₄ and CO₂ to constitute a modeled bio-gas feed (CH₄/CO₂ = 60/40, H₂O/CH₄ = 3/1-5/1). A pre-heater has made possible the vaporization of water, which has been mixed with CH₄ and CO₂ besides a constant flow rate of nitrogen (~ 22 mL/min) as internal standard gas prior to enter into the annulus of the MR as reaction zone. Concerning the outlet streams, the retentate was cooled through a cold-trap (ice bath) to condensate the unreacted water. Then, both permeate and retentate streams have been directed to a temperature programmed HP 6890 GC.

III. RESULTS AND DISCUSSION

Firstly, pure gas permeation tests have been performed using such gas as H₂, He and N₂ at T = 380 °C and ΔP in the range 0.5 - 1.0 bar. Table 1 reports the permeating fluxes of each gas investigated as well as the hydrogen/other gas ideal selectivity.

Table 1. H₂/other gas ideal selectivity and permeating flux at T = 380 °C and various ΔP.

<table>
<thead>
<tr>
<th>Gas</th>
<th>ΔP [bar]</th>
<th>J [mol/m²·s]</th>
<th>α_{H₂/other gas}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.5</td>
<td>4.64E-02</td>
<td>1</td>
</tr>
<tr>
<td>He</td>
<td>0.5</td>
<td>3.03E-05</td>
<td>1500</td>
</tr>
<tr>
<td>N₂</td>
<td>0.5</td>
<td>1.08E-05</td>
<td>4300</td>
</tr>
<tr>
<td>H₂</td>
<td>1.0</td>
<td>9.79E-02</td>
<td>1</td>
</tr>
<tr>
<td>He</td>
<td>1.0</td>
<td>8.49E-05</td>
<td>1200</td>
</tr>
<tr>
<td>N₂</td>
<td>1.0</td>
<td>2.48E-05</td>
<td>4000</td>
</tr>
</tbody>
</table>

Regarding the reaction tests, they are still in progress, but at T = 380 °C and p = 2.0 bar methane conversion was around 70% with a hydrogen recovery of around 30%.

REFERENCES


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LOW TEMPERATURE CATALYTIC OXIDATION OF H$_2$S OVER V$_2$O$_5$/CeO$_2$ CATALYSTS

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Abstract – Vanadium-based catalysts supported on CeO$_2$ with different amount of V$_2$O$_5$ (2.55%-20%) were studied for the selective catalytic H$_2$S oxidation to sulfur at low temperature (150-250°C). These samples were prepared by wet impregnation method and were characterized by XRD, Raman Spectroscopy and SSA techniques. All the samples showed the characteristic peaks of CeO$_2$ while the typical V$_2$O$_5$ reflections were not detected likely due to the low metal loading and the good dispersion on the support; in particular for the samples having a loading exceeding the 5 wt%, they have been identified peaks attributable to polyvanadate forms and crystalline forms of vanadium. The experimental tests were carried out to varying the temperature by feeding a stoichiometric molar feed (200 ppm H$_2$S, 100 ppm O$_2$). All among the samples, the 20% V$_2$O$_5$/CeO$_2$ catalysts exhibited the best catalytic performances relatively to the activity, stability and selectivity to sulfur (99%).

Index Terms – Biogas Clean-Up, H$_2$S selective catalytic oxidation.

I. INTRODUCTION

Hydrogen sulfide, a major contaminant in biogas produced from anaerobic digestion of organic materials, can cause high corrosion of metal parts, degrade engine oil and has a negative environmental impact. For this reason, in order to increase the practical use of biogas, H$_2$S must be economically removed [1].

Several methods for H$_2$S removal are available, including physical-chemical treatment (adsorption, absorption in aqueous solutions, physical solvent) that have been used to treat tail gases containing low concentrations (<5% vol); the main problem of these purification processes is linked to the high costs and to the limited efficiency [2].

The direct and selective catalytic oxidation of H$_2$S to elemental sulfur may be an interesting alternative to the traditional processes if a good catalyst is allowable.

In the previous study the vanadium-based catalysts supported on different metal oxides (Al$_2$O$_3$, TiO$_2$, CuFe$_2$O$_4$, CeO$_2$) were prepared, characterized and tested for H$_2$S selective oxidation at low temperature [3]. These catalysts have shown a good catalytic activity in terms of H$_2$S abatement and a low selectivity to SO$_2$; however the better performance was exhibited from the V$_2$O$_5$/CeO$_2$ catalyst that it has shown a low selectivity to SO$_2$ (4%) and a high H$_2$S conversion (~98%) at the higher temperature (250°C).

Further investigations were carried out on this sample by varying the temperature and the vanadium metal loading from 2.55% to 20% wt, to identify the optimal formulation of the catalyst that can minimize the SO$_2$ formation and maximize the H$_2$S conversion.

The most promising catalyst was the sample with the highest vanadium oxide load (20 wt% V$_2$O$_5$/CeO$_2$) that showed 99% of sulfur selectivity and an equilibrium conversion even at 150°C.

II. EXPERIMENTAL RESULTS

A. Catalysts Characterization

The fresh catalysts were characterized by XRD, Raman Spectroscopy and SSA techniques.

From the results of the X-Ray Diffraction and the Raman Spectroscopy, it was observed that the vanadium oxide was well dispersed on the support when the loading was low (2.55-10 wt% V$_2$O$_5$), while in the case of samples having a loading exceeding the 10 wt%, they have been identified peaks attributable (1,023 cm$^{-1}$) to polyvanadate forms of vanadium (VO$_4^{3-}$) and crystalline forms of vanadium (998 cm$^{-1}$).

The results of the measures of specific area of the vanadium-based catalysts have shown a decrease of the surface upon the V$_2$O$_5$ addition and after the catalytic tests likely due to the occlusion of the porosity of the CeO$_2$ by the sulfur.
B. Catalytic Activity Tests

The attention was focused on the V$_2$O$_5$/CeO$_2$ catalysts and in particular to the influence of the V$_2$O$_5$ loading on the catalytic performance.

In the Figure 2 it is showed the catalytic activity in terms of H$_2$S conversion in the range of temperature 150 - 244°C.

The figure shows that, for all the samples, the higher H$_2$S conversion values were obtained at the lower temperature (150°C), except to the sample 2.55 wt% V$_2$O$_5$/CeO$_2$, for which the H$_2$S conversion was ~90%; the H$_2$S conversion was about 100 % for the other samples.

At temperature of 200°C, they are not appreciable significant difference, because all the catalysts have shown a H$_2$S conversion about 96 %, while the catalyst with the highest metal loading (20 wt% V$_2$O$_5$) has shown a higher value (98%). At high temperature (240°C), the catalyst with higher V$_2$O$_5$ loading (8 - 20 wt%) have exhibited values of H$_2$S conversion higher than 90 %; in particular for the 20 wt% V$_2$O$_5$/CeO$_2$ the value was ~93 %.

From the data of the Figure 3 it is clear that for all catalysts the formation of SO$_2$ increases with increasing temperature, but it is also important to observe that the catalyst 20 % V$_2$O$_5$/CeO$_2$ showed a SO$_2$ formation tendency slightly lower respect to the other samples.

In particular, at 150°C, the catalysts with the higher vanadium load exhibited a very low SO$_2$ selectivity of only 1 %.

III. Conclusion

In this work, vanadium-based catalysts supported on CeO$_2$ with different vanadium loading, were used for the H$_2$S removal by selective partial oxidation at low temperature.

From the characterization techniques, it was obtained that the vanadium oxide was well dispersed on the support when the loading was low, while in the case of samples having a loading exceeding the 5 wt%, they have been identified peaks attributable to polyvanadate forms of vanadium and crystalline forms of vanadium.

The screening carried out on catalysts has shown that the effect of the vanadium loading has affected especially on the value of SO$_2$ selectivity, but not on the catalytic activity because all the samples showed high conversions of H$_2$S (> 90 %) in the range of temperature 150 - 250°C. The catalyst more selective to sulfur (99 %), for the partial oxidation reaction at low temperature (150°C), was 20 wt% V$_2$O$_5$/CeO$_2$, suggesting that the polyvanadate species are the most active and selective.

REFERENCES

EXPERIMENTAL ANALYSIS OF COMMERCIAL HIGH TEMPERATURE PROTON EXCHANGE FUEL CELLS

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Abstract – In this work the experimental analysis and comparison of two commercial high temperature proton exchange membrane single fuel cells is reported. The observed differences are addressed to different manufacturing processes and characteristics.

Index Terms – HT-PEM, experimental, impedance spectroscopy.

I. INTRODUCTION

In 1996 phosphoric acid doped polybenzimidazole was first proposed and successfully demonstrated as a polymer electrolyte suitable for application in high temperature proton exchange membrane fuel cells (HT-PEMFC) [1-3]. In the last decade, research succeeded in improving the performances and the durability of membrane electrode assembly (MEA) and few commercial prototypes are available nowadays. HT-PEMFCs suffer mainly two issues: first, the presence of phosphoric acid within the electrode affects the power density and thus high catalytic loading is necessary. Second, the degradation rate in continuous operation is higher than low temperature polymer fuel cell and it must be reduced to meet the requirements for micro-CHP system durability. Further experimental and modeling activity is necessary in order to deepen the understanding of the phenomena involved and thus to suggest actions which could mitigate the drawbacks. In this work we present the experimental results of single cell testing performed on two different commercial MEAs. The test consists in a set of polarization curves and electrochemical impedance spectra with different operating parameters: temperature, anode and cathode stoichiometry, fuel and oxidant dilution. In addition global mass transport phenomena are characterized by measurements of humidity and flow composition at the anode and cathode outlets.

II. EXPERIMENTAL

Tested MEAs are a 20.4 cm² active area Celtec® P2100 (BASF Fuel Cells) and a 23.04 cm² active area Dapozol® MEA (Danish Power System). The experimental activity is carried out on an in-house designed and assembled setup [4]. The experimental techniques applied are the polarization curve, the electrochemical impedance spectroscopy, the linear sweep voltammetry, the cyclic voltammetry and the hydrogen pumping. Water concentrations are measured at the anode and cathode outlets to quantify the water transport across the membrane.

III. RESULTS AND DISCUSSION

A. Polarization curve

The polarization curves recorded at 160°C, cathode (anode) stoichiometry 2 (1.2) with pure hydrogen and air, are reported in Figure 1. The voltage of Celtec® MEA is always higher than the voltage of Dapozol MEA, in the activation and ohmic regions. At high current densities Celtec® MEA shows a lower limiting current. This effect was demonstrated with a low oxygen concentration feed (10.5%) instead of air (not reported).

Fig. 1. Polarization curves recorded on Celtec P2100 and Dapozol MEAs.

B. Impedance Spectra

In figure 2 we compare two impedance spectra recorded at 0.2 A cm⁻². The main differences are listed below:

- The high frequency resistance is lower for Celtec® P2100
MEAs, indicating a lower electrolyte resistance.

- Celtec P2100 has a larger 45° high frequency linear branch, associated to the proton transport within the electrode. This result suggests that the electrode is thicker or the use of a different binder, more hydrophobic for Celtec® P.

- The cathode charge transfer resistance is slightly higher for Dapozol® MEA, which may justify higher activation loss observed in Section A. No appreciable difference is reported for the anode charge transfer resistance (see Section F).

- Celtec P2100 cathode charge transfer loop has an elliptic shape, while Dapozol MEA is circular. The distortion of the cathode kinetic loop is associated to limited diffusion in the cathode electrode. This may be due to a lower porosity or a partial flooding of the electrode (because of phosphoric acid).

- A higher low frequency capacitive loop is observed for Celtec® P2100 MEA. This result may be due to a presence of cathode MPL or the partial flooding of the electrode.

- The double layer capacitance of Dapozol® MEA is lower.

- The total low frequency resistance is similar in the two MEAs at low current density. At high current density (not reported), the Celtec® P2100 MEA shows a higher total resistance, because of the increase in the low frequency feature. This is coherent with a lower limiting current as observed in Section A and suggests the presence of MPL.

\[ \text{Fig. 2. Impedance spectra recorded at 0.2 A cm}^{-2} \text{ in reference conditions.} \]

**C. Linear Sweep Voltammetry**

The measurement of crossover currents from linear sweep voltammetry indicates homogeneous values of hydrogen crossover for the two HT-PEMFCs. The short circuit resistance is lower for Dapozol® MEA than for Celtec® P2100.

**D. Cyclic voltammetry**

Cyclic voltammetry indicates a larger active area for Celtec® P2100 membrane (21 m² gPt⁻¹) than for Dapozol MEA (15 m² gPt⁻¹), coherently with what observed in Section A and B. The active area of Celtec® P2100 MEA is sensitive to the humidification level, while Dapozol® active area is independent of the humidification level. This supports the idea of a different binder, probably more hydrophobic for Celtec® MEA.

**E. Water Transport across the membrane**

The water transport across the membrane was quantified for both HT-PEMFC. The water crossover flux has a diffusive nature in both the HT-PEMFC indicating that the electroosmotic drag is negligible. The water transport across the membrane is higher for Celtec® P2100 MEA in the same operating conditions.

**F. Hydrogen Pumping**

Hydrogen pumping polarization data indicate that the anode is working in the linear regime in both cases. Anode activation loss is higher for Dapozol® MEA, and this may be due to the much higher Platinum loading at the anode of Celtec® P2100.

**IV. CONCLUSION**

The experimental results from Dapozol® and Celtec® P2100 MEAs have been compared. The differences in the manufacturing process and characteristics have thus been evidenced:

1. The direct casting method employed in the manufacturing process of Celtec® membranes allows for higher acid doping levels and it results in a lower electrolyte resistance.
2. The cathode catalyst activity of Celtec® MEAs is higher, probably because Platinum alloy is employed instead of pure Platinum.
3. The proton conductivity of the electrode is higher for Dapozol® MEA. This may be due to the binder employed in the electrode manufacturing or high hydrophobicity of the Celtec® electrode. This is confirmed by the fact that the active surface measured by cyclic voltammetry depends on the humidification level.
4. Celtec® MEA shows a higher mass transport loss at the cathode, probably due to the presence of MPL.
5. Anode activation is linear for both MEAs under test. Celtec® P2100 shows a higher activity, explained by the much higher catalytic loading employed.

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**REFERENCES**


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MICROBIAL FUEL CELLS FED BY SOLID ORGANIC WASTE: A PRELIMINARY EXPERIMENTAL STUDY

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Abstract – Microbial Fuel Cells are electrochemical reactors based on the metabolism of particular strains of microbes. A battery composed of seven microbial fuel cells has been realized, using glass bottles of 500 mL internal volume; solid organic waste, taken from an urban disposal site, has been employed as fuel, without any sort of pretreatment. Electric potential and current intensity have been monitored showing a very good performance of our Microbial Fuel Cell system.

Index Terms – Clean Energy, Microbial Fuel Cell, Solid Organic Waste

I. INTRODUCTION

The solid organic waste management has become a very crucial issue in many countries, due to the ever-increasing amount of waste material. The main strategies to face the problem of waste management are the increase of material recovery (MR) and the improvement of energy recovery (ER) from waste.

The conventional technologies for the energy recovery are based on thermo-chemical and biochemical processes. The thermo-chemical conversion methods, such as combustion, gasification and pyrolysis are suited to relative dry organic waste and herbaceous biomass (the C/N ratio must be higher than 30 and the moisture content less than 30%) whereas biochemical technologies, such as the anaerobic digestion and alcohol (or hydrogen) fermentation can also handle biomass with high moisture content.

The ER technologies, based on both thermochemical and biochemical processes, generate electric power by using the produced biogas as fuel in conventional or innovative technologies [1,2,3,4,5].

An innovative biochemical technology, that is able to produce electricity from organic waste in a direct way, is the Microbial Fuel Cell (MFC). This technology is considered as a new pathway for bioconversion processes towards electricity.

Briefly, anaerobic heterotrophic bacteria carry out the degradation of provided (organic) fuel, transferring electrons to an anode placed in an anaerobic or anoxic environment. As co-product of the microbial catabolism, protons are formed. As in a traditional fuel cell, protons move through an electrolyte till reacting with the oxygen on the surface of a cathode, placed in an aerobic environment. For their ability to exchange electrons with inorganic matter, such bacteria are called electrogenic or electro-active, [6, 7]. Moreover, the presence of biofilms at the cathode can avoid the utilization of catalyst like Pt, with economic advantages, [8, 9].

This work deals with a preliminary experimental characterization of a single-chamber MFC fed by Organic Fraction of Municipal Solid Wastes (OFMSW).

The experimental results have been compared to numerical and experimental data available in technical literature [10].

II. EXPERIMENTAL SETUP

The experimental set-up (Figure 1) consists of 7 cells connected in series in which each cell is a single chambered membraneless glass bottle, whose volume is equal to 500 mL. The electrode are realized by using the graphite from standard pencils for artistic drawings (9B undermines).

The current and the voltage were measured by means of a Valex multimeter and the date were recorded by an Arduino® “Nano” card, controlled by means of an ad-hoc realized LabView® dashboard.
The fuel consists of solid organic waste, taken from an urban disposal site, without any sort of pretreatment.

Figure 1. Experimental Setup

III. PERFORMANCE ANALYSIS

The focus of the experiments was to analyze the ability of the cell in producing electric power.

Figure 2 shows the polarization curve and the power density as function of the current density.

Figure 2. Polarization and Power Curves

The maximum electric power is obtained at approximately 1500mA/m². At this current value the internal resistance of the whole stack (that is equal to the resistance of the external load) is equal to 420 Ω.

IV. CONCLUSIONS

The results shown in this paper are the preliminary experimental data of electric power production, acquired with a stack of membraneless MFC’s.

Even adopting solid organic waste without any sort of pretreatment, our fuel cells have shown good energetic performance, compared to other solutions present in literature. The technology of Microbial Fuel Cells, thus, can be considered as a promising solution for waste management in the next future.

REFERENCES


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OPTIMIZATION STRATEGIES FOR MICRO-CHP SYSTEMS BASED ON HT-PEM FUEL CELLS.

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Abstract - A procedure for the optimal energy management of distributed generation plants is applied to Micro-CHP systems based on HT-PEM Fuel Cells.

A typical residential load is considered for the optimization, with special focus to the overall economic and energy performances. The HT-PEM based plant is compared to traditional energy systems, that relies on reciprocating internal combustion engines and fuel boilers.

Index Terms - HT-PEM, Micro-CHP, Optimization, Distributed generation.

I. INTRODUCTION

Polymer Electrolite Membrane (PEM) Fuel Cells (FC) are characterized by high maturity and they are probably the kind of fuel cells closest to mass production [1]. In particular, high temperature PEMFCs may play a key role in the distributed energy generation, thanks to their high efficiency and low pollutant emissions and the possibility of using reformate gas as a fuel, being CO tolerance dramatically increased with respect to traditional PEMFCs. Moreover, waste heat can be recovered for cogeneration or trigeneration purposes [2].

Therefore, much research is needed to study their integration in power plants for distributed power generation, which is to say complex systems made up of different components, and their performances in satisfying the energy requirements (heat, electricity, and cooling) within the actual energy market. We report here the results obtained through a combined experimental and numerical activity aimed at investigating the optimal operation of PEMFCs in distributed energy systems, also with respect to traditional technologies. The potential advantages of PEMFCs part-load operation, as their ability to meet and follow the highly non-coincident electric and thermal loads, are discussed.

II. MATERIALS AND METHODS

A. Experimental Setup

The experimental tests have been performed on a HT PEM fuel cell stack with 1 kW (@ 31.5V) of nominal power whose characteristics are reported in Table I. The cell is fuelled using a laboratory mixture of H₂ and CO. The experimental activity has regarded a series of tests, in order to measure the performance under various load conditions (see Fig. 1).

<table>
<thead>
<tr>
<th>Number of Stacks</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cells/Stack</td>
<td>65</td>
</tr>
<tr>
<td>Nominal Power</td>
<td>1000 W</td>
</tr>
<tr>
<td>Nominal Voltage</td>
<td>31.5 V &lt;sub&gt;DC&lt;/sub&gt;</td>
</tr>
<tr>
<td>Nominal Current</td>
<td>32 A</td>
</tr>
<tr>
<td>Cathode Temperature</td>
<td>0-40°C – atmospheric air</td>
</tr>
<tr>
<td>Anode: Fuel</td>
<td>H₂ (99.9%) - Reformate (max 3%CO)</td>
</tr>
<tr>
<td>Operating Temp.</td>
<td>100°C-175°C</td>
</tr>
</tbody>
</table>

Table 1: HT PEM Stack characteristics.

Fig. 1. HT-PEM efficiency curve.

B. Numerical setup

Following the approach introduced and validated in [3-5], the energy systems are modeled through a phenomenological approach, that accounts for equipments rated and off design...
performances, as well as their integration issues. In this respect all the energy fluxes, are considered as model constraints.

The optimal control strategy, that is, the management policy that minimizes the total daily cost, is determined using backward dynamic programming having discretized and represented the problem as a weighted and oriented graph [4,5]. To this aim, costs and revenues related to the energy fluxes are accounted for, as well as maintenance and equipment start-up costs.

III. CASE STUDY

A typical residential winter energy demand is considered as a case study. Energy demand is represented in Fig. 2.

![Fig. 2. Energy demand.](image)

The HT-PEM based plant is compared to a traditional CHP, that utilizes a reciprocating Diesel engine as prime mover. In both cases the power unit is complemented with a natural gas boiler. The plant is grid-connected and thermal energy can be stored in a 243 MWh capacity tank. Both the prime movers has 10 kW of rated electrical power. The HT-PEM is operated at a constant temperature of 170°C.

IV. RESULTS

Daily cost, resulting from fuel, electricity, maintenance, and start-up costs, and PEC relative to the three considered plants are reported in Tab. II.

<table>
<thead>
<tr>
<th></th>
<th>Cost [€]</th>
<th>PEC [kJ]</th>
<th>Cost Variation</th>
<th>PEC Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>27.5</td>
<td>1.06x10^6</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>ICE</td>
<td>19.4</td>
<td>9.16x10^5</td>
<td>-29%</td>
<td>-14%</td>
</tr>
<tr>
<td>PEM-HT</td>
<td>13.5</td>
<td>9.83x10^5</td>
<td>-51%</td>
<td>-7.5%</td>
</tr>
</tbody>
</table>

Both configurations allow significant cost and PEC reductions with respect to the reference case. Nevertheless, the PEM-HT based configuration leads to the lowest global cost, with a 50% energy supply cost reduction with respect to the reference case. On the other hand, the minimum PEC is obtained using the Diesel engine based plant that is characterized by a higher full-load efficiency.

The PEM-HT load time trace is compared to the Diesel engine one in Fig.3. Comparing Fig.3 and Fig.2, it is noted that both the fuel cell and the engine are basically operated following an electrical-tracking strategy. Thereafter the PEM-HT takes a significant advantage from the inherent flexibility of the fuel cell (i.e. the PEM-HT efficiency increases as its load is decreased). This point is further clarified noting that, the Diesel generator is turned off (thus electricity is bought from the grid) for electrical demand lower that 1 kW, while the PEM-HT allows electricity self-production also for a demand as low as 0.5 kW.

![Fig. 3. ICE vs FC set-point time-trace.](image)

Finally it is pointed out that thermal demand is completely satisfied using cogeneration (i.e. recovering heat from prime mover exhaust) for both the configurations, thanks to the possibility to store thermal energy, and thus decouple electricity and heat demand.

V. CONCLUSION

In this paper we presented the application of PEM-HT based micro-cogeneration plant to a residential load. The plant control strategy is optimized to minimize the daily cost and the fuel cell performances are compared to then Diesel engine ones, demonstrating its economical feasibility. It is noted that the fuel cell based plant benefits also of the absence of vibrations, noise and pollutant emissions that hinder the usage of reciprocating engines in residential and domestic applications.

ACKNOWLEDGEMENTS

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REFERENCES

ADVANCED CONTROL FOR PRESSURIZED SOFC HYBRID SYSTEMS: EXPERIMENTAL VERIFICATION

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Abstract - This paper focuses on advanced controls for a pressurized SOFC hybrid system, based on a model predictive control (MPC) approach.

A MIMO (multi input multi output) MPC controller was synthesised and implemented in the hybrid system emulator test rig developed by Thermochemical Power Group (TPG) at the University of Genoa.

Experimental tests were carried out to compare MPC against classical PID method which was used in previous tests on the hybrid system emulator. In particular, tests focused on the emulator behaviour changing the fuel cell power target. Ramping fuel cell load from 100% to 80% and back, keeping constant the target of the cathode inlet temperature, MPC controller was able to reduce the mismatch between the actual and the target values of the cathode inlet temperature from 7 K maximum of the PID controller to 3 K maximum, showing, in general, a more stable behavior.

Index Terms – Dynamics and Control, Fuel Cell, Model Predictive Control, Hybrid system.

I. INTRODUCTION

Model predictive control (MPC) has been an operative field of research during the last decades, driven by numerous successful applications of the technology [1-2] and by the research interests of the academia. MPC is an interesting control approach because of its ability to control multivariable systems under constraints in an optimal way. In model predictive control, the control action is computed by solving an optimization problem at each sampling period. This is the main difference from traditional control, where a precomputed control law is employed [3].

An MPC was developed and applied to the hybrid system emulator test rig developed by Thermochemical Power Group (TPG) at the University of Genoa.

II. TEST RIG DESCRIPTION

In TPG laboratories located at Savona an emulator test rig for fuel cell hybrid systems has been running since 2007 (Fig. 1).
The test rig is based on the coupling of a micro gas turbine and a specially designed vessel which emulates the behavior of a fuel cell working close to 4 bar. The mGT is a Turbec T100, able to operate in stand-alone configuration or connected to the electrical grid. The fuel cell physical emulator is based on a thermally insulated vessel connected between the recuperator outlet and the combustor inlet.

The test rig is equipped with a real-time model for emulating components not present in the laboratory (SOFC block, anodic circuit, cathodic blower, reformer, off-gas burner). Using a UDP based connection with the test rig control and acquisition software, it generates a real-time hardware-in-the-loop (HIL) facility for hybrid system emulation (Fig. 2) [4].

III. MODEL PREDICTIVE CONTROL

In this work MATLAB Simulink Model Predictive Control toolbox was used in order to control the HIL facility described above. In Fig. 3 a flow diagram of Matlab MPC toolbox is shown, with the possible variables managed by the MPC. This toolbox is able to generate a discrete-time controller - one that takes action at regularly spaced, discrete time instants. The complete documentation about this toolbox is available in the documentation developed by MathWorks™.

![Fig. 3. Flow diagram of the Matlab MPC toolbox](image)

MPC needs a model of the controlled plant to compute the control signal: a linearized model was implemented starting from the non linear real-time model (previously built by TPG) used in the hybrid system emulator HIL and was fed to the MPC Simulink block.

A MIMO (multi input multi output) MPC controller was obtained: fuel cell power and cathode inlet temperature are the controlled variables; cathode flow, electrical current and fuel mass flow rate (the utilization factor kept constant) are the manipulated variables.

IV. TESTS AND RESULTS

Experimental tests were performed to compare MIMO MPC controller against classical PID method which was used in previous tests on the hybrid system emulator (the PID coefficients were calculated using the Ziegler-Nichols tuning method based on the open loop reaction curve).

In Fig. 4 and 5 there are the results of two tests (one with MPC and one with PID) in which fuel cell load varies from 100% to 80% and back, keeping constant the target of the cathode inlet temperature. MPC controller was able to reduce the mismatch between the actual and the target values of the cathode inlet temperature from 7 K maximum of the PID controller to 3 K maximum (see Fig. 5). Moreover the root-mean-square error (RMSE) between the actual and the target cathode inlet temperatures during the tests is 1.9°C using MPC and 2.3°C with PID. Finally MPC shows a smoother cathode inlet temperature profile with a more stable behavior along the whole transient.

![Fig. 4. SOFC output power](image)

![Fig. 5. SOFC inlet temperature](image)

V. CONCLUSION

MPC controller showed to be able to improve the performance of the PID in the experimental tests because:

- the mismatch and the RMSE between the actual and the target values of the cathode inlet temperature are reduced.
- a smoother and more stable cathode inlet temperature profile is obtained.

ACKNOWLEDGMENT

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REFERENCES


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NUMERICAL CHARACTERIZATION OF MICRO-CHP SYSTEM BASED ON HT-PEM FUEL CELLS

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Abstract – A 3D CFD complete model to evaluate the performance of a Micro-CHP system based on a single HT-PEM Fuel Cell is proposed. In previous papers, we described the development of the channel design, optimized for the best gas diffusion with the lowest pressure losses, and the set-up of our electrochemical model.

A detailed 3D model of the coolant paths has been realized and different cooling liquids have been accounted for.

The overall energetic performances, in terms of power output and heat production, have been evaluated and compared to similar data in literature.

Index Terms – Clean Energy, Fuel Cell, Numerical Model, Heat Recovery

I. INTRODUCTION

In the field of renewable energies, great interest is devoted to the study and development of Fuel Cell (FC) technologies, [1]. In recent years, different technological solutions have been investigated to find a solution to pollutant emissions in a convenient and sustainable way, such as solar and wind energy, geothermy and Fuel Cell technologies.

Among the different types of Fuel Cells, those characterized by Polimer Electrolyte Membranes (PEM) are considered as the closest to wide commercialization, due to their several peculiarities.

High Temperature (HT) PEM FC represent an enhancement of standard (low temperature) PEM: their operating temperature, in fact, is above 100°C, with considerable advantages in terms of chemical kinetics, CO tolerance and water and heat management.

HT PEM FC's have membranes based on particular polymers, suited for dry operating conditions, such as PBI or Pyridine, doped by means of phosphoric acid, that allow efficient proton transport in a temperature range of 140°-180°C at atmospheric pressure: the choice of operating temperature is directly related to the feeding gas composition, and to the content of CO in the anode gas. Thanks to the considerable increase in tolerance towards CO, HT PEM's can be fed by means of Syngas, with great saving in the overall system cost in comparison to traditional PEM systems.

In this work, a complete 3D model to study the internal fluid dynamics coupled to the electrochemistry of a HT PEM stack is proposed. Starting from the fluid dynamic optimization of anode and cathode channels performed by the authors in a previous work, a complete set of electrochemical equations has been implemented in Ansys 13 environment.

II. STACK MODELING

Figure 1 reports the main elements of our computational domain. The green and gold plates are the mono-polar collectors at the extremes of the cell; the red plates are bipolar and the light-yellow in the middle is a bipolar plate with channels for heating/cooling, as shown in Fig. 2.

The grey sections represent the four Membrane Electrode Assemblies (MEA’s) of our stack.

Table 1 reports the main geometrical characteristics of our computational domain: for further details on the mesh realization, the Reader is addressed to [2].

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Channel height 1.1 mm
Channel average length 235 mm
Anode channel width 1.1 mm
Cathode channel width 1.1 mm
Anode GDL thickness 0.34 mm
Cathode GDL thickness 0.34 mm
Membrane thickness 0.065 mm
Membrane active area 45.2 cm²
Anode Catalyst Layer thickness 0.04 mm
Cathode Catalyst Layer thickness 0.11 mm
Average Cell dimension inside Channels 0.11 mm

III. SIMULATIONS AND RESULTS

Figure 3 reports the velocity magnitude in [m/s] in anode (a) and cathode (b) compartments: the cell anode compartments are fed with pure H₂, with an overall mass flow rate of 0.08 slpm, providing a total current output of 10 A. The air mass flow rate in the cathode compartment is set to have the perfect stoichiometric quantities. The production of water in the cathode compartment is evident from Fig. 4, which shows H₂O mass fraction, [-].

IV. CONCLUSION

A complete 3D CFD-electrochemical model has been proposed, to study the performance of a micro-CHP system based on a HT-PEM FC stack. The detailed description of both the internal fluid dynamics and the electrochemical reactions allows a deep investigation on the energetic performance of micro-CHP systems based on the cell stack.

REFERENCES

NON-PRECIOUS METAL OXYGEN REDUCTION CATALYSTS FOR FUEL CELLS: A GOOD OR A BAD IDEA?

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Abstract - Non-precious metal catalysts (NPMCs) have shown promising activity towards oxygen reduction reaction (ORR), both in basic and acidic media. However, the use of NPMCs in acidic Nafion®-based polymer electrolyte fuel cells has been hampered by relatively low activity and stability when compared to platinum-based catalysts. In order to overcome these issues, a new class of ORR NPMCs was developed that involves heat treatment as a key step in the NPMC synthesis. This presentation provides a review of the progress in research on heat-treated non-precious metal catalysts, with an emphasis on the efforts focusing on the active site identification and correlation between catalyst performance and morphology.

Index Terms - Polymer electrolyte fuel cells, oxygen reduction, electrocatalysis, non-precious metal catalysts

I. INTRODUCTION

With the growing awareness that the use of platinum needs to either be significantly reduced or completely eliminated from the polymer electrolyte fuel cell (PEFC), non-precious metal catalysts for oxygen reduction reaction (ORR) have received lots of attention in recent years as a possible replacement of precious-metal catalysts, especially at the fuel cell cathode, the electrode process that demands substantially higher Pt loadings than the much faster hydrogen oxidation reaction at the anode. A successful cathode catalyst must combine high ORR activity with good long-term stability—a major challenge in the strongly acidic environment of the PEFC cathode. In response to the catalyst cost challenge we have developed non-precious metal ORR catalysts capable of minimizing the performance gap to platinum-based catalysts at a cost sustainable for high-power fuel cell applications. We used several organic compounds, polymeric and non-polymeric, as nitrogen and carbon precursors for high-temperature synthesis of catalysts in the presence of transition metals (Fe and/or Co). When used at a sufficiently high loading, the most active catalysts come within ca. 60 mV of the activity exhibited by state-of-the-art carbon-supported Pt catalysts. At the same time, they exhibit promising stability and four-electron selectivity on par with Pt-based catalysts. In this presentation, we will offer a critical overview of the current state of non-precious metal catalysis of oxygen reduction. We will also discuss the limits of the present high-temperature approach and requirements for non-precious metal ORR catalysts to become viable for polymer electrolyte fuel cells.

A. Catalyst synthesis and active site identification

Even though the heat treatment of virtually any mixture of nitrogen, transition metal and carbon species can yield a material with some ORR activity, better-performing catalysts require a careful and creative choice of precursors, supports, and synthesis conditions (control over precursor reactions in solution, heat-treatment temperature and atmosphere, post-treatment conditions, etc.) [1, 2]. Heat-treated transition-metal-nitrogen-carbon (M-N-C) NPMCs can be divided into three main groups: (1) catalysts obtained from transition-metal-based macrocycles; (2) catalysts derived from metal salts and gaseous nitrogen precursors, such as NH₃; and (3) catalysts synthesized from inorganic transition metal salts and simple nitrogen-containing molecules [3]. Recent advances in the development of high-performance NPMCs show that M-N-C catalysts (with M being typically Fe or Co), obtained by simultaneously heat-
treat ing precursors of a transition metal, nitrogen, and carbon at 800-1000°C yields the most promising NPMCs.

Although catalysts with measurable ORR activity can be prepared without any detectable metal content, the presence of Fe and/or Co is essential for generating catalysts with high activity and best durability observed to date [3-5]. However, the exact nature of the active site(s) in M-N-C catalysts synthesized using a heat-treatment approach remains unknown. Also lacking is a direct evidence of the transition-metal participation in the ORR active site. In either case, while nitrogen species embedded within the carbon structures are likely critical to the active-site performance, the bonding character and structure of active sites are yet to be conclusively identified.

B. State-of-the-art NPMCs

We reported on a family of NPMCs that utilize polyaniline (PANI) as a precursor of a carbon/nitrogen template in high-temperature synthesis of Fe- and Co-based catalysts [6]. PANI-Fe-C catalysts turned out to be the most active and four-electron-selective NPMCs, as determined in rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) tests, respectively. The catalysts catalyze the ORR in acid media at half-wave potentials within ca. 60 mV of those delivered by the state-of-the-art carbon-supported Pt catalysts (Figure 1a) [6].

Recently, we introduced a new type of nitrogen-doped carbon nanotube/nanoparticle composite ORR electrocatalyst obtained from iron acetate as an iron precursor and from cyanamide (CM) as both the nitrogen and carbon-nanotube precursor. The catalyst, obtained in a simple, scalable and single-step method, has the highest ORR activity in alkaline media of any non-precious metal catalyst (Figure 1b) [2].

![Fig. 1. RDE polarization plots recorded with LANL ORR catalysts at 25°C and 900 rpm in (a) 0.5 M H2SO4 for PANI-derived catalyst and (b) in 0.1 M NaOH for CM-derived catalysts.](image)

C. Carbon nanostructures in NPMCs

M-N-C catalysts are rich in carbon nanostructures formed during synthesis. The nanostructures involve, for example, carbon tubes, onion-like carbon, and carbon platelets (multi-layer graphene) (Figure 2) [7, 8]. The active PANI-derived ORR catalysts are especially rich in nitrogen-doped graphene, generated directly in the graphitization process of PANI in the presence of transition metal species (Co and/or Fe). These highly-graphitic structures can serve as a matrix for hosting ORR-active nitrogen or metal moieties. The effect of these nanostructures on the ORR activity and fuel cell performances is in need of further studies.

![Fig. 2. Drawings and micrographs of in situ nitrogen-doped carbon nanostructures in M–N–C catalysts.](image)

II. CONCLUSION

Heat-treated NPMCs, synthesized from earth-abundant transition metals, nitrogen, and carbon, are capable of catalyzing the ORR and efficiently generating electricity from fuels via a direct electrochemical conversion.

The major challenge of non-precious metal electrocatalysis of oxygen reduction reaction continues to be the lack of knowledge of the active catalytic sites and reaction mechanism. Other challenges are the role of graphitized carbon nanostructures in the ORR and gains potentially stemming from the optimization of electrode structure.

Further progress in the development of NPMCs will likely depend on the ability to characterize and understand the source(s) of the activity of the catalysts that have already been developed and presently are under development today.

ACKNOWLEDGMENT

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REFERENCES


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Abstract – Activated Carbon (AC) have been used as cheap alternative cathode for microbial fuel cell (MFC) applications. Different parameters (applied pressure and temperature treatment) have been changed and the cathode performances have been studied in half electrochemical cell and in single chamber MFC. The best cathode polarization was achieved at 2 mT applied pressure and temperature treatment of 200°C. The cathodes were also tested in microbial fuel cell (MFC) fed with phosphate buffer and sodium acetate.

Index Terms - activated carbon cathode; fabrication protocol; cathode polarization curves; SCMFC

I. INTRODUCTION

Microbial fuel cell (MFC) is a promising bioremediation device capable of converting organic substances into clean electric energy. The greatest challenge is to develop cost-effective electrode materials to increase the power output. Usually the cathode is the limiting electrode due to the high activation losses and further studies need to be addressed. Platinum (Pt) is the most common catalyst used in MFCs systems to increase the oxygen reduction reaction (ORR) kinetic on cathodes [1]. But the high cost hinders the large-scale MFC application. In the past years, activated carbon (AC) cathode gained attention due to the low cost and high catalytic activity towards the ORR [2]. Unfortunately, the fabrication protocol is not clear and further developments need to be addressed. In this work, different parameters (applied pressure and temperature treatment) have been changed and the cathode performances have been optimized in half electrochemical cell and in single chamber MFC.

II. MATERIALS

The AC cathodes prepared under different pressures, pressing times, and heating temperatures were examined. Specifically, the AC and PTFE (20%wt) were mixed and pressed with different pressure forces (0.25-5 mT) on carbon cloth used as the electrons collector. The final AC cathode was thermally treated for 1 hour at different temperatures (ambient 25, 90, 150, 200 and 340°C).
III. METHOD

Half cell electrochemical tests have been performed in phosphate buffer solution at pH≈7.2 using linear sweep voltammetry (LSV) with scan rate of 0.2 mV/s. Each cathode has been run in triplicate. Power curves have been measured applying different external resistances ($R_{ext}$) between anode and cathode, recording the voltage after stabilization and applying the Ohm law where the power was $V^2/R_{ext}$ and the current was $V/R$. Power and current density were referred to the projected cathode area (3.5 cm$^2$).

IV. RESULTS AND DISCUSSION

The tests in the half electrochemical cells and in MFC showed that both the parameters investigated (applied pressure and temperature treatment) had a significant effect on the cathode and overall performances. The best performances were achieved at the applied pressure of 2mT and the treatment temperature of 200°C.

It can be noticed a certain linear dependence between current generated and applied pressure until 2 mT and this could be explained by the increase in contact among the AC particles and consequently a reduction in materials ohmic resistance (Figure 1). However, in our case, a further increase in pressure up to 5mT instead led to a decrease in performance and this was probably due by the complete perforation of the electron collectors (carbon cloth) leading to abundant anodic solution leakage. The highest power recorded was the 2mT pressed cathode MFC ($\approx 70 \mu W \text{ cm}^{-2}$) and similar power was reached when the cathode was pressed at 1mT ($\approx 68 \mu W \text{ cm}^{-2}$) and 3.5 mT ($\approx 67 \mu W \text{ cm}^{-2}$). Lower power was reached at lower pressure 0.25mT ($\approx 62 \mu W \text{ cm}^{-2}$) and 0.5mT ($\approx 63.5 \mu W \text{ cm}^{-2}$) and at the highest pressure of 5 mT ($\approx 62 \mu W \text{ cm}^{-2}$).

The change in performances of the cathodes with the temperature treatment can be attributed to the PTFE agent and the different behaviour and structure with the temperature. It can be noticed an almost linear relationship between current generated and increase in temperature until 200°C but a significant drop in performance with high T treatment (Figure 2). In fact, the increase in temperature led the PTFE to a state transition from hard/solid state (at ambient temperature), to vitrification (between 115 and 250°C) to the complete melting (after 327°C). This phase transition creates different interaction between PTFE particles and activated carbon. An increase in temperature (up to 150-200°C) led to the vitrification of the PTFE and slight expansion of the PTFE crystals that probably enhance the complete coverage with AC particles. Instead, the heating treatment of the mixing AC/PTFE at 340°C slightly over the PTFE melting point (327°C) led to the complete disintegration of the crystal structure of the PTFE. It can be assumed that the PTFE covered the activated carbon decreasing substantially the porosity and decrease the pore size distribution. The highest power recorded was the MFC with cathode treated at 200°C ($\approx 70 \mu W \text{ cm}^{-2}$) and comparable power was reached when the cathode was treated at 200°C ($\approx 69 \mu W \text{ cm}^{-2}$). The power generation decreased to $\approx 62 \mu W \text{ cm}^{-2}$ and 60 $\mu W \text{ cm}^{-2}$ with cathode treatment at temperature of 90°C and ambient temperature (90°C) respectively. The worst performances were achieved with temperature treatment close to the PTFE melting point with a power generated of $\approx 55 \mu W \text{ cm}^{-2}$.

V. CONCLUSIONS

The study developed novel Pt-free AC cathodes and optimized the fabrication protocols, which showed the great potential of reducing MFC costs. High power generation was achieved in SCMFCs with AC cathode that was optimized varying applied pressure and temperature treatment. The best performances were achieved at the applied pressure of 2mT and the treatment temperature of 200°C.

![Fig. 1. Current density generated with different applied pressure (a) and temperature (b) treatment.](image)

REFERENCES

LOAD CYCLING AND REVERSIBLE SOE/SOFC OPERATION IN INTERMEDIATE TEMPERATURE STEAM ELECTROLYSIS


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Abstract - Intermediate Temperature Steam Electrolysis (ITSE) aims at optimising the electrolyser life time by decreasing its operating temperature while maintaining satisfactory performance level and high energy efficiency at the level of the complete system including the heat and power source and the electrolyser unit.

In this work, we present the results of electrochemical measurements performed on SOFCpower stacks operating in ITSE conditions. These measurements were focused on the stack durability upon very rapid load cycling in SOE-mode and reversible SOE/SOFC operation.

Index Terms - High temperature electrolysis; solid oxide fuel cells, renewable energy sources

I. INTRODUCTION

SOFCpower SPA provides efficient energy solutions based on its proprietary planar SOFC technology. Main products of the company are combined heat and power generation (CHP) unit and distributed power generation units with high electrical efficiency; both systems run on natural gas. In this respect, the company develops and manufactures SOFC power modules in close collaboration with European heat appliance OEMs and utilities. Furthermore, the company is evaluating strategic technology options for planar electroceramic membrane reactors; for example, the use of its SOFC stacks technology for high temperature solid oxide electrolysis (SOE). In this field, HTceramix leads the European FCH-JU project ADEL (ADvanced EElectrolysers). The ADEL project works on intermediate temperature steam electrolyser that ideally matches available electricity and heat sources. HTceramix coordinates this project covering several aspects including materials and stack development over system appliance design and specification up to the level of energy flow sheeting to evaluate several options of energy ranging from nuclear to renewable sources such as solar, geothermal and wind.

In the present work we present the results of electrochemical measurements performed on SOFCpower stacks operating in ITSE conditions. These measurements were performed in order to investigate the capability of the stack to modulate its power, to be adapted to operation conditions typically occurring when coupling the electrolyser with renewable energy sources. In addition, the reversibility of the stack to produce hydrogen by working in SOE-mode when an excess of energy is available, to be switched to produce electricity in SOFC-mode when energy production is required and hydrogen is available, was also investigated.

II. EXPERIMENTAL

SOFCpower technology is based on planar anode supported solid oxide cells for SOFC and SOE applications. Cells consist of a thin (ca. 10 µm) 8YSZ electrolyte supported by a porous Ni/YSZ fuel-electrode (ca. 250 µm). The Oxygen electrode is based on (La,Sr)(Co,Fe)O_{3-δ} (LSCF) perovskite and Gadolinia doped-Ceria (GDC) barrier layer.

The stack consists of an assembly of 6 cells interfaced with proprietary SOFCCONNEX™ gas diffusion layers and Crofer 22 APU metallic interconnectors. The single cell active area, corresponding to the oxygen electrode, is 48 cm². The testing bench is designed to test stacks in the power range of 20-200W and it is composed by three main parts: Reformer Bench, Short Stack Test Bench and Water Gas Shift Reactor. Stack performances were studied by performing current/voltage (IV) polarization curves in the range 650°C-750°C and by feeding 10vol%H_{2}/H_{2}O and air on the fuel- and oxygen-electrode sides, respectively. Gas flow rates were 0.012Nl cm⁻² min⁻¹ for both electrodes. The IV curves were recorded by
increasing the current by -1A cm\(^{-2}\) min\(^{-1}\) steps up and limiting the exothermal conditions to 1.5V. After reaching the maximum value, the current was stepwise decreased to the OCV by using the same ramp. The temperature of the stack during the measurement was monitored by observing the air temperature downstream the stack, measured by a thermocouple.

The stack durability under transient operation conditions was investigated at 700°C. On/off “fast” load cycles in SOE mode were performed by starting from the OCV and increasing the current up to 38% steam conversion (SC), corresponding to -0.6 A/cm\(^2\). These load conditions were selected in order to achieve an average voltage of the stack close to the thermal neutral conditions. The current was increased from 0 to -0.6A/cm\(^2\) in 1 sec and maintained for 10 min. After that, the current is suddenly interrupted to restore OCV conditions were a new cycle started after a 10 min plateau.

“Slow” load cycles were performed in the same conditions and using a 10 min plateau at OCV and at -0.6A/cm\(^2\). In this case, the stack was loaded and unloaded by a 1A/cm\(^2\) ramp.

SOFC/SOEC cycles were performed at 700°C, under a 50vol%H\(_2\)/H\(_2\)O atmosphere and by ranging the load between 0.21 and -0.21 A/cm\(^2\). The current was applied by a 0.21 mA cm\(^{-2}\) min\(^{-1}\) ramps, followed by a 10 min plateau at the maximum load. The calculated steam conversion is 24% at -0.21A/cm\(^2\).

### III. RESULTS AND DISCUSSION

Average stack performances under SOE conditions at different temperatures and the temperature profile of the stack during the measurements are given in Fig. 1. As expected, the stack temperature slightly increase when the voltage reaches the exothermal operation conditions. This temperature increase affects the stack performances, resulting in a significant hysteresis in the IV curve. The ASR\(_{sec}\) calculated between the OCV and the TNV, was 0.65 and 0.70 V Ohm cm\(^2\) at 750°C and 700°C, respectively. This average resistance is affected by a large ohmic resistance, related to a contact issue, observed on one of the six repeating elements. The ASR\(_{sec}\) at 700°C ranges from 0.6 to 0.9 Ohm cm\(^2\), for the best and the worst repeating elements, respectively. The average ASR\(_{sec}\) at 650°C is 1.25 Ohm cm\(^2\).

An overview of the stack behavior under transient operation conditions and SOE/SOFC cycles is given in Fig. 2. The durability test was performed over the course of 80h, during which 50 fast cycles, 19 slow cycles and 22 SOE/SOFC cycles were performed. The stack demonstrated a very good capability to be adapted to transient operation as well as a good reversible behavior under SOE/SOFC conditions. Moreover, no significant degradation was observed over the complete characterization campaign.

### IV. CONCLUSION

The present work shows that an electrolyser based on Solid Oxide Cells can demonstrate good performances, at intermediate temperatures (700°C), running under thermal neutral conditions. The stack demonstrated a good capability to modulate its power to be adapted to transient operation conditions which are typically required when coupling the electrolyser with renewable energy sources. Moreover, the stack demonstrated a very good flexibility to be used under reversible Solid Oxide Electrolysis/Solid Oxide Fuel Cell operations.

### ACKNOWLEDGMENT

Authors are grateful to the European Commission for financial support through the FP7 FCH-JU ADEL (Nr. 256755) project.
Abstract - The present work refers to a first series of obtained results on how Au and/or Mo addition can affect the stability of modified Ni/GDC anodes for the reaction of internal CH₄ steam reforming, in the presence of H₂S. Specifically, it is shown that Ni/GDC is stable in the presence of 10 ppm H₂S, but only in the case where 100 vol% of H₂ is the anode feed. In the case where CH₄ and H₂O (diluted in Helium carrier gas) comprise the anode feed then at S/C = 2 or S/C = 0.13 ratios the performance of Ni/GDC shows severe degradation, while the Au-Mo-Ni/GDC anode has the best and most stable performance.

Index Terms – Au and/or Mo modified Ni/GDC anodes, H₂S poisoning, Internal CH₄ Steam Reforming, Solid Oxide Fuel Cells

I. INTRODUCTION

Solid oxide fuel cells (SOFCs) are among the most promising energy systems as they produce electric power and heat with higher efficiency as well as lower noise and pollutant emissions than conventional heat engines [1]. So far, Ni-based cermet is the most popular anode in SOFC systems due to its low cost, ease of fabrication and relatively high electrochemical activity. However, Ni cermets consisting of Ni and YSZ ceramic (Ni/YSZ) experience severe degradation in fuels containing only a few ppm of H₂S, due to the high vulnerability of Ni to sulphur poisoning. Studies using Ni/GDC [2] have shown that this composition might be a very good candidate for operating in the presence of H₂S, since the degradation in performance for the H₂ oxidation in H₂S-containing H₂ fuels is substantially smaller compared to that on Ni/YSZ anodes [2]. Along this direction, it was recently published [1, 3] that modification of NiO/GDC anode powder via deposition-precipitation of fine dispersed Au and/or Mo nano-particles resulted in a material with high tolerance to carbon formation and improved electrocatalytic activity under carbon forming conditions, for the reaction of CH₄ internal steam reforming (ISR). The present work refers to a first series of obtained results on how Au and/or Mo addition, with the above preparation methods, can affect the stability of modified Ni/GDC anodes for the reaction of CH₄ (ISR) in the presence of H₂S.

II. EXPERIMENTAL

Preparation of cermets

Binary Au – NiO/GDC and Mo – NiO/GDC anode powders with nominal loading 3wt.% Au or Mo, respectively, were prepared via the deposition-precipitation (D.P.) method. The ternary Au – Mo – NiO/GDC anode powder was prepared with the deposition-coprecipitation (D.CP.) method, while the nominal loading of Au and Mo remained at 3 wt.%, respectively. After filtering, the precipitate was dried at 110 °C for 24 h. All dried powders were calcined at 600 °C for 90 min.

Preparation of Solid Oxide Electrode Assemblies

The Solid Oxide Electrode Assemblies (SOEAs) comprised circular shaped planar electrolyte-supported SOFC membranes manufactured by Kerafol with a diameter of 25 mm. The mechanical support consisted of approx. 300 µm thick 8YSZ electrolyte. The anode was deposited by means of stepwise addition of droplets of slurry with a precision micropipette. The anode slurry contained an amount of NiO/GDC anode powder (modified with Au, Mo and Au-Mo), terpineol (Sigma-Aldrich) as the dispersant, PVB (polyvinylbutyral, Sigma-Aldrich) as binder and iso-propanol as solvent. After the deposition of the slurry, the anode assembly was dried and finally sintered at 1250°C with a heating and cooling ramp rate of 2 °C/min. The loading of the examined anodes lied in the range between 15–25 mg/cm² with 1.7 cm² geometric surface area. The cathode side comprised porous LSM from Fuel Cell Materials (FCM) and was deposited by means of screen printing. The electrocatalytic experiments were carried out on galvanostatic mode at 850 °C under various H₂O/CH₄ (S/C) ratios with the addition of 10 ppm H₂S. Pt-mesh was used as current collector on the anode and cathode side. Other details regarding the experiments are mentioned in the corresponding figures.
III. RESULTS AND DISCUSSION

Stability studies

The following Figures depict the stability diagrams of blank and of Au and/or Mo modified Ni/GDC anodes under different reaction conditions. In the presence of 10 ppm H₂S/H₂ (Fig. 1), the worst cell was the one that comprises 3wt.% Mo-Ni/GDC as anode, showing the lowest electrocatalytic activity. Nevertheless, under 10 ppm H₂S in H₂, all cells presented a stable behavior suggesting that Ni/GDC is sulphur tolerant in the case where H₂ is the main reactant fuel. Fig. 2 depicts the performance under CH₄ (ISR) with S/C=2 and the addition of 10 ppm of H₂S. It is clearly observed that 3wt.% Mo-Ni/GDC presented the worst performance both in terms of durability and electrocatalytic activity. Ni/GDC showed a bit better performance, but still degraded very fast. On the other hand, 3wt.% Au-Ni/GDC showed a bit better performance, but still degraded very fast. The latter was quite stable for almost 130 minutes and remained more active compared to the other cells. The electrocatalytic activity and tolerance of the studied cells changed when S/C=0.13 plus 10 ppm H₂S (Fig 3).

The main problem in this case was carbon deposition in combination with H₂S poisoning. Ni/GDC was the worst anode having the less operating potential and the shorter life time. On the other hand, 3wt.% Au-3wt.% Mo-Ni/GDC is once again the best performing anode, for almost 200 minutes. Au and Mo-modified anodes performed similarly, with Au-Ni/GDC slightly better, but both were not as stable as the ternary anode.

IV. CONCLUSION

Ni/GDC is stable in the presence of 10 ppm H₂S, but only in the case where H₂ is the main anode fuel. For the CH₄ internal steam reforming reaction with ratios of H₂O/CH₄=2 or 0.13 the performance of Ni/GDC is severely deteriorated in the presence of 10 ppm H₂S, while the ternary Au-Mo-Ni/GDC anode had the best and more stable behavior. The latter remark suggests a positive synergy between Au, Mo and Ni, resulting in sulphur and carbon tolerant anodes that could prove to be promising candidates for SOFCs fueled with CH₄, H₂O and H₂S.

ACKNOWLEDGMENT

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REFERENCES


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TWO-DIMENSIONAL MODELING OF A SOFC STACK REPEATING UNIT

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Abstract - For a SOFC stack in a highly integrated micro SOFC system a two-dimensional model of one repeating unit is presented. The stack, with an electric power output of 150 W, comprises 40 planar cells in cross-flow configuration. The model includes the species and energy balances, reforming reactions and additionally an electrochemical sub model based on measured area-specific resistances (ASR). A porous media approach is used to minimize computational costs. The model is implemented in the finite volume solver FiPy [1] based on programming language Python. With help of the model, different cell designs and operating conditions were compared with respect to their influence on cell performance. Furthermore, the effect of predefined cell defects (e.g. a crack of the electrolyte with hydrogen combustion or deactivated electrolyte regions) has been investigated.

Index Terms – finite volume, plane model, SOFC, LTE

I. PLANE SOFC MODEL

In the following we would like to introduce the geometry and setup of our plane SOFC model as well as the mathematical approach and want to present some selected results.

A. Model geometry and setup

Figure 1 displays an example for the model domain and the mesh obtained from Gmsh mesh generator [1]. The stack design shows a cross flow configuration with an electrochemical active area of 40x40mm². We consider a stack operating in an environment with constant temperature (800–850°C) which interacts by thermal radiative heat transfer with the outer faces of the stack. The inner surfaces of the gas manifolds can also exchange radiative heat. There are three functionally different regions in the model: a passive frame region consisting of packed solid materials contributing only to heat conduction being connected to a passive gas distribution region (fuel and air path) which encloses the active stack region, where electro-chemical oxidation takes place. The anisotropic effective heat conductivity values were obtained by a detailed 3d FE unit cell analysis of the stack structure.

![Fig. 1. Model geometry and mesh](image)

B. Mathematical Equations

The repeating unit of the micro SOFC stack is treated as an anisotropic porous medium with parameters for several physical properties. Mass transport of fuel and air can both be described by Darcy’s law:

\[ \nabla \left( - \frac{\rho_{gas}}{\eta_{gas}} \kappa_{gas} \cdot \nabla p_{gas} \right) = S_{m}^{gas} \]  

(1)

\[ \rho_{gas}, \ \eta_{gas}, \ \kappa_{gas}, \ S_{m}^{gas} \text{ and } p_{gas} \text{ represent the density, viscosity, permeability, mass source term and the pressure of either fuel or air. The source term } S_{m}^{gas} \text{ is a result of the net mass transport of oxygen to the anode side due to electrochemical oxidation of hydrogen and is defined by the Eq. (2).} \]

\[ S_{m}^{fuel} = -S_{m}^{air} = M_{O_2} \frac{1}{2} r_{emi} \]  

(2)

\[ M_{O_2} \text{ and } r_{emi} \text{ are the molar mass of oxygen and the reaction rate of the electrochemical oxidation is related by} \]

\[ r_{emi} = \frac{1}{h_{UC}} \frac{f_s}{2F} \]  

(3)

to the transverse electric current density \( j_s \) (\( h_{UC} \) and \( F \) are...
unit cell height and Faraday’s constant. Due to the good lateral conductivity of the interconnector, a constant cell potential $U_{\text{Load}}$ is assumed over the whole cell plane. The current density is defined by

$$j = \frac{1}{R_a} \left( U_{\text{Nernst}} - U_{\text{Load}} \right), \quad (4)$$

with $U_{\text{Nernst}}$ referring to the local Nernst voltage and $R_a$ to the area specific cell resistance, which is assumed to have the form

$$R_a = R_a^0 \cdot \exp \left( \frac{E_a}{k_B} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \quad (5)$$

and is obtained by fit of experimental data. The heat balance is included by a local thermal equilibrium (LTE) approach.

$$\nabla(-k_{\text{eff}} \nabla T) + C_{\text{p, gas}} \rho_{\text{gas}} \dot{u}_{\text{gas}} \nabla T + C_{\text{p, solid}} \rho_{\text{solid}} \dot{u}_{\text{solid}} \nabla T = \dot{q}_{\text{rec}} \quad (6)$$

Here $k_{\text{eff}}, C_{\text{p, gas}}, \rho_{\text{gas}}, \dot{u}_{\text{gas}}$ and $\dot{q}_{\text{rec}}$ are the effective heat conductivity tensor, fuel/air heat capacity, fuel/air velocity, the reaction heat from both gas-phase reactions and electrochemical oxidation. $T$ is the local temperature.

The species fractions at both fuel and air side obey

$$\nabla(-D_{ij} \rho_{\text{gas}} \nabla y_i) + \nabla \left( \rho_{\text{gas}} \dot{u}_{\text{gas}} y_i - D_{ij} \rho_{\text{gas}} \frac{\nabla T}{M_{\text{gas}}} y_j \right) = M_j \sum_{\text{reaction}} \dot{y}_j \quad (7)$$

whit $y_i$ standing for the mass fraction of either $\text{CH}_4, \text{H}_2\text{O}, \text{H}_2, \text{CO}, \text{CO}_2, \text{N}_2$ on fuel side or $\text{O}_2, \text{N}_2$ on air side. $D_{ij}, \frac{\nabla T}{M_{\text{gas}}} y_j$ are effective anisotropic diffusion coefficient, mean molar mass of fuel/air and the stoichiometric coefficients.

C. Results

Temperature, current density and species distribution in the interior of the stack are of particular interest. As an example a result for the temperature distribution is shown in Fig. 2 for a reference load case (see Table I).

<table>
<thead>
<tr>
<th>Boundary conditions</th>
</tr>
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<tbody>
<tr>
<td>$V_{\text{fuel}} = 6.325 \text{ Nl/min @676°C}$</td>
</tr>
<tr>
<td>$H_2$: 47.6vol.%, $\text{H}_2\text{O}$: 3.8vol.%, $\text{N}_2$: 48.6vol. %</td>
</tr>
<tr>
<td>$V_{\text{air}} = 15.1 \text{ Nl/min @655°C}$</td>
</tr>
<tr>
<td>$\text{O}_2$: 21vol.%, $\text{N}_2$: 79vol.%</td>
</tr>
<tr>
<td>$U_{\text{Load}} = 0.73V$</td>
</tr>
<tr>
<td>$I_{\text{stack}} = 5A$</td>
</tr>
<tr>
<td>$P_{\text{stack}} = 3.75W$</td>
</tr>
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</table>

A maximum temperature of around 880°C is observed near to the center of the stack plane. The value corresponds well to measurements from an instrumented stack with a pattern of internal temperature sensors under comparable conditions. From an analysis of several design variations (active area size, manifold shape, interconnector thickness) an improved design variant was obtained, which was selected as basis for the current hardware revision of the eneramic system.

Fig. 2. Temperature distribution

Fig. 3 shows the appropriate current density for the above load case. The highest current densities of around 480mA/cm² appear close to the fuel inlet as may be expected for pure hydrogen load. The slightly higher current densities at top and bottom of the picture are a result from hydrogen, diffusing from a passive region both at top and bottom into the active area.

Fig. 3. Current density distribution

II. CONCLUSION

With the presented planar stack model which includes fluid flow, species transport with reforming reactions, energy transport and an electro-chemical sub model based on ASR we were able to satisfactorily reproduce SOFC-stack behavior for practically relevant load cases.

ACKNOWLEDGMENT

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REFERENCES


ANALYSIS OF ELECTRODE PERFORMANCE IN A MOLTEN CARBONATE ELECTROLYSIS CELL

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Abstract - The performance of the state-of-the-art cell operating as reversible molten carbonate fuel cell was investigated in half-cell and full-cell tests. The electrochemical measurements were performed by polarization curves coupled with current interrupt. The full-cell tests showed that it was feasible to run the reversible molten carbonate fuel cell and that the cell exhibited better performance in electrolysis cell mode than in fuel cell mode. In the temperature range from 600 to 675 °C the polarization of the Ni hydrogen electrode showed to be slightly higher in electrolysis cell mode. The NiO oxygen electrode on the other hand showed better behaviour in electrolysis cell mode than in fuel cell mode within the temperature range.

Key words: electrolysis cell mode, Ni hydrogen electrode, NiO oxygen electrode, reversible molten carbonate fuel cell

I. INTRODUCTION

The molten carbonate fuel cell (MCFC) technology has reached a level of maturity enough for commercialization and in total more than 100 MW is installed in about 60 different places worldwide [1-2]. When MCFC is run in reversible mode, it can operate as a molten carbonate electrolysis cell (MCEC) to generate hydrogen or syngas (H_2+CO) from electrolysis of water and carbon dioxide. Both hydrogen and syngas are today considered as important fuels in the future energy system. Traditionally these fuels are produced from fossil fuels and natural gas reforming [3-4]. There is a growing interest in high temperature water electrolysis, since it is considered as a feasible and more environmentally friendly option for hydrogen production, at least when using renewable electricity. Another advantage of the high temperature electrolysis (about 650°C in this case) is the reduction of applied voltage due to favourable thermodynamic and kinetic conditions when compared to low temperature electrolysis. Therefore, if the cell can be regarded as a mutual energy converter that operates as fuel cell to produce electricity and as electrolysis cell to generate fuel gases, it could improve the efficiency of the system and the economic benefits.

II. ELECTROCHEMICAL STUDY

Experimental data was obtained from the laboratory cell unit with a geometrical electrode area of 3 cm². The state-of-the-art components were produced by Ansaldo Fuel Cells in Italy and consisted of a porous Ni-Cr alloy as hydrogen electrode and a porous nickel as oxygen electrode, oxidized and lithiated in situ. The electrodes were separated by a porous LiAlO₂ matrix, which also supported the electrolyte, a eutectic mixture of 62/38 mol% Li₂CO₃/K₂CO₃. Two reference electrodes (Au wires with a 33/67% O₂/CO₂ gas mixture) were placed in separate chambers filled with the same electrolyte as in the cell. They were connected to the cell through a capillary with a gold plug.

Standard gas mixtures consisting of 64/16/20% H₂/CO₂/H₂O and 15/30/55 O₂/CO₂/N₂ were used for the Ni hydrogen electrode and the NiO oxygen electrode respectively. The polarization curves were run in potentiostatic steps by using Solartron Interface SI1287 with supporting CorrWare software. To separate the ohmic losses from other types of polarization, the current interrupt technique was used.

Fig. 1 shows polarization curves, with and without iR-corrected, of the cell in MCFC and MCEC mode at 650 °C. The continuity of the polarization curves observed close to OCV when shifting from fuel cell to electrolysis
cell mode, shows that it is feasible to operate the reversible molten carbonate fuel cell. The total cell resistances \((R_{\text{tot}})\), calculated from the slope of the curves without iR-corrected, were 1.096 and 0.894 \(\Omega \cdot \text{cm}^2\) in MCFC and MCEC mode respectively. Also the polarization resistance \((R_p)\) estimated from the slope of the iR-corrected curves showed a lower value in MCEC mode (0.584 \(\Omega \cdot \text{cm}^2\)) than in MCFC mode (0.781 \(\Omega \cdot \text{cm}^2\)). It shows that the cell was operated with a better performance in electrolysis cell mode. At the same time, the cell showed almost the same ohmic resistance (~0.31 \(\Omega \cdot \text{cm}^2\)) in these reversible operating conditions, indicating that running reversible molten carbonate fuel cell did not affect the properties of the electrode materials at least in this short-term test.

The polarization of the NiO oxygen electrode is investigated in both fuel cell and electrolysis cell modes with varying temperatures from 600 to 675°C, as shown in Fig. 3. As expected the polarization of the NiO electrode decreased in both operating modes with increasing the temperature. The electrode exhibited asymmetrical behaviour between the fuel cell and electrolysis cell modes. The NiO electrode as an MCEC anode showed significantly better performance than that as MCFC cathode.

The electrochemical performance of the state-of-the-art cell as MCFC and MCEC was compared, showing that it was feasible to run a reversible molten carbonate fuel cell. The cell exhibited better performance in MCEC mode than in MCFC mode.

The polarization of the Ni hydrogen electrode and the NiO oxygen electrode was investigated within the temperature range from 600 to 675°C. The Ni hydrogen electrode showed slightly higher polarization in electrolysis cell mode. However, the NiO oxygen electrode exhibited better performance in electrolysis cell mode than in fuel cell mode.

III. CONCLUSIONS

The financial support by China Scholarship Council (CSC) is appreciated. The cell components are provided by Ansaldo Fuel Cells in Italy.

ACKNOWLEDGMENT

The polarisation of the NiO oxygen electrode is investigated in both fuel cell and electrolysis cell modes with varying temperatures from 600 to 675°C, as shown in Fig. 3. As expected the polarization of the NiO electrode decreased in both operating modes with increasing the temperature. The electrode exhibited asymmetrical behaviour between the fuel cell and electrolysis cell modes. The NiO electrode as an MCEC anode showed significantly better performance than that as MCFC cathode.

Fig. 1. Polarization curves for the cell in MCFC and MCEC mode, working at 650 °C.

Fig. 2 shows the iR-corrected polarization curves of the Ni hydrogen electrode at different operating temperatures with the standard gases. In this temperature range, the Ni electrode showed an asymmetrical behaviour for hydrogen oxidation and water electrolysis. The performance of the Ni electrode for hydrogen oxidation is slightly better than that for water electrolysis. Using a constant polarization loss of 50 mV at 600, 625, 650 and 675 °C, the current densities are 0.23, 0.26, 0.27 and 0.31 A·cm⁻² while the electrolysis cell current densities are -0.22, -0.24, -0.25 and -0.26 A·cm⁻² respectively. Higher temperatures favour the performance of the Ni electrode in both fuel cell and electrolysis cell mode as expected.

Fig. 2. iR-corrected polarization curves for the Ni electrode in fuel cell and electrolysis cell mode at temperatures from 600 to 675 °C.

Fig. 3. iR-corrected polarization curves for the NiO electrode in fuel cell and electrolysis cell mode at temperatures from 600 to 675 °C.

REFERENCES

SOLID OXIDE FUEL CELL WITH MoNi-CeO₂ CERMET ANODE FOR DIRECT METHANE OXIDATION

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Abstract - In this work, MoNi in combination with CeO₂ (MoNi-Ce) has been evaluated as anode material for direct methane solid oxide fuel cells (SOFCs). For this purpose, a single cell of MoNi-Ce/LDC/LSGM/LSCF was fabricated and tested under humidified H₂ and CH₄ as fuel and stationary air as oxidant at 1023, 1073 and 1123 K. The electrochemical behavior was evaluated by current-voltage curves, impedance spectroscopy and durability tests. No performance degradation was detected in both studied fuels (H₂ or CH₄), which suggested that MoNi-Ce is a suitable anode material for direct methane solid oxide fuel cell.

Index Terms - Anode, direct methane oxidation, electrochemical performance, SOFC.

I. INTRODUCTION

The development of ceramic anodes for the direct use of hydrocarbon fuel is one of the most important goals in SOFC technology. Among the various materials investigated, doped ceria is being as promising anode for the direct oxidation of CH₄ [1]. Ceramics based on CeO₂ exhibit mixed ionic and electronic conductivity in a reducing atmosphere and show an excellent electrocatalytic activity on various fuels (e.g. H₂, CH₄). Ceria also presents high resistance to carbon deposition, which permits the direct supply of dry hydrocarbon fuels to the anode. However, the major concern is the low electronic conductivity of ceria-based anodes, which increases the resistance decreasing the cell performance. Therefore, introducing transitions elements into CeO₂ could provide additional pathways for redox reactions at the anode surface, facilitating its electrocatalytic reaction for oxidation of fuels. In this context, Ni-CeO₂/YSZ anodes showed excellent stability during CH₄ reforming and some tolerance to H₂S contamination and doping additional metals in the Ni-YSZ anode such as Mo, Pt, Au and La are beneficial to the reforming reaction of hydrocarbons, due to their functions of breaking the C-H bond more easily [2]. In addition, molybdenum appeared in the composition of promising anode materials for running on hydrocarbons fuels, such as double perovskites based on Sr₃MMoO₉ family [3].

Based on these studies, doping with hexavalent Mo to Ni-CeO₂ could improve the catalytic activity of hydrocarbon oxidation and reduce the carbon deposition. In a previous work MoNi-Ce, was studied in terms of structural properties as SOFC anode material and revealed that this compound exhibited an acceptable electrical conductivity and a thermal expansion coefficient close to other SOFC cell components [4]. In the present paper, we have investigated its electrochemical performance as alternative SOFC anode in a single cell based on LSGM electrolyte in H₂ and CH₄ as fuels at 1023, 1073 and 1123 K.

II. EXPERIMENTAL

Mo-Ni combined with CeO₂ (MoNi-Ce) with a total loading of 30 wt.% (5/1 atomic ratio for Ni/Mo system) was prepared by coprecipitation within reverse microemulsion and calcined in air at 1123 K for 2 h. Full details of preparation method and its characterization by XRD, XPS and SEM-EDAX can be found elsewhere [4].

A single cell with an active area of 0.28 cm² was fabricated with La₀.₃₈Sr₀.₆₂Co₀.₂Fe₀.₈O₃−δ (LSCF) as cathode and La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₂.₈₅ (LSGM) as electrolyte and MoNi-Ce as anode material. A thin buffer layer of La₀.₄Ce₀.₆O₄−δ (LDC) was placed between the electrolyte and anode, in order to prevent formation of unwanted phases at the anode electrolyte interface. The cell was tested under humidified H₂ and CH₄ as fuel and stationary air as oxidant at 1023, 1073 and 1123 K. The electrochemical behavior was evaluated by IV curves, impedance spectroscopy (IS) and durability tests.

III. RESULTS AND DISCUSSION

MoNi-Ce was tested as anode in a single cell running on humidified H₂ and CH₄ as fuel to evaluate its electrochemical performance. Fig. 1 shows the cell voltage and power density as a function of current density at several temperatures. The cell reached maximum power densities of 298, 443 and 589 mW/cm² in H₂ and 149, 234 and 358 mW/cm² in CH₄ at 1023, 1073 and 1123 K, respectively, as well as the maximum current densities (cell voltage= 0 V) were 1.24, 1.82 and 2.34 A/cm² in H₂ and 0.49, 0.82 and 1.34 A/cm² in CH₄ at the above mentioned temperatures. The lower values of maximum power
densities obtained in methane could be related to CH₄ is much less reactive than H₂ in heterogeneous oxidation, thus resulting in a higher polarization resistance associated with slower electrochemical oxidation of methane versus hydrogen.

**Fig. 1.** Cell voltage and power density as function of current density at 1023, 1073 and 1123 K in (a) H₂ and (b) CH₄.

The total polarization resistances of the cell measured by IS were 1.07, 0.61 and 0.34 Ω cm² in H₂ and 1.77, 1.26 and 0.48 Ω cm² in CH₄ at 1023, 1073 and 1123 K, respectively.

Long-term tests were performed in order to evaluate the resistance to carbon deposition. The cell was tested in pure CH₄ for 10 h at constant current density of 157, 356 and 654 mA/cm² at 1023, 1073 and 1123 K; and reached power densities of 95, 180 and 330 mW/cm², respectively (Fig. 2). The current density demanded in each test corresponded to the intensity required to achieve 90% of the maximum power, the values were obtained of IV curves. The cell performance remained stable in these time periods indicating no carbon deposition on the anode surface. Similar IV curves and impedance diagrams were measured before and after the endurance tests.

Generally, the oxidation reaction of methane on the anode of a SOFC can be expressed as [4]

\[ CH_4 + 4O^{2-} \leftrightarrow CO_2 + 2H_2O + 8e^- \]  

In fact, the oxidation of methane to CO₂ is through a series of intermediate steps. For example, the reaction

\[ CH_4 + 3O^{2-} \leftrightarrow CO + 2H_2O + 6e^- \]  

at an oxide-electrode surface is followed by (3) and the competing reaction (4)

\[ CO + O^{2-} \leftrightarrow CO_2 + 2e^- \]  

\[ 2CO \leftrightarrow C + CO_2 \]  

Reaction (4) results in C–C bond formation. If reaction (3) is faster compared with reaction (4) on an oxide anode, the electrode surface may remain free of coke build-up. Removal of CO from the surface by adding steam to the feed gas, reaction (5), can be accompanied by (6):

\[ CO + H_2O \leftrightarrow CO_2 + H_2 \]  

\[ H_2 + O^{2-} \leftrightarrow H_2O + 2e^- \]  

Therefore, it is reasonable to propose that the high performance for MoNi-Ce in wet CH₄ fuel is due to the reformer reaction (5) that not only removes the CO resulting from reaction (2) but also releases H₂ to create via reaction (6) the extra oxide-ion vacancies needed for good oxide-ion conductivity.

**Fig. 2.** Power density of the cell as a function of the operating time in wet CH₄ fuel and static air at 1023 1073 and 1123 K.

### IV. Conclusion

The electrochemical results evidenced that the cell performance was stable in H₂ and CH₄. The power output of this cell improved with increasing temperature and CH₄ as fuel. No degradation in the cell performance was detected when it was running in pure CH₄ under a constant current density for 10 h at each studied temperature. Then, MoNi-Ce compound exhibited a good tolerance to carbon deposition when was operated in wet pure CH₄ at high current density and could be a promising anode material for direct oxidation of methane.

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ATOMIC LAYER DEPOSITION, A RISING TECHNIQUE FOR SOFC AND MCFC DEVICES

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Abstract – This paper deals with the application of atomic layer deposition in the field of high-temperature fuel cells, mainly solid oxide fuel cells (SOFCs) which have been mentioned regularly in the last fifteen years and more recently molten carbonate fuel cells (MCFC). The use of the high-quality ALD-processed thin layers of less than 1 µm may have different roles in these fuel devices: electrolytes, catalysts, corrosion protection or barrier layers. Only few examples will be given to show the potentialities of ALD technique in the considered field. Ceria-based compounds will be studied, in particular, because of their interesting properties in both SOFC and MCFC systems.

Key words: ALD, fuel cells, thin layers, SOFC, MCFC

I. INTRODUCTION

Atomic layer chemical vapor deposition (ALCVD), commonly known as atomic layer deposition (ALD), is a CVD-type technique developed in Finland in the 1970’s by Suntola [1]. The technique lies in the interaction of different precursors in a self-limiting sequential surface chemistry which makes it possible to tailor at atomic level highly conformal, pinhole free thin films on various substrates. It is one of the most successful techniques for processing high-quality nanostructured thin-layered materials for electronic devices, electroluminescence, photovoltaic applications and most probably also for the next-generation lithium batteries and high-temperature fuel cells (SOFC & MCFC). Furthermore, the scalability of ALD is already proven and the reduction of costs for mass production is becoming a reality when the functional role of ultra-thin layers is compulsory.

SOFCs offer a very open and varied field of investigations and uses [2-4]. The feasibility of processing usual or new electrolyte materials with some single cell tests has been fully proven but ageing and thorough analyses are still required. Electrode materials, more difficult to process, are beginning to attract a particular attention, not much as a bulk material but as active interfaces. Nevertheless, the most important trend reside in processing interlayers, as catalysts, diffusion barriers or protective films, which corresponds perfectly to the features of ALD. The control of the interface catalytic properties of the anode towards hydrogen oxidation or even direct hydrocarbons oxidation is one of the most challenging topic. Geometry and engineering of the deposits as well as the large area capacity of ALD are also very promising.

ALD layers can also play different roles in MCFC devices: as protective coatings for cathode and bipolar plate corrosion and as anode catalysts. Interesting results have already been obtained with ALD-processed oxide coatings, such as TiO2, CeO2, Co3O4, onto the porous Ni cathode. These coatings not only may reduce significantly Ni solubility, which is a limiting factor for MCFCs, but as they are extremely thin and conformal they allow maintaining the well-known electrocatalytic properties of Ni towards oxygen reduction. Some results on titania coatings have recently been published [5].

II. ALD FOR SOFC AND MCFC APPLICATIONS

A. Experimental

Only the case of ceria will be considered here. Ceria films were deposited in a Picosun Sunale flow type reactor using commercial Ce(thd)4(tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionatoCe(IV)) (STREM chemicals). Ozone (70%) was used as an oxidizing source. High purity N2 was used as a carrier and purge gas. 1x1cm² gold plates or YSZ (100) doped at 9.5 mol% from Crystal Gmbh were used as substrates. The temperature within the reaction chamber was set to 300°C and
the precursor was warmed up to 180°C. The pulsing sequence is Ce(mhd)(3)/N₂O₃/N₂ with 3/2,5/4,5/2,5 s as pulsing times. Characterization of the as-deposited Ceria thin films was carried out on a Rigaku Smartlab X-Ray diffractometer using Cu Kα₁ (1.5406 Å). The thickness of the deposits was found to be 5 nm and 30 nm by SEM-FEG and reflectometry. A Gemini DSM 982 SEM-FEG was used to check the good quality of the film deposited and its thickness.

B. SOFC

i. General applications

ALD has been used for different SOFC components, as shown by Cassir et al [4]. We will give a very short overview on the present literature. In the case of electrolytes, yttria-stabilized zirconia has been processed by ALD and tested in single cells with interesting performance, reaching 1.34 W/cm² at 500°C [6-8]. Proton-conductive materials, such as Y-doped BaZrO₃, were also integrated in promising single cell devices that would allow a significant decrease in the operating temperature [9,10].

Also ceria and gadolinia- or yttria doped ceria have been successfully prepared by ALD, but mainly as interlayers [3,11-13]. Finally, there are fewer studies concerning electrode materials. Only cathode perovskite materials, such as La₆Sr₁₋ₓCaₓMnO₃ (LSM), La₃Ca₂MnO₇ or La₃Sr₂FeO₇, have been built by ALD, but the studies are still far to be complete [14].

ii. Epitaxial Ceria Catalyst Layers

Polycrystalline thin-layered ceria mainly exposes its most stable surface (111), which is poorly reactive as an oxidizer of hydrogen. DFT modeling and experiments carried out by Temperature-Programmed-Reduction (TPR) showed that orientation of ceria particles has a significant effect on their catalytic properties [15]. Therefore, controlling the surface orientation of ceria thin layers would be an interesting solution for reducing SOFC working temperature and improve the fuel consumption efficiency. In this work we have shown the feasibility of processing epitaxial thin layers of ceria on YSZ(100) . * indicate the peaks of the substrate. In all the cases, solubility of ceria is below 1 wt.ppm.

Table 1- Ni Solubility in CeO₂ recovered cathodes compared to bare Ni.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solubility (wt. ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous Ni</td>
<td>15</td>
</tr>
<tr>
<td>CeO₂-27 nm</td>
<td>10</td>
</tr>
<tr>
<td>CeO₂-120 nm</td>
<td>8</td>
</tr>
</tbody>
</table>

III. CONCLUSION

ALD is well-adapted to energy devices such as SOFCs and MCFCs. We have shown that this technique may have a favorable impact on the efficiency of SOFC components and on the global efficiency. In particular, ceria thin layers with oriented structures could have interesting catalytic properties towards hydrogen reduction. ALD-processed thin layers are also useful in MCFCs in order to protect the Ni cathode.

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Copyright © 2013
REFORMATE FROM BIOGAS USED AS FUEL IN A PEM FUEL CELL

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Abstract – The performance of a PEM fuel cell can be easily degraded by introducing impurities in the fuel gas. Since reformate of biogas from olive mill wastes will contain at least one third of carbon dioxide, its influence was studied on a PtRu catalyst. A clean reformate gas for the anode (67% H₂ and 33% CO₂) without any traces of other compounds was used and electrochemical measurements showed that the performance of the fuel cell was hardly affected. However, diluting the hydrogen with higher amounts of CO₂ will reduce the performance remarkably.

Index Terms – Biogas, carbon dioxide, dilution, PEM fuel cell.

I. INTRODUCTION

The proton exchange membrane (PEM) fuel cell is seen as an attractive alternative for clean electricity production for transportation and stationary power since it possesses advantageous features such as high efficiency, high power density and low emissions, and these features make it competitive with the internal combustion engine [1]. Other advantages are quiet operation, improved power density compared to batteries and modularity (similar efficiencies for small and large units) [2].

The principle of the PEM fuel cell is to convert hydrogen directly into electrical energy and heat through the electrochemical reaction of hydrogen and oxygen into water [2, 3].

Biogas is a renewable source that can be processed in a steam reformer obtaining about 65 – 69% of hydrogen with 26 – 29% of carbon dioxide and small amounts of impurities. Olive mill wastes can be digested to produce biogas that will in a later step be reformed to a hydrogen rich gas. In this study such reformate gas will be used as anode gas in a PEM fuel cell. For the cathode gas, air will be used.

The aim of this investigation is to study how the reformed biogas, including carbon dioxide and ammonia, will affect the performance of the fuel cell.

II. EXPERIMENTAL SET-UP

The measurements were performed in a cell from Fuel Cell Technologies Inc. The cell hardware was coupled to the humidifiers with fittings from Swagelok. The cell temperature was 70 °C and the gases were humidified to 90% with an external control before they entered the fuel cell. The gas flow rates were controlled by mass flow controllers (Brooks Instruments B. V.). The cell was connected to an IM6 Zahner elektrik potentiostat. For the electrochemical impedance spectroscopy (EIS) measurements the cell was connected to an IM6 unit with an EL101 Booster (Zahner Elektrik). The frequency range used was 10 kHz – 100 mHz at an amplitude of 10 mV. A Gore MEA of thickness 25μm was used. The catalyst loading was 0.45 mg/cm² Pt-Ru alloy on the anode and 0.4 mg/cm² Pt on the cathode. Carbel™ was utilized as gas diffusion media.

III. RESULTS AND DISCUSSION

First the cell was operated with pure hydrogen and oxygen, and then different combinations of gases were studied; 67%H₂/33%N₂ – air, 67%H₂/33%CO₂ – air and H₂/air. The polarization curves of these experiments are shown in Fig. 1. Each experiment
was made with the same length step in the current density.

![Fuel cell polarization curves](image1)

**Fig. 1.** Fuel cell polarization curves of pure H₂ - O₂ and of mixtures with other gases at a temperature of 70 °C.

The results show similar performance degradation for all tests with air at the cathode. When comparing the two experiments using pure hydrogen on the anode side a large difference in performance can be noted when changing the cathode gas from pure oxygen to air. This is due to the dilution of oxygen (decreasing from 100% to 21%) in the cathode gas that results in increasing mass transfer losses in the fuel cell.

In one of the experiments the hydrogen was diluted to 67% by adding inert nitrogen to the anode gas. That polarization curve is placed almost exactly on top of the curve with pure hydrogen, showing that dilution of the hydrogen gas flow, at least not to this degree, has no visible impact on the fuel cell performance. Changing the inert nitrogen to carbon dioxide gives the same result: No noticeable effect on the fuel cell performance could be seen and this means that there are no problems with poisoning by carbon dioxide of the PtRu catalyst used in this study. These results are in agreement with Tingelöf et.al [4] and Nachiappan et.al [5].

In order to investigate the effect of higher degrees of hydrogen dilution, different levels of CO₂, ranging from 0 to 95% in volume, were measured. The dilution experiment was made at a constant current density of 0.2 A/cm². Fig. 2 shows a clear drop of the voltage as a function of increasing CO₂ concentration. At first the curve is almost flat but the voltage drop becomes much more pronounced at higher concentrations of CO₂. However, the decreased efficiency is partly a consequence of the lower partial pressure of hydrogen, but also a small poisoning of the anode catalyst by CO may occur. The CO is formed in the reversible water gas shift reaction (RWGS) but this reaction is to a large extent inhibited by ruthenium (Ru).

**Fig. 2.** Cell voltage as a function of dilution of hydrogen by CO₂. Current density is 0.2 A/cm².

**IV. CONCLUSIONS**

Electrochemical measurements performed in a lab scale fuel cell with PtRu catalyst show that using clean reformate gas for the anode, i.e. 67% H₂ and 33% CO₂ without any traces of other compounds, will hardly at all affect the performance of the fuel cell. However, diluting the hydrogen with higher amounts of CO₂ will reduce the performance remarkably. The performance loss is mainly in accordance with thermodynamics. The loss is partly a consequence of the lower partial pressure of hydrogen, but also a small poisoning of the anode catalyst by CO may occur. The CO is formed in the reversible water gas shift reaction (RWGS) but this reaction is to a large extent inhibited by ruthenium (Ru).

**ACKNOWLEDGMENT**

This work was supported by the European project Biogas2PEM-FC (FP7).

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THE INFLUENCE OF ENERGY POLICIES ON EXPECTATIONS OF PREMIUM RISK IN ELECTRICITY GENERATION. AN LCOE SIMULATION ANALYSIS FOR MCFC, ICE AND SGT

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Abstract - The competitiveness conditions for out-of-market technologies are largely affected by financial factors. In the conventional framework of LCOE analysis approach this work performs an impact analysis of a simple energy policy hypothesis about the price tax credit on electricity production performed in a three-technology market: a molten carbonate fuel cell (MCFC), a conventional internal combustion engine (ICE) and a small gas turbine (sGT); the results concern an elaboration on the Monte Carlo simulation outcome of the effects under investor’s point of view, using the payback-time as a proxy of the investment attractiveness. Final results show the correlation between the chosen energy policy measure and the target variable.

Index Terms - LCOE, simulation, energy policy, investor’s point of view.

I. NOMENCLATURE

LCOE: levelised cost of energy; PTC: Production Tax Credits; P-T: Payback Time; INV: investment cost.; O&M: Operation and Maintenance Cost; Eff: plant efficiency (total); P: Power; F: Fixed Cost; V: Variable Cost; dr: discount rate; CF: capacity factor; t: lifetime of the plant.

II. INTRODUCTION

Despite several limitations [1], LCOE is the standard tool in measuring tech’s competitiveness in electricity generation [4, 13, 14]: this approach can be extended to account for uncertainty simulating the variability connected to main cost components and testing some hypothesis related to financial parameters excluded from standard LCOE equation. In the present work a dynamic standard LCOE model is applied to three technologies to get a first order assessment evaluation about the relationships between an energy policy measure, the PTC (Production Tax Credits) [9, 10, 11] and a financial key parameter, the PT (Payback-Time).

Final results show the relationship between the energy policy input and the output variable, representative of lenders evaluation point of view on the profitability of the investment [12].

III. DATA, MODEL AND MONTE CARLO SIMULATION

A. Data

The dataset cover main model variables for three technologies: MCFC (1 MW plant with electrical efficiency range of 47-55%) [2, 5, 6]; ICE (1 MW plant Jenbacher) [7, 8]; Small Gas turbine (characteristics for “typical” commercially available gas turbines generator system, 1 MW) [3].

TABLE I

<table>
<thead>
<tr>
<th>Main variables</th>
<th>Cell</th>
<th>ICE</th>
<th>sGT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of plant</td>
<td>MCFC</td>
<td>TYPICAL</td>
<td>TYPICAL</td>
</tr>
<tr>
<td>P(MW)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>INV(€/kW)</td>
<td>4.928</td>
<td>1107</td>
<td>1096</td>
</tr>
<tr>
<td>O&amp;M(€/kW)</td>
<td>12.7</td>
<td>7.5</td>
<td>9.8</td>
</tr>
<tr>
<td>Eff(%)</td>
<td>51</td>
<td>44</td>
<td>35</td>
</tr>
<tr>
<td>t(years)</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>CF (%)</td>
<td>92</td>
<td>91</td>
<td>91</td>
</tr>
</tbody>
</table>

B. Model

The basic equation in LCOE approach is [4]:

\[
LCOE = INV + \sum_{i=1}^{i=1} \frac{I}{(F + V_i)(1 + dr)^i} / 8760 \sum_{i=1}^{i=1} \frac{I}{(F + CF_i)(1 + dr)^i}
\]

the above formula has been detailed to meet the calculation requirements as will be explain in the final version of the paper.

The conventional name of the model used in this work is EPFE (Energy Policy Financial Evaluator).

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C. Simulation

The simulation is based on Monte Carlo method. The main parameters of LCOE formula (INV, O&M, Fuel cost, dr) have a specific range of values and continuous uniform probability distribution is assumed. In each calculation, one value is selected randomly according to preset probability distribution for each parameter and LCOE is calculated. Calculation is repeated 10,000 times. The results are rounded to the nearest full euro. The results of LCOE calculations are presented as frequency and are displayed in charts.

IV. RESULTS

A. Basic simulation

The main results are reported below.

![Fig. 1. Probability distribution for LCOE curves](image)

A subsequent step has been performed taking the mean of this distribution as an input in calculating the effects of PTC application on PT.

![Fig. 2. Effects of PTC changes on LCOE and PT](image)

Results show an application of the model on a simple hypothesis (application of a PTC from 1 to 50 €/MWh) without any other parameter change (equation terms fixed at their average value). Under the condition examined, we can see the parity grid point and the consequent PT decrease. At PTC of 45 €/MWh the cell get competitive with the sGT; at the same point, PT move to less than a half of its initial value.

V. CONCLUSION

It is possible to connect energy policy measure application to financial parameters relevant for investors. EPFE model was developed to investigate simultaneously effects on LCOE and PT of the application of PTC. As a subsequent step, a GAMS optimization routine using parity grid as a constraint in minimizing PT is under development.

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**Abstract** - In the present work the results of a field test on HT-PEM cells and stacks fed with biogas are reported and discussed. A mobile laboratory was set up at the premises of a waste treatment plant in the North East of Italy where the organic fraction of municipal solid waste, sludge and various organic wastes from industry are fed to an anaerobic digester.

**Index Terms** – Anaerobic digestion, Biogas, HT-PEM fuel cell

**I. INTRODUCTION**

The use of biomass for electrical generation can be an attractive solution especially when integrated with high efficiency energy conversion devices such as fuel cells. H₂S content in biogas as high as thousands ppmv and, when using a single shift reformer, CO content of 2-3 %, are the main challenges in this fuel cells application.

Biological filters seem to offer a cost effective option for H₂S removal compared with chemical and physical processes. High Temperature PEM (HT-PEM) fuel cell, based on polybenzimidazole (PBI) polymer and phosphoric acid, is a promising technology when using high CO content reformates. Nevertheless, experimental data on such systems are scarce in literature.

A prototypal HT-PEM system, fed with biogas cleaned up through a biofilter and processed in a single shift reformer, is outlined in this work. Experimental data are presented and discussed.

**II. EXPERIMENTAL SETUP**

The complete system consists of a biological biotrickling filter, a reformer, a fuel cell stack and ancillary equipment needed for safe and unmanned operation in an industrial environment. The system has been installed into a mobile laboratory unit and fed with biogas produced by an anaerobic digester in the North East of Italy (Fig. 1).

The available raw biogas mainly contains 60-66% of methane and 33-37% of carbon dioxide. Sulfur contaminant is present as hydrogen sulfide, ranging within few tenths and few hundreds ppmv.

A simplified schematic of the system is presented in Fig. 2.

**Biotrickling filter.** The filter unit for H₂S removal compared with chemical and physical processes. High Temperature PEM (HT-PEM) fuel cell, based on polybenzimidazole (PBI) polymer and phosphoric acid, is a promising technology when using high CO content reformates. Nevertheless, experimental data on such systems are scarce in literature.

A prototypal HT-PEM system, fed with biogas cleaned up through a biofilter and processed in a single shift reformer, is outlined in this work. Experimental data are presented and discussed.

**Fuel processor.** The fuel processor is composed of a burner, a steam reforming reactor and a single CO purification stage (Water Gas Shift Reactor - WGSR). The burner unit consists of a start burner and a flameless burner based on a catalytic bed. Therefore, fuels with different heating values, such as fuel cell anode off gas and biogas can be used.

The tests were carried out with a single cell and a 22 cells stack, both assembled with BASF Celtec P1000 MEA. The reforming system engineering and the stack have been developed by the Italian company Cenergy.

Additional details regarding the reformer and the fuel cell can be found in [2]
During the HTPEM cell and stack operating periods, the H$_2$S removal efficiency of the biotrickling filter was usually found better than 95%, in agreement with literature data on this kind of filters [1].

The single cell was operated with biogas for a total time of 821 h, at 160 °C. The current was set at 10 A during the first 170 hours, while for the rest of the test period the current was set to 5 A. The stack was operated for a total of 417 hours, with current loads from 2.5 A up to 10 A. During the test period different thermal management options have been assessed.

Fig. 3 shows the stack polarization curves with different fuels: hydrogen, a synthetic biogas named “MIX” (66.5%vol CH$_4$, N$_2$ rest) and the digestion plant biogas. The performance with biogas is lower but this is in part due to a lower stack operating temperature. As it was decided not to over stress the stack with higher temperature, the data at 160°C have not been collected.

Tab.1 presents the voltage degradation rates and the fuel processor efficiencies in different system configurations. With biogas, the stack average cell degradation rate was found to be 10% greater than the single cell values (66 μV/h against 60 μV/h). During the tests the stack cell voltage distribution was measured. Fig. 4 highlights the effect of load on cell voltage dispersion.

**Table 1. MEA degradation data and main components efficiencies**

<table>
<thead>
<tr>
<th>MEA Degradation</th>
<th>Stack and reformer efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single cell (821h biogas)</td>
<td>60 μV/h</td>
</tr>
<tr>
<td>Stack (471h biogas)</td>
<td>66 μV/h</td>
</tr>
<tr>
<td>Producer data (H$_2$, const. load, 18.000n)</td>
<td>6 μV/h</td>
</tr>
</tbody>
</table>

**ACKNOWLEDGMENT**

This work has been financed by the Research Fund for the Italian Electrical System under the Contract Agreement between RSE and the Ministry of Economic Development – General Directorate for Nuclear Energy, Renewable Energy and Energy Efficiency stipulated on July 29, 2009 in compliance with the Decree of March 19, 2009.

**REFERENCES**


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IMPEDANCE ANALYSIS OF THE CONDITIONING OF PBI–BASED ELECTRODE MEMBRANE ASSEMBLIES FOR HIGH TEMPERATURE PEM FUEL CELLS

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Abstract - This work analyses the conditioning of single fuel cell assemblies based on different membrane electrode assembly (MEA) types, produced by different methods. The analysis was done by means of electrochemical impedance spectroscopy, and the changes in the fitted resistances of all the tested MEAs are studied. The ohmic resistances increase in most cases, implying that the proton conductivity of polybenzimidazole (PBI) membrane degrades during the conditioning process. On the other hand, the intermediate frequency resistances generally decrease showing enhancement in cathodic activities during the process.

Index Terms – Break-in, Conditioning, High temperature PEM fuel cell, PBI

I. INTRODUCTION

Fuel cell break-in/conditioning is the process of stabilizing the performance of a fuel in the initial stages of its operation before it can be used for performance and endurance tests or other purposes. It is an inconvenient and costly process, which can take more than 100 hours of operation with continuous consumption of hydrogen. However, running a fuel cell, especially on reformate gases, without conditioning first can cause loss in performance or even premature failure of the fuel cell. Better understanding of the phenomenon could provide with better guidelines for faster conditioning or even help to investigate ways to eliminate the need for break-in.

Even though it is not clear what goes on during a break-in process, a number of hypotheses have been put forward. It is suspected that impurities introduced during manufacturing are removed from the catalyst and catalyst residue are removed from the membrane [1]. In polybenzimidazole (PBI)-based high temperature PEM fuel cell (HT-PEMFC) redistribution of phosphoric in the membrane electrode assembly (MEA) is a part of the conditioning process [2].

Tingelöf & Ihonen [3] identify two main types of break-in procedures for PBI-based HT-PEMFCs, galvanostatic and potential cycling. In the current work a galvanostatic break-in, which is done at constant current, typically at 0.2 A/cm² for more than 100 hours, is used as it is more appropriate for such PBI-based fuel cells [3].

II. EXPERIMENTAL

A. Test station

An in-house prepared unit cell setup was used to study the break-in phenomenon in PBI-based HT-PEMFCs. For this purpose two sets of MEA types with different production and doping methods were tested. The first set of MEAs is from BASF, Celtec®-P2100 and Celtec®-P1000. According to Schmidt & Bauernmeister [4] in Celtec®-P membranes the polymerization of the monomers is done in polyphosphoric acid (PPA) at elevated temperatures producing a sol containing PBI/PPA, and thereby doping the membrane with phosphoric acid during the polymerization process. Afterwards from the PBI/PPA sol the membrane is casted and further hydrolyzed, and during the process the membrane undergoes a sol–gel transition which results in the final membrane used in Celtec® MEAs [4].

The other set of MEAs is from Danish Power Systems (DPS), which are made of film cast that are heat treated, dried and afterwards doped with phosphoric. The work examines the activation regimes of these differently produced membranes.

B. Break-in procedure

Break-in, as already mentioned is the initial activation stage of a fuel cell’s operation. For this work the break-in process was done on pure hydrogen and at a relatively low current density of 0.2 A/cm², and temperature of 160 °C.

A galvanostatic break-in was performed, where electrochemical impedance spectroscopy (EIS) of the different MEAs was recorded during the entire break-in period. The measured data is then analyzed by fitting to an equivalent circuit model consisting of an inductor in series with a resistor, and in series with three loops. The three loops consist of two resistors in parallel with two capacitors (one of the resistors is
also in series with a bound Warburg diffusion element) and one resistor in parallel with an inductor.

III. RESULTS AND DISCUSSION

The fitted resistances are given in Fig. 1. It can be noticed that the ohmic resistances, usually associated with membrane conductivity, have a generally increasing trend with the exception of the fuel cell with DPS2 MEA after around 60 hours of break-in. This could be because the phosphoric acid, responsible for proton conduction in the PBI membrane, is leached during the process.

![Fig. 1. Fitted resistances of the break-in processes of PBI-based single cell assemblies.](image)

High frequency resistances, usually associated with anode kinetics, slightly increase for the DPS-based fuel cells and remain almost unaltered, with only slight decrease in the beginning for the BASF-based fuel cells. On the other hand, the intermediate frequency resistances, usually associated with cathode activities, have a generally decreasing trend. This shows that the main enhancement in the fuel cell performance, especially on the BASF-based fuel cell assemblies is the result of increased cathode activities.

The free nature of the phosphoric acid in the MEA might be the reason for most of the changes during break-in process. In [5] it is reported that there is exchange of phosphoric acid between the membrane and the catalyst layers. The same report also states that impregnating the cathode with phosphoric acid reduces the time needed before an MEA reaches its best cell performance, which usually coincides with the end of the break-in process. This can justify the decrease in intermediate frequency resistances seen in this work as a result of redistribution of phosphoric acid from the membrane to the cathode.

IV. CONCLUSIONS

Break-in of PBI-based single cell assemblies was analyzed by means EIS and equivalent circuit fitting. The results show that the ohmic resistances increase in the process, implying that the proton conductivity of the fuel cell decreases in most cases, possibly as a result of acid leaching. It is also seen that the decrease in intermediate resistances or increase in cathode activities is the main contributor to the increase in performance of a fuel cell during the break-in process.

REFERENCES


STUDY OF THE ETHANOL STEAM REFORMING REACTION AT LOW TEMPERATURE OVER CERIA-SUPPORTED CATALYSTS

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Abstract - The steam reforming of ethanol (ESR) is considered an environmentally benign route to sustainable energy, combining hydrogen production for fuel cell applications to the advantages of biomass-derived ethanol: the latter is renewable, non-toxic, sulfur free and directly usable as an aqueous solution.

In this study, the behavior of homemade catalysts, supported on CeO2, for the ESR reaction at low temperature (300–600 °C), in terms of activity, selectivity and stability. The effect of the preparation method, temperature, GHSV and feed composition was taken into account; the results were compared with the equilibrium and the outcomes of characterization techniques.

The tests showed that CeO2 gives a crucial contribution, due to its stability and the not nearly trifling activity in the ESR reaction.

The most promising catalysts were selected for additional tests, aimed to hypothesize a specific set of reactions, resulting in a mathematical kinetic model of the system.

Index Terms – Hydrogen, Bio-Ethanol Steam Reforming.

I. INTRODUCTION

Hydrogen’s share in the energy market is increasing with the implementation of fuel cell systems and the growing demand for zero-emission fuels. As a consequence, hydrogen production is keeping pace with this growing market [1].

Even if thermodynamic analysis has indicated that high temperatures can enhance the H2 yield and avoid coke formation in the ESR reaction, the low temperature range can increase the overall thermal efficiency and minimize CO content, enabling ethanol steam reforming (ESR) for the coupling with PEM fuel cells [2]. Nevertheless, in these conditions the catalyst can deactivate, due to preferential formation of by-products [3]. Efforts were made in developing new catalysts [4] but challenges in catalyst stability, due to sintering of the active component and coking tendency during the reaction persist [5].

There has not been extensive research of catalytic performance studies for low temperature steam reforming of ethanol. In those studies, monometallic and bimetallic catalysts based on noble (Pt, Rh, Pd) and non-noble (Ni, Co, Cu) metals, supported on ionic oxides, mainly CeO2, have been proposed for hydrogen production from ethanol. The noble metals are used for their ability to promote dehydrogenation, decomposition and WGS reactions that are in favour of hydrogen production, while the non-noble metals are employed for their capability in the C-C bond rupture [6]. The reason for the successful use of ceria in catalysis is connected to its ability to take up and release oxygen: this function is called oxygen storage/release capacity, following variations in the stoichiometric composition of the feedstream [7].

The aim of this work is to find an optimal catalyst for the low temperature ethanol steam reforming reaction among Pt-based bimetallic catalysts, containing Ni or Co, supported on CeO2, in order to obtain a complete ethanol conversion, a high H2 selectivity, a low CO content in the outlet gas stream and a high catalyst durability. The activity described in this paper is included in the FP7-CoMETHy project, aimed to exploit ethanol as H2 source for fuel cells and others applications.

II. EXPERIMENTAL

The Pt-Ni and Pt-Co catalysts were prepared through two different methods, wet impregnation and co-precipitation, using in both cases a noble metal content of 3 weight% and a non-noble metal content of 10 weight%. All the samples were characterized by different techniques such as X-Ray Diffraction (XRD), N2 adsorption at -196°C, Temperature Programmed Reduction
(TPR). The catalytic activity tests were performed in a lab-scale plant, using diluted and concentrated reaction mixture. In the first case, the operating conditions were: \( P = 1 \) atm, \( T = 300^\circ\text{C} \), \( \text{GHSV} = 15000 \text{ h}^{-1} \), \( Q_{\text{TOT}} = 1000 \text{ Ncm}^3/\text{min} \), feed gas composition = EtOH/H\(_2\)O/N\(_2\) = 0.5/1.5/98 vol\%\(. In concentrated conditions, different r.a. and r.d. values were used to better simulate the raw bio-ethanol stream; the temperature range was 300-500\(^\circ\text{C}\), and the GHSV one is 7500-15000 h\(^{-1}\). The effect on catalysts activity and selectivity of the catalyst preparation method and main operating conditions, such as temperature, GHSV and reactants mixture composition, were evaluated.

### III. RESULTS

The preliminary results were very interesting and promising. The 3\%Pt/10\%M/CeO\(_2\) catalyst obtained through impregnation seems to be very promising for the low temperature ESR reaction, in terms of activity and selectivity among the investigated catalysts, since the experimental values agree with the equilibrium data, in particular by increasing contact time. In particular, the 3\%Pt-10\%Ni/CeO\(_2\) sample exhibited a high activity, selectivity and agreement with the equilibrium at 500\(^\circ\text{C}\), 15000 h\(^{-1}\) and with the following feed stream composition: 5\%C\(_2\)H\(_5\)OH/15\%H\(_2\)O/80\%N\(_2\). Its stability is affected by a few coke deposition, but with any effect on the activity.

The behaviour of the products distribution at 370\(^\circ\text{C}\) in the range 0-600 ms revealed that at very low contact time, for values lower than 4 ms, no ethanol and steam conversion was obtained. This could be an index of a characteristic time for the adsorption of the reactants before activating the reaction. Few ms later, only the acetaldehyde appears in the gas phase, and simultaneously the ethanol concentration decreased. Starting by 8 ms, the hydrogen was revealed in the gas phase, together with the CH\(_4\) and CO, and a lower CO\(_2\) concentration. The CO profile reached a maximum at about 16 ms and after decreased, while the CO\(_2\) and H\(_2\) concentrations still increased, in very good agreement with the stoichiometry of the WGS reaction. In the range 20-45 ms, CO, CO\(_2\), CH\(_4\) and H\(_2\) still increased while C\(_2\)H\(_5\)OH and C\(_2\)H\(_2\)O was totally converted up to about 100 ms, where a maximum is observed for CO\(_2\) and H\(_2\). After this point, another reaction occurred between the CO\(_2\) and the H\(_2\), driving the system to the equilibrium composition. In fact, in the range 100-400 ms the concentration changes in the gas phase followed the stoichiometry of the methanation reaction. At contact time \( \geq 400 \) ms, the gaseous composition was in perfect agreement with the equilibrium. This evolution of products distribution suggests a set composed by different reactions, activated at different contact times: ethanol dehydrogenation, ethanol decomposition, acetaldehyde steam reforming, acetaldehyde decomposition, CO-WGS and CO\(_2\)-methanation reaction.

These hypotheses were used to implement a model for the simulation of the reaction pathway. The calculation was initially optimized 370\(^\circ\text{C}\), where the evolution of the specie seems more clearly linked to a possible reaction mechanism.

The results of the optimization are shown in Figure 1, in which there are the volumetric compositions of each component as a function of contact time.

![Fig. 1. Experimental (Points), Model (Line) and Equilibrium (Dotted lines) Products distribution vs. contact time in the range 340–480\(^\circ\text{C}\)](image)

There is a very good fitting of the experimental data, index that the hypothesized set of reaction is possible.

The set of reactions involved in the process was detected and it was proposed a possible reactions sequence at 370\(^\circ\text{C}\) including the following steps: ethanol adsorption followed by dehydrogenation to acetaldehyde; intermediate decomposition and reforming to CH\(_4\), CO, H\(_2\) and CO\(_2\); CO-WGS and CO\(_2\)-methanation reaction.

### REFERENCES


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Abstract - The primary purpose of this work is to explore the electrode behavior of this new material (Rh/Cu-Ca_{0.1}Ce_{0.9}O_{2+δ}, anode) in H_{2}S-containing fuels as well as its characterization at structural level upon interaction with H_{2}S. Different sulfur tolerance tests in dry and humidified hydrogen (up to 1000 ppm H_{2}S) were carried out and analyzed in order to elucidate the reactions of hydrogen sulfide at the anode.

Single cell tests endorse this approach and demonstrate the ability of Rh/Cu–Ca doped ceria anode to directly operate on H_{2}S-containing hydrogen and methane fuels at relative low temperature (1023 K). The sulfur content in hydrogen fuel to ensure a stable and durable single cell performance was 500 ppm. Higher S-contents had a dramatic effect on the cell voltage.

Index Terms – Hydrocarbon fuels, IT-SOFC anode, Rh-Cu doped ceria, sulfur tolerance.

I. INTRODUCTION

An important research target in SOFCs is to find better anode materials that are catalytically active and less-prone to poisoning by coke formation and sulfur impurities to enable the direct use of readily available hydrocarbon fuels such as natural gas or biogas [1]. Emphasis has been placed on Cu- ceria based anode materials and positive results have been achieved. In previous works, we have demonstrated the ability of nanocrystalline Cu-ceria based anodes to operate with different fuels: hydrogen, methane and simulated biogas mixtures containing H_{2}S [2-4]. The employment of bimetallic anode formulations such as Cu-Co, Cu-Ni or Cu-Ag doped ceria induced changes in the properties of material in terms of enhanced catalytic activity, stability and poisoning tolerance when compared to monometallic Cu-ceria. On the other hand, doping a basic copper-ceria formulation, Cu (40 at. %)/CeO_{2}, with an alkaline rare-earth (divalent cation Ce^{2+}) increased the oxygen vacancy concentration and concomitant oxide ion conductivity that enhanced the anode performance.

Although several improvements have been achieved, with the structural modifications of ceria, it is still needed to improve the anode activity for direct electrochemical oxidation of hydrocarbon fuels. In this context, small quantities (0.4 wt. %) of rhodium were added to an optimized formulation based on Cu-Ca doped ceria in order to enhance the catalytic activity of the conductive layer. Cu-Ca_{0.1}Ce_{0.9}O_{2+δ} (Cu- CeCa) was considered because of its thermal-stability, compatibility with the electrolyte, good sulfur and coke tolerance and improved O^{2−} conductivity when compared to Cu-ceria [5].

II. EXPERIMENTAL

The Rh/Cu-CeCa (0.4 wt.% Rh) was prepared by incipient wetness impregnation of the Cu-CeCa (40 at.% Cu combined with Ca_{0.1}Ce_{0.9}O_{2+δ}) previously synthesized by inverse microemulsion method [2], with an aqueous Rh(NO_{3})_{3} solution. After impregnation, sample was dried at 373 K and calcined under air at 1023 K for 2 h. Material was characterized by XRD, XPS, Raman, ICP-AES and electrical conductivity measurements along with analysis of its chemical compatibility with SDC electrolyte, by mixing anode and electrolyte materials (1:1 w/w) and firing in pure H_{2} for 50 h at 1023 K. Sulfur tolerance tests were carried out in a tubular quartz reactor, feeding 50 ml/min of H_{2}S-containing H_{2} (500 ppm H_{2}S in dry and humidified atmosphere) for 50 h at 1023 K.

For a better understanding of the performance and sulfur tolerance of Rh/Cu-CeCa its single cell evaluation was carried out. For this purpose, a single cell with an active area of 0.3 cm^{2}, was prepared using SDC as electrolyte and LSM as cathode. Details of the preparation method can be found elsewhere [3]. Single cell was galvanostatically operated at 1023 K for 862 h at 0.55 A cm^{-2}, under humidified H_{2}, CH_{4} and was exposed to H_{2}S at increasing concentrations (300-1000 ppm), for at least 1 h each fuel composition. Impedance spectra and current-voltage curves were regularly collected.
III. RESULTS AND DISCUSSION

Rh/Cu-CeCa is mainly constitutes by a fluorite phase of CuCe1-xO2 and oxides (CuO and RhO) which coexist with the mixed oxide (Fig. 1a). It presents optimal electrical characteristics, excellent thermal compatibility, based on the TEC values (air: 11.4·10^-6 K^-1; 5 % H2/N2: 13.3·10^-6 K^-1) that are closed to those for common SOFC electrolytes as well as good chemical compatibility with SDC electrolyte (Fig. 1c), no new phases are detected after test.

Fig. 1. XRD patterns of Rh/Cu-CeCa after different treatments at 1023 K, a) air; b) H2; c) electrode-electrolyte compatibility test; d) dry H2/H2S; e) humidified H2/H2S

Sulfur tolerant test revealed that the exposition of Rh/Cu-CeCa to 500 ppm-H2S in dry H2 produces a total structural change in the sample (Fig. 1d), the complete sulfidation of sample occurs. Fluorite and cubic metallic phases in Rh/Cu-CeCa disappear to form new specimens such as cerium oxysulfide (CeO2S2) and other sulfides (Cu2S, CuS, CaS and RhS2), what is corroborated by XPS and Raman. However, when steam is introduced in the anodic chamber, 500 ppm-H2S in humidified H2 (3% H2O), see Fig. 1e, reactions with hydrogen sulfide are inhibited and Rh/Cu-CeCa sample remains in its reduced form.

Fig. 2 shows the main results of the evaluation of Rh/Cu-CeCa in single cell at 1023 K and different fuel compositions. Cell voltage remained stable under a current density of 0.55 A/cm^2 during all process. The maximum current density, at 0 V, under humidified H2 was 1.18 A/cm^2, while in the presence of H2S it drops to 0.62, 0.60 and 0.59 A/cm^2 for 500, 750 and 1000 ppm of H2S in H2, respectively. In the case of using CH4 as fuel, different compositions were used. The maximum current density for 40:60 and 20:80 CH4/H2 mixtures were 0.91 and 0.51 A/cm^2, respectively. However, when pure methane was fed to the anode voltage drastically dropped (Fig. 2), due to chemical limitations. Nevertheless, it was possible to operate in a stable mode using a CH4-rich gas mixture containing H2S, although the maximum power density was 5 mW/cm^2 (Fig. 2g).

In the present work all these results are discussed on the basis of the different chemical reactions taken place in the Rh/Cu-CeCa anode as function of fuel composition.

IV. CONCLUSION

The capability of Rh/Cu-CeCa to operate in humidified H2, H2S-containing H2 (up to 1000 ppm) as well as methane-rich gas mixture containing H2S at relatively low temperature (1023 K) has been demonstrated. The incorporation of Rh to Cu-CeCa anode enhances the electrical conductivity, sulfur and coke tolerances as well as the catalytic activity for methane oxidation of the anode formulation, what improves the final electrical efficiency of the fuel cell.

ACKNOWLEDGMENT

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NUMERICAL STUDY OF CO POISONING EFFECTS IN HIGH TEMPERATURE PROTON EXCHANGE MEMBRANE FUEL CELLS BASED ON PHOSPHORIC ACID DOPED POLYBENZIMIDAZOLE MEMBRANES

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Abstract - We present a carbon monoxide (CO) poisoning model for high-temperature proton exchange membrane fuel cells (HT-PEMFC) utilizing phosphoric acid (PA) doped polybenzimidazole (PBI) membranes in which the adsorption/desorption processes of CO and hydrogen on the anode Pt catalysts and subsequent electrochemical oxidation are rigorously taken into consideration. The CO poisoning model is incorporated into a previously developed 3-D HT-PEMFC. The simulation results generally agree well with the experimental data. Furthermore, polarization, activation loss and species coverage curves, and key distributions in anode CL are shown to illustrate CO poisoning mechanisms and characteristics in HT-PEMFC under various operating conditions.

Index Terms - High-temperature proton exchange membrane fuel cell, CO poisoning, modeling, Polybenzimidazole (PBI).

I. NOMENCLATURE

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>1.0</td>
<td>(10^5) m(^{-1})</td>
</tr>
<tr>
<td>(b)</td>
<td>1000</td>
<td>Pa</td>
</tr>
<tr>
<td>(k_f)</td>
<td>637.405</td>
<td>A m(^{-2}) Pa(^{-1})</td>
</tr>
<tr>
<td>(k_{eh})</td>
<td>7.553 \times 10^7</td>
<td>A m(^{-3})</td>
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<tr>
<td>(k_{fh,0})</td>
<td>889.323</td>
<td>A m(^{-2}) Pa(^{-1})</td>
</tr>
<tr>
<td>(\delta(\Delta E_{H2}))</td>
<td>6.35</td>
<td>kcal/mol</td>
</tr>
<tr>
<td>(\eta)</td>
<td>1000.0</td>
<td>Pa</td>
</tr>
<tr>
<td>(\rho)</td>
<td>37.771</td>
<td>245</td>
</tr>
</tbody>
</table>

kinetic parameters are assumed to be constant listed in Table 1. Eqs. (1) through (4) in conjunction with the species balance laws can be used to derive the expressions of the fractional coverage of catalyst sites adsorbed by CO and hydrogen.

\[
p_{OH_{\alpha}} = k_f \rho_{H_{\alpha}} (1 - \theta_{\alpha_{\alpha}} - \theta_{\alpha_{\beta}}) - b_{\alpha_{\alpha}} \theta_{\alpha_{\alpha}} - k_{\alpha_{\alpha}} \rho_{H_{\alpha}} e^{\delta(\Delta E_{H2})} = 0 \quad (5)
\]

\[
p_{\alpha_{\beta}} = k_f \rho_{H_{\alpha}} (1 - \theta_{\alpha_{\alpha}} - \theta_{\alpha_{\beta}}) - b_{\alpha_{\beta}} \theta_{\alpha_{\beta}} - k_{\alpha_{\beta}} \rho_{H_{\alpha}} (e^{\delta(\Delta E_{H2})} - e^{\delta(\Delta E_{H2})}) = 0 \quad (6)
\]

II. INTRODUCTION

In PEMFC, it is known that even small amount of CO in the reformate anode feed stream is preferentially adsorbed onto the Pt based anode catalysts, significantly reducing active Pt sites for hydrogen oxidation reaction (HOR). The effect of CO poisoning on the anode electrode can be greatly mitigated by high temperature operations because the kinetics of CO desorption from Pt catalyst particles is favored with increasing temperature [1]. Although HT-PEMFCs feature superior CO tolerance, CO poisoning seems to be still major concerns for the commercialization of HT-PEMFC technologies.

In this study, CO poisoning processes in HT-PEMFCs are newly modeled and implemented into the previous model [2] based on the early work of Springer et al. [3].

III. NUMERICAL MODEL

Readers are referred to our previous papers [2] for detailed description of the HT-PEMFC model. The present CO poisoning model accounts for four reaction steps as follows:

\[
CO + M \leftrightarrow (M - CO) \quad (1) \quad (M - H) \rightarrow H^+ + e^- + M \quad (2)
\]

\[
H_2 + 2M \leftrightarrow 2(M - H) \quad (3) \quad H_2O + (M - CO) \rightarrow M + CO_{\beta} + 2H^+ + 2e^- \quad (4)
\]

where M represents the anode catalyst.

TABLE I

<table>
<thead>
<tr>
<th>Physical parameters used for the analysis of CO poisoning effects at 160°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>(k_f)</td>
</tr>
<tr>
<td>(b)</td>
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<tr>
<td>(k_{eh})</td>
</tr>
<tr>
<td>(k_{fh,0})</td>
</tr>
<tr>
<td>(\delta(\Delta E_{H2}))</td>
</tr>
</tbody>
</table>

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In Eq. (6), \( n \) denotes the order of hydrogen adsorption step (n=2).

The analytical expressions of \( \theta_{\text{CO}} \) and \( \theta_{\text{H}_2} \) can be obtained at the steady state condition in which the transient terms of Eqs. (5) and (6) are equal to zero:

\[
\theta_{\text{CO}} = \left[ \frac{2b(1-\theta_{\text{CO}}) + b_1 - \left[ 2b_h(1-\theta_{\text{H}_2}) + b_1 \right]^2 - 4b_h(b_h - b_b)(1-\theta_{\text{CO}}) \right]}{2(b_h - b_b)} \right] \]

\[
\theta_{\text{H}_2} = \frac{a_1(1-\theta_{\text{H}_2})}{a_1 + a_2 + a_3} \]

where coefficients \( a_1 \), \( a_2 \), \( a_3 \), \( b_1 \), \( b_2 \), and \( b_3 \) are given in the following equations:

\[
a_1 = k_\text{p}_{\text{FC}} \frac{P_{\text{CO}}}{C_{\text{FC}} RT} \]

\[
a_2 = b_2 k_\text{p}_{\text{FC}} \]

\[
a_3 = b_3 \exp \left( \frac{\alpha_{\text{CO}} F}{RT} \right) \exp \left( -\frac{\sigma}{RT} F \eta_c \right) \]

The consequence of surface coverage by hydrogen and CO on the active catalyst sites results in reduction in the a node side and thus requires the modification of the volumetric current density expression for HOR

\[
j_{\text{CO}} = \theta_{\text{CO}} \cdot k_\text{e} \left( \exp \left( \frac{\alpha_{\text{CO}} F}{RT} \right) - \exp \left( -\frac{\sigma}{RT} F \eta_c \right) \right) \]

In addition, the species equation for CO and relevant source term should be also considered in the model to account for the transport and consumption of CO.

\[
\nu_0 \dot{\omega}_{\text{CO}} + \nabla \cdot \left( \nu_{\text{CO}} D_{\text{CO}} \nabla \omega_{\text{CO}} \right) + S_{\text{CO}} = 0 \]

\[
S_{\text{CO}} = -j_{\text{CO}} + \frac{j_{\text{CO}}^*}{\omega_{\text{CO}}} \]

Further, in reality, hydrogen adsorption rate is varying with CO coverage:

\[
k_\text{p}(\theta_{\text{CO}}) = k_\text{p} \exp \left( \frac{\delta\Delta E_0}{RT} \left( 1 - \frac{\theta_{\text{CO}}}{\theta_{\text{CO}}^0} \right) \right) \]

IV. RESULT AND DISCUSSION

Fig. 1. shows the voltage and activation loss curves for comparison of experimental data and simulation results. Generally, good agreement between the simulations and experiments is seen with the reformate gas whereas the agreement is relatively poor with pure hydrogen in which the calculated cell voltage is lower than the measured value. On the other hand, the activation loss was over-predicted by the model with pure hydrogen while it was under-predicted with the reformate gas.

Hydrogen/CO concentration and coverage distributions are shown in Fig. 2. With the reformate gas, hydrogen concentration and coverage are lower compared to those with pure hydrogen. When using various hydrogen adsorption rate, hydrogen depletion increases due to the reduced kinetic by the CO coverage, which results in decreases of hydrogen coverage.

REFERENCES


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NUMERICAL INVESTIGATION OF COLD START BEHAVIOR OF POLYMER-ELECTROLYTE FUEL-CELLS FROM SUBZERO TO NORMAL OPERATING TEMPERATURES – PART I: EFFECTS OF CELL BOUNDARY AND OPERATING CONDITIONS

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Abstract - In this study, we performed transient cold start simulations of polymer-electrolyte fuel-cells (PEFCs) under a wide range of PEFC operating temperatures, from subzero (–20°C) to normal operating temperatures (80°C). The model successfully predicts various stages of PEFC cold starts, i.e., ice formation/growth, constant ice accumulation with undersaturated vapor, ice melting. In addition, the results for simulations performed under various cold start operating conditions clearly address the effects of key cold-start factors such as cathode stoichiometry, external thermal boundary condition, inlet relative humidity, co- and counter-flow configurations on PEFC cold start behavior, especially ice freezing/melting processes. This numerical investigation attempts to develop effective cold start strategies that can simultaneously suppress ice formation/growth, thereby ensuring rapid and stable startup of a PEFC from subzero temperatures.

Index Terms – ice melting, polymer-electrolyte fuel-cell, transient cold start model, water freezing

I. NOMENCLATURE

\[ a \] water activity
\[ C \] molar concentration, mol m\(^{-3}\)
\[ P \] pressure, Pa
\[ R_u \] universal gas constant, 8.314 J mol\(^{-1}\)K\(^{-1}\)
\[ T \] temperature, K

Greek symbol

\[ \zeta \] stoichiometry

\[ \lambda \] water content, mol\(\text{H}_2\text{O}\)/mol\(\text{SO}_3\).}

II. INTRODUCTION

During the last decade, key cold start phenomena occurring in PEFCs have been clarified by many numerical and experimental studies. Most of these studies explored the ice formation/growth characteristics inside PEFCs under different cold start conditions [1]. In this study, a three-dimensional, multiphase, non-isothermal, transient, cold start PEFC model is simulated for transient PEFC simulations under a wide range of PEFC operating temperatures, from subzero (–20°C) to normal operating temperatures (80°C). The main emphasis is on exploring ice melting and the resultant dynamic responses of a PEFC under various PEFC operating conditions. The results suggest that an effective cold start strategy that can simultaneously suppress ice formation/growth ensures rapid and stable startup of a PEFC from subzero temperatures.

A. A multi-dimensional cold--start fuel cell model

The three-dimensional (3-D), non-isothermal cold start PEFC model developed in the previous study [2] has been enhanced by including ice melting and constitutive relations for PEFC transient simulation above 0°C. The cell geometry and its computational mesh for present simulations are given Fig. 1. We defined five simulation cases which are given in Table 1. The transport properties of electrolytes are correlated with the water content of the membrane, \(\lambda\), which is in turn a function of the water activity, \(a\), as follows;

\[
a = \frac{C \cdot R_u \cdot T}{P_{sat}}
\]
\[
\lambda = \begin{cases} 
0.043 + 17.8a - 39.85a^2 + 36.0a^3 & 0 < a \leq 1 \\
14 & a = 1 \\
0.043 + 17.8a - 39.85a^2 + 36.0a^3 & 1 < a \leq 3 \\
16.8 & 3 < a 
\end{cases} \quad \text{when } T < 273.15 \\
\lambda = (a-1) & 1 \leq a \leq 3 \\
16.8 & 3 < a 
\] when \( T \geq 273.15 \) \hfill (2a)

where the water vapor partial pressure can be calculated in a wide temperature range from subzero to normal temperatures as follows;

\[
\log_{10} P_{sat} = -9.0718 \times \left(273.16/T - 1\right) - 3.56654 \log_{10} \left(\frac{273.16}{T}\right) 
\]
\[+ 0.876793 \left(1 - T/273.16\right) \log_{10} 6.07172 + 2 \] when \( T < 279.15 \) \hfill (3a)

\[
\log_{10} P_{sat} = -2.1794 + 6.02905 \left(T - 273.15\right) - 3.1837 \times 10^4 \left(T - 273.15\right)^2 
\]
\[+ 1.4454 \times 10^5 \left(T - 273.15\right)^3 \] when \( T \geq 279.15 \) \hfill (3b)

Fig. 1. Configuration of computational domain and mesh with boundary conditions

TABLE I

<table>
<thead>
<tr>
<th>Cases</th>
<th>Thermal boundary</th>
<th>RH/RHc</th>
<th>Flow direction</th>
<th>( \zeta_a / \zeta_c )</th>
<th>Initial temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case1</td>
<td>adiabatic</td>
<td>0/0</td>
<td>co- flow</td>
<td>1.5/2.0</td>
<td>-20°C</td>
</tr>
<tr>
<td>Case2</td>
<td>convective</td>
<td>0/0</td>
<td>co- flow</td>
<td>1.5/2.0</td>
<td>-20°C</td>
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<tr>
<td>Case3</td>
<td>adiabatic</td>
<td>50/50</td>
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<td>1.5/2.0</td>
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<tr>
<td>Case4</td>
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<tr>
<td>Case5</td>
<td>adiabatic</td>
<td>0/0</td>
<td>co- flow</td>
<td>1.5/10.0</td>
<td>-20°C</td>
</tr>
</tbody>
</table>

III. RESULT AND DISCUSSION

Fig. 2 shows the average cell temperature and ice accumulation evolution curves in the cathode catalyst layer (CL) for five different cases. The rates at which the cell temperature increases are similar for Cases 1, 3, and 4, reaching around 70 °C within 500 s, which indicates that the effects of inlet humidification (Case 3) and flow configuration (Case 4) on cell temperature evolution are not significant. In contrast, a much slower temperature rise is observed in Cases 2 and 5; this can be attributed to significant heat loss to the cold ambient environment (−20 °C) in Case 2, and a more substantial cooling effect driven by the higher air flow rate in Case 5.

The ice accumulation curves for Cases 1–5 exhibit three distinct stages during the cold-start period, namely freezing, undersaturated, and melting stages. During the first 20 s, a fast ice-growth rate is observed because the vapor saturation pressure is low due to the low cell temperature; therefore, the water produced by ORR mostly freezes in the cathode CL. However, as the cell temperature increases, the vapor saturation pressure increases significantly, making the cell undersaturated. Finally, once the cell temperature approaches 0 °C, residual ice in the cathode CL undergoes melting by absorbing the waste heat released during PEFC operation, therefore the ice accumulation curve drops dramatically.

The ice accumulation curves for Cases 1 and 4 are similar to each other, indicating that the co- and counter-flow configurations do not significantly affect ice accumulation behavior. The effect of inlet humidification at −20 °C (Case 3) is significant, leading to higher ice accumulation inside the cell compared with Case 1. This implies that the cell water storage capacity in the vapor phase is reduced by even a very low inlet vapor pressure (31.537 Pa, corresponding to 50% RH at −20 °C). Comparing Cases 1 and 2 show that the ice accumulation is greatly increased by the convective boundary condition of Case 2, mainly because of the lower rate of cell temperature rise in Case 2. In contrast, the higher air flow rate in Case 5 has a minor influence on ice accumulation, showing slightly higher ice accumulation in Case 5 than that in Case 1.

IV. CONCLUSION

In this paper, we presented an extended cold-start PEFC model for transient simulations under a wide temperature range from subzero to normal temperatures. The model can predict ice formation and growth inside a cell at subzero temperatures, and additional key cold-start phenomena such as ice melting. Especially, the model successfully captured the three distinct stages of ice accumulation: the freezing, undersaturated, and melting stages.

ACKNOWLEDGMENT

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SYNTHESIS AND PROPERTIES OF SULFONATED POLYMER CONTAINING N-METHYLISATIN BY SUPERACID-CATALYZED POLYHYDROXYALKYLATION REACTION

Youngtae Jeon*, Soonho Lee*, Youngdon Lim*, Hohyoun Jang*, Younggil Cho*, Hyunho Joo* and Whangi Kim*

* Department of Applied Chemistry, Konkuk University, Chungju, (Korea)

Abstract – High molecular weight polymer containing n-methyl isatin was synthesized by superacid-catalyzed polyhydroxyalkylation reactions. Their functionality with sulfonic acid groups and the measurement of apposite parameters for PEMs are described. Sulfonic acid groups were introduced by sulfonation reaction with chlorosulfonic acid. All these membranes were casted from dimethylsulfoxide (DMSO). The membranes were studied by thermogravimetric analysis (TGA), ion exchange capacity (IEC), water uptake, dimensional stability and proton conductivity assessment. The chemical stability was investigated by Fenton’s reagent, and compared with Nafion 211. These polymers have no ether linkage on polymer backbone and were chemically stable against nucleophiles (such as H2O, hydrogen peroxide, hydroxide anion and radical).

Index Terms – PEMFC, Electrolyte, Membrane, Superacid

I. INTRODUCTION

Polymer electrolyte membrane fuel cell (PEMFC) can be efficiently generating high power densities, thereby making it an attractive technology for automobile and portable applications. At present, perfluorinated polymer membranes, such as Nafion® and Flemion®, are widely used for PEM materials because of their excellent chemical & physical stability, and high proton conductivity [1,2]. Their characteristics are derived from fluoro atoms and carbon-carbon bonded chemical structures which attribute relatively long lifetime compared to hydrocarbon membranes. Most hydrocarbon membranes are generally lower ionic conductivities at comparable ion exchange capacities than Nafion [3] and more susceptible to oxidative or acid-catalyzed degradation than Nafion by structural ether linkage [4]. Chemical degradation of membranes is generally thought to play the most important role for abating fuel cell performance. Research in the field of hydrocarbon membranes has made great strides throughout the years. Performances of proton conductivity and power density etc. of hydrocarbon membranes are close to those of perfluorinated sulfuric acid membranes, and also their cost is lower. However, the durability of hydrocarbon membranes is not as high as that of Nafion. To overcome these kinds of drawbacks, the carbon-carbon backbone structured polymers were studied [5-7]. Since Olah and co-workers explain the high reactivity of electrophilic species in superacid media, numerous reactions have been carried out using superacids as a reaction medium [8].

Our aim is to prepare the carbon-carbon linked polymer in main chain without ether group and isatin moieties for improving chemical stability and good solubility in polar solvent. This work is an attempt to synthesize polymer from n-methylisatin and biphenyl with trifluoromethane sulfonic acid as a superacid followed by sulfonation with chlorosulfonic acid to prepare sulfonated polymer. The sulfonated polymer membranes were studied by the measurements of ion exchange capacity (IEC), water uptake, and proton conductivity.

II. EXPERIMENTS

A. Preparation of poly(phenylene) (PP) and sulfonated poly(phenylene) (SPP)

A solution of isatin (1.6 g, 20.39 mmol), potassium carbonate (3.38 g, 24.47 mmol) and methyl iodide (3.47 g, 24.47 mmol) in acetonitrile 50 mL was refluxed at 82 °C for 24 h. The reaction mixture was allowed to cool to room temperature and then filtered. The filtrate was evaporated under reduced pressure and dissolved in ethyl ether. After evaporation of ethyl ether, the crude product was recrystallized from ethanol to afford a red solid; yield: 2.85 g (95%). A typical polyhydroxyalkylation procedure as follows (Scheme 1). TFSA (8.8 mL) was added to an ice-cooled mixture of n-methyl isatin (1.63 g, 10.09 mmol), biphenyl (1.56 g, 10.09 mmol) and

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dichloromethane (4.9 mL). Thereafter, the temperature was raised to 20 °C over a period of 30 min and reaction was continued at this temperature for 15 h to afford a highly viscous dark-green solution. The resulting mixture was decanted dropwise into methanol. After drying, white fibre like polymer was obtained ($\eta_{inh} = 0.89$ dL/g in NMP at 30 °C). To a solution of polymer (1.5 g, 5.05 mmol) in dichloromethane (30 mL), chlorosulfonic acid (2.7 mL, 40.35 mmol) in dichloromethane (8 mL) was added at 0 °C over a period of 30 min. The reaction mixture was stirred for 2 h 30 min at room temperature. The resulting mixture was poured slowly into distilled water and the precipitate was washed several times with water until the residual water was pH neutral, and finally dried under vacuum at 80 °C for 24 h.

III. RESULTS

Sulfonation reaction of poly(phenylene) was controlled by chlorosulfonic acid molar ratio. The ion exchange capacity of the SPP 1, 2 and 3 membranes were 1.55, 1.84 and 2.48 meq/g and Nafion 211® is 0.91 meq/g. Water uptake of the SPP 1, 2 and 3 membranes were 31.8%, 42.5% and 62.5% compared with 32.13% of Nafion 211® at 80°C for 24h. Other membrane properties, such as TGA, proton conductivity, dimensional and chemical stability are in progress.

ACKNOWLEDGMENT

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REFERENCES

SYNTHESIS AND CHARACTERIZATION OF SULFONATED POLY(ETHER SULFONE)S CONTAINING DCTPE FOR PEMFC

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Abstract - Sulfonated poly(4,4′-dichlorotetraphenylethylene)-random-poly(ether sulfone) copolymers (SMBPDs) were synthesized by Ni-catalyzed copolymerization of 4,4′-dichlorotetraphenylethylene (DCTPE) and 4,4′-dichloropheynlsulfone-endcapped oligo(ether sulfone), and followed sulfonation reaction with chlorosulfuric acid. Thus sulfuric acid groups were selectively attached to side phenyl rings of tetraphenylethylene unit. These polymers have all carbon-carbon linkages without any ether linkage on polymer backbone, which were not attacked by nucleophiles (H2O, hydrogen peroxide, hydroxide anion and radical). A series of membranes were studied by 1H-NMR spectroscopy, thermo gravimetric analysis (TGA), ion exchange capacity (IEC), water uptake, and proton conductivity.

Index Terms – PEMFC, membrane, Ni-catalyst, C-C coupling

I. INTRODUCTION
Polymer electrolyte membranes (PEMs) based on sulfonated perfluoropolymers, Nafion and Flemion have been widely used for polymer electrolyte membrane fuel cells (PEMFCs) because of their high proton conductivity and high stability [1,2]. However, they suffer from such disadvantages as limited operation temperature (0-80 °C), high cost, insufficient durability and high methanol permeability. To overcome these obstacles, extensive efforts have been made to develop alternative acid-functionalized aromatic hydrocarbon-based polymers [3,4]. And there have been significant advances in the synthesis of sulfonated aromatic polymers as alternative proton exchange membrane [5]. Most of the chemical structure of polymer membranes had sulfonic acid groups directly attached on aromatic rings of main polymer chain. These kinds of polymer structures are susceptible to nucleophile attack by hydrogen peroxide or peroxide radical formed from oxygen and hydrogen. The chemical modification to sulfonic acid attached on aromatic rings of polymer side chain provides better stability due to less reactivity of nucleophile substitution reaction [6]. Furthermore, IEC values of polymers are quite an important factor because proton conductivity is strongly affected by IEC values. Although sulfonated aromatic membranes with high IEC values can achieve high proton conductivity, such membranes show excess water swelling or even dissolve in water [3,7]. Therefore we proposed block copolymer membrane have no ether linkage nearby phenyl rings attached sulfuric acid groups by Ni-catalyzed polymerization. This structure is a promising to good stability and proton mobility. The sulfonated polymer membranes were studied by ion exchange capacity (IEC), water uptake, and proton conductivity.

II. EXPERIMENTAL
A. Synthesis of 4,4′-dichlorotetraphenylethylene (DCTPE)
DCTPE was synthesized with diphenylmethane (10.1 g, 60mmol) and 4,4′-dichlorobenzophenone (11.3 g, 45 mmol) followed by Rathore’s method [8].

B. Synthesis of oligomer
4,4′-dichlorophenylsulfone (2.842 g, 9.90 mmol), bis(4-hydroxyphenyl)sulfone (2.298 g, 9.00 mmol), potassium carbonate (1.492 g, 10.80 mmol), sulfolane (18 mL), and chlorobenzene (18 mL) were placed in a 100 mL round bottomed flask, and the reaction mixture was heated with a Dean–Stark trap at 160 °C for 2 h, and then at 180 °C for 30 min. The resulting mixture was poured to water/methanol (150 ml/ 150 ml) solution. The filtrated oligomer was washed with water and methanol several times. The oligomer was dried in 80 °C vacuum oven for 24h.
C. Synthesis of block copolymer (MBPD)

To a flask was evacuated and filled with nitrogen several times. NiBr2 (0.091g, 0.41 mmol), triphenylphosphine (0.761g, 2.90 mmol), and zinc dust (1.576g, 24.86 mmol) were placed in a flask by using glovebox. A septa-rubber cap was placed over one neck of the flask, a stopcock adapter in another and a nitrogen inlet adapter in the other. Dried DMAc (4ml) was added via syringe through the septa-rubber cap. The reaction was heated to 80 °C with stirred mechanically at nitrogen atmosphere. After the red-brown catalyst had formed, a nitrogen-purged solution of DCTPE (1.217g, 3.03mmol) and oligomer (0.753 g) in the DMAc was added via syringe to the reaction mixture. The mixture was stirred at 80 °C for 4h, until the reaction system became significantly viscous. The resulting mixture was cooled, and then poured into 1M HCl aqueous solution to precipitate a white powdery polymer. The precipitated polymer was washed with hot water and methanol several times. Washed polymer was dried in 60 °C vacuum oven for 24h.

D. Sulfonation of block copolymer (SMBPD)

The dried MBPD (2 g) was dissolved in 30 mL of conc. H2SO4 (95%) under nitrogen and vigorous stirring for 1 h. After the formation of a homogenous solution, the solution was stirred for 12 h at 45 °C temperature, and the mixture was gradually precipitated into a large excess of ice-cold deionized water. The polymer precipitate was filtered and washed several times to remove the acidic residue. The received SMBPD was dried in 80 °C vacuum oven for 24h.

III. RESULTS AND DISCUSSION

Scheme 1. Synthesis of SMBPD

The reaction mechanism for the preparation of the SMBPD is presented in scheme 1. SMBPD was synthesized by Ni-catalyzed polymerization and followed sulfonation reaction with conc. H2SO4. The sulfonation was taken selectively on tetraphenylethylene units with conc. H2SO4. Degree of sulfonation was controlled by DCTPE monomers ratio. The ion exchange capacity (IEC) of the SMBPD 30, 40, and 50 were 1.43, 1.95, and 2.54 meq/g. In increasing the percentage of pendant sulfuric acid groups, the IEC of membrane was increased. The theoretical IECs and the titrated IECs were in reasonably good agreement. The water uptake of SMBPD 30, 40, and 50 membranes were 24.69, 47.25 and 77.21 % at 80 °C. The SMBPD membranes show low water uptake in spite of high IEC. Proton conductivities of the SMBPDs were measured as a function of the mole fraction of sulfuric acid groups. As expected, the conductivity of polymers increases as the degree of sulfonation was increase. The resulting of SMBPD 30, 40, and 50 membranes were 64.3, 94.9 and 104.9 mS/cm compared with 104.3 mS/cm of Nafion 211 at 80 °C under 90% humidity. The conductivity values and other properties of the SMBPDs are acceptable to use in fuel cell performance compare to the previous reported PEMFCs. And now, we are going to testing of durability and cell performance of membranes.

ACKNOWLEDGMENT

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REFERENCES

PREPARATION AND CHARACTERIZATION OF GRAFTED PROPANE SULFONIC ACID ON POLYPHENYLENE PREPARED BY SUPERACID-CATALYZED REACTION

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Abstract - A series of polyphenylene-based polyelectrolytes were synthesized from 2,2-biphenol, and isatin by superacid catalyzed polyhydroxyalkylation reactions. Grafted sulfonated polyphenylenes were synthesized by K₂CO₃ catalyzed condensation reaction with 3-bromopropane sulfonic acid potassium salt. These polymers have all carbon-carbon linkages without any ether linkage on polymer backbone, which were not attacked by nucleophiles (H₂O, hydrogen peroxide, hydroxide anion and radical). Particularly, chemical modification to flexible sulfoalkyl groups attached to a biphenol unit and formed side chain structure afforded better stability due to less reactive towards nucleophilic substitution reaction, and good proton mobility because of well phase separation. The structure properties of the synthesized polymers were investigated by ¹H-NMR spectroscopy. The membranes were studied by ion exchange capacity (IEC), water uptake, dimensional stability and proton conductivity. The chemical deterioration test was performed by Fenton reagent, and compared with normal sulfonated poly(ether sulfone)s and Nafion.

Index Terms – PEMFC, membrane, grafting, super acid

I. INTRODUCTION
Polymer electrolyte membranes (PEMs) based on sulfonated perfluoropolymers, Nafion and Flemion have been widely used for polymer electrolyte membrane fuel cells (PEMFCs) because of their high proton conductivity and high stability [1, 2]. Their characteristics are derived from fluoro atoms and carbon-carbon bonded chemical structures which attribute relatively long lifetime compare to hydrocarbon membranes. Most hydrocarbon membranes are generally lower ionic conductivities at comparable ion exchange capacities than Nafion, and more susceptible to oxidative or acid-catalyzed degradation than Nafion by structural ether linkage [3, 4]. Chemical degradation of membranes is generally thought to play the most important role for fuel cell failure. Research in the field of hydrocarbon membranes has made great strides throughout the years. Performances of proton conductivity and power density etc. of hydrocarbon membranes are close to those of perfluorinated sulfuric acid membranes, and their cost is lower. However, the durability of hydrocarbon membranes is not as high as that of Nafion. To overcome these kinds of drawbacks, the carbon-carbon backbone structured polymers were studied. Sulfonated polyphenylenes generally synthesized by Ni-catalyzed polymerization and Diels-Alder polymerization [5-7]. These all carbon structured polymer backbone based polymer membranes have excellent oxidative and chemical stability and good performance [7]. However, they are very expensive process of monomers, catalyst, and demanding reaction conditions. Since Olah and co-workers explain the high reactivity of electrophilic species in superacid media, numerous reactions have been carried out using superacids as a reaction medium [8, 9].

The purpose of this work is to prepare the carbon-carbon linked polymer in main chain without ether group, and also contain grafting structured moieties for improving good solubility and good proton mobility. The copolymer synthesized by superacid catalyzed polymerization and pendant sulfonation were characterized by FT-IR, ¹H NMR spectroscopy, thermogravimetric analysis (TGA), proton conductivities, water uptake, and ion exchange capacity (IEC), and also studied cell performance.

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II. EXPERIMENTAL

A. Synthesis of polymer

To a flask, trifluoromethane sulfonic acid (11 mL) was added to an ice-cooled mixture of isatin (1.59 g, 10.85 mmol), 2,2-biphenyl (1.87 g, 10.05 mmol) and trifluoroacetic acid (6.2 mL). After addition, the temperature was raised to 20 °C over a period of 30 min and reaction was continued at this temperature for 18 h to afford a highly viscous dark-green solution was obtained. The resulting mixture was poured into methanol. The filtered polymer was washed with water and methanol several times, and dried in 80 °C vacuum oven for 24h.

B. Synthesis of bromopropane-sulfonic acid potassium salt

To a solution of potassium bromide (4.76 g, 40 mmol) in water (15 ml) heated to 60 °C was added 1,3-propanesultone (3.51 mL, 40 mmol). After the sultone completely dissolved (about 10 min), the water was removed via distillation. The crude residue was washed with cold ethanol (2 x 10 mL). The crude solid was recrystallized from 3:1 EtOH/H₂O, giving white crystalline solid, and dried in 80 °C vacuum oven for 24h.

C. Pendant sulfonation of polymer (PSPP)

To a flask, synthesized polymer (1.5 g), excess amount of bromopropanesulfonic acid potassium salt (4.80 g, 19.90 mmol), potassium carbonate (2.75 g, 19.90 mmol), toluene (20 ml) and DMAc (20 ml) were charged. The mixture was refluxed for 3 h at 130 °C. After the produced water was azeotroped off with toluene, the mixture was heated at 160-180 °C for about 4-5 h. After reaction, the mixture was poured into 0.5 M HCl solution and stirred vigorously. The polymer was washed in water several times and dried in 60 °C vacuum oven.

III. RESULTS AND DISCUSSION

![Scheme 1. Synthesis of PSPP](image)

The reaction mechanism for the preparation of the PSPP is presented in scheme 1. PSPP was synthesized by superacid catalyzed polymerization and followed pendant sulfonation by condensation reaction with bromopropane sulfonic acid. Degree of sulfonation was controlled by added amount of bromopropanesulfonic acid at the reaction. The ion exchange capacity (IEC) of the PSPP 1, 2, and 3 were 1.81, 2.37, and 3.21 meq/g. In increasing the percentage of pendant sulfuric acid groups, the IEC of PSPP membrane was increased. The water uptake (WU) of PSPP 1, 2, and 3 membranes are 38.24, 65.32 and 109.27 % at 80 °C. The PSPP membranes show low water uptake in spite of high IEC. Proton conductivities of the series of PSPPs were measured as a function of the mole fraction of sulfuric acid groups. As expected, the conductivity of polymers increases as the degree of sulfonation was increase. The resulting of PSPP 1, 2, and 3 membranes were 70.5, 98.2 and 119.8 mS/cm compared with 104.3 mS/cm of Nafion 211 at 80 °C under 90% humidity. The conductivity values and other properties of the PSPPs are acceptable to use in fuel cell performance compare to the previous reported PEMFCs. And now, we are going to testing of durability and cell performance of membranes.

ACKNOWLEDGMENT

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REFERENCES

HIGH PRESSURE ONBOARD HYDROGEN STORAGE: PUBLIC PERCEPTION OF SAFETY

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Abstract - In this presentation author speaks as a member of public having access to published information of safety of onboard high pressure hydrogen storage. Test results of catastrophic failure of tanks of type 3 and 4 are shown, including fireballs, long flames, data on blast waves and projectiles. Some new statistical data are presented demonstrating that a catastrophic failure of a tank cannot be ruled out from the probabilistic risk assessment as was thought previously. It is suggested that most of safety concerns can be resolved if fire resistance rating of storage tank without activation of TPRD would be reaching 1-2 hours. This would allow TPRD diameters below 1 mm and thus shorter flames and realistic separation distances, self-evacuation and rescue operations.

Index Terms – Hydrogen safety engineering, high pressure onboard storage, fire resistance rating, life and property safety.

I. INTRODUCTION

Brief overview of existing regulations is given and their shortfalls are discussed, including suggestions to amend the regulations. It is underlined that regulations are supposed to be developed by public as opposed to standards which are driven by industry. Author argues that current concept of a bonfire test in the Global Technical Regulations (GTR) 2013 is misleading on the actual level of safety of hydrogen-powered vehicles in fire. In particular, the bonfire test is insufficiently specified to provide expected by public level of safety and property protection. Indeed, the public would not be informed about an actual duration of fire during which the structural integrity of the tank is guaranteed (fire resistance rating). Unfortunately, the duration of the localized bonfire test is limited by GTR-13 by 10 minutes only. This time is close or in many real cases shorter compared to time of fire recognition and evacuation, e.g. at night from a residential building with a garage where a fire is possible (only in USA there are thousands of fires in garages every year initiated not by a car), and time of first responders arrival. Consequences for life safety of driver/passengers and first responders then would be dramatic. The ignoring of actual fire resistance rating of hydrogen storage tank (without TPRD activation) issue generates serious problems for property protection as well.

II. MAIN SAFETY ISSUES

Fire resistance rating (FRR) is defined as an actual time during which a tank being a subject to fire conditions remains intact (after this time it either loses integrity and starts to leak through vessel walls or catastrophically ruptures). However, the concept of FRR is missing in current regulations. The absence of “fire resistance rating” concept in the regulations creates large uncertainties in the prediction of tank behavior in fire conditions and thus compromises life safety of public and first responders. Instead of clear requirement about FRR of onboard storage tank, the public will be informed that a vehicle passed the bonfire test (probably supposed to mean that a type-approval is done and a vehicle is “safe” for use by customers, i.e. ready for sale).

Life safety of public still can be compromised both before and after 10 minutes of realistic fire (this time is identified as localised bonfire test duration in current regulations). Temperature activated pressure relief devices (TPRDs) have at the moment internal diameter of about 4-6 mm to quickly release hydrogen from the tank before its catastrophic failure, i.e. rupture of a shell. As a result, a release from such TPRD gives unacceptably large flame length up to 15 m and a separation distance of about 50 m. This makes self-evacuation and rescue operations impossible in many practically situations, especially in conditions of false initiation of TPRD. Catastrophic failure of a tank after time registered at the “successful” bonfire test, e.g. due to blocking TPRD in the accident, could kill people by decaying blast wave, engulfment to and radiation from the fireball of size of tens of meters, and
by a huge fire storm if the tank fails with a large hole or crack.

TPRD can fail to be initiated, e.g. when a fire affects only a part of the tank where there is no TPRD. To address this, author suggests introduction of two FRR for a tank: with TPRD activation and without TPRD activation.

Property protection issues include but not limited to the recently discovered pressure peaking phenomenon characteristic for only one fuel – hydrogen [1]. Hydrogen unignited or ignited (fire) release from a currently applied TPRD with large exit diameter of 4-6 mm at storage pressure of 350-700 bar in a civil structure such as a garage will destroy it by overpressure in just 1-2 seconds due to extremely high flow rate of an order of 400 g/s. This means that an idea of fast release of hydrogen from a tank to prevent its catastrophic failure creates unacceptable conditions for people within any enclosure where such “fast” release with large mass flow rate is “pre-designed”, e.g. garages, maintenance shops, tunnels, etc. Public and customers who will buy and use hydrogen-powered vehicles should be informed about this potential situation in their property directly related to their life and property safety.

Moreover, currently there is no control over an increase of permeation and small leaks from on-board storage tanks with time of vehicle exploitation. This creates uncertainty in when the tank has to be changed without potential threat for life and property.

It seems that the bonfire test protocol has not been reviewed sufficiently by wider fire and hydrogen safety community representing public opinion and having concerns about safety provisions in hydrogen-powered cars. This should be addressed and mentioned above concerns resolved ASAP to exclude misleading and compromising the public acceptance of this inevitable technology. Public and first responders have to know what will happen to storage vessel in fire if TPRD is not initiated and what are two FRR. Unfortunately, the regulations require only passing bonfire test and getting a certificate which value for safety provisions is questionable.

It is suggested that innovative safety strategies and engineering solutions have to be developed to provide expected level of life safety and property protection, i.e. to underpin public acceptance of hydrogen-powered vehicles. These have to include higher FRR for tank without activation of TPRD compared to current 3-12 minutes (recent unconfirmed information mentions tanks with 20 minutes fire resistance yet it has to be published and placed to public domain), tank aging control that is fully absent at the moment, mitigation measures providing tank stability beyond standard crash test conditions, bullet-proof design of a tank, and fast filling of tank without pre-cooling. Outline of how it can be achieved is given.

Thus, what is necessary to do for the provision of acceptable for public level of hydrogen-powered vehicle safety is the reduction of TPRD diameter to reduce flame length to about 1 m that implies increase of fire resistance rating to about 1-2 hours. This is technically feasible and R&D has to be performed in collaboration with OEMs.

It is suggested to modify or amend the regulations as follows:

• Introduce two fire resistance ratings (FRR) of a hydrogen storage tanks – with and without TPRD.

• Change the bonfire test protocol and continue the localised bonfire test beyond current 10 minutes until the tank fails by either losing its integrity (leaks through walls) or by catastrophic rupture of the tank shell. The time of tank failure is the actual FRR that has to be registered during testing.

• In a bonfire test with TPRD the overpressure should drop to low level, e.g. 0.1 MPa, without catastrophic failure of the tank and limited flame length of the order of 1 m (to be established) during the whole duration of release to provide conditions for self-evacuation and rescue operations, and integrity of civil structures such as garages.

• For a tank without TPRD the bonfire test should be performed until the tank fails in the bonfire. Time of failure has to be registered. This time represents actual FRR for a tank without TPRD. The bonfire test protocol has to include the registered during testing size of the fireball, maximum jet flame length and blast wave pressure decay with distance when relevant.

• The following requirement should be included into the regulations. Car manufacturers and OEMs must demonstrate safe performance of their products outdoors and indoors, including a whole vehicle assembly, in fire conditions with clear proof that safe conditions for self-evacuation and safety of performing rescue operations people are provided.

• The regulation must include a requirement that FRR of a storage tank and associated flame length from TPRD should provide conditions for driver/passengers self-evaluation, safety of public nearby, e.g. in a house adjacent to a garage, safety of first responders working on a scene, etc.

• A new requirement to test TPRD, as an essential safety component of the safety system of hydrogen-powered vehicle, should be introduced to exclude otherwise unacceptable frequency of false TPRD initiation.

• On-board hydrogen storage system has to have a sub-system of permeation/small leaks control that is used to monitor tank aging with time of its exploitation.

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REFERENCES

INTEGRATED SYSTEM OF A PROTON-CONDUCTING SOFC AND ETHANOL AUTOTHERMAL REFORMER: DESIGN AND PERFORMANCE EVALUATION

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Abstract – In this study, an integrated system of SOFC-H+ and ethanol autothermal reformer is proposed. The optimal design and operating parameters are carefully determined to obtain the best possible performance of the integrated SOFC-H+ system satisfying a desired power output of 25 kW.

Keywords - Autothermal reforming, Ethanol, Proton-conducting SOFC, Performance evaluation

I. NOMENCLATURE

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<th>Symbol</th>
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II. INTRODUCTION

A proton-conducting solid oxide fuel cell (SOFC-H+) in which the electrolyte made of a proton conductor becomes the most promising fuel cell technology for power generation. In SOFC-H+, water vapor is generated at the cathode side and this factor can improve the open-circuit voltage and electrical efficiency of cell [1]. In general, there are two approaches to incorporate a fuel processor in the SOFC operation: external reforming and internal reforming. Although the internal reforming system has higher efficiency than the external one, this approach faces some difficulties: the possibility of carbon formation on the anode and the presence of a large thermal gradient within SOFC stack [2]. Thus, a power system consisting of SOFC-H+ integrated with an ethanol autothermal reformer is proposed in this study. The attractive feature of this system is that the SOFC-H+ always provides a high-temperature exhaust gas which can be used for other heat-requiring units in the SOFC system, leading to a decrease in the external energy demand.

The present study is aimed at designing the integrated system by considering the SOFC-H+ stack configuration and operating parameters where a desired power output is 25 kW.

III. SOFC-H+ SYSTEM INTEGRATED WITH ETHANOL AUTOTHERMAL REFORMER

Fig. 1 demonstrated the integrated system of SOFC-H+ and ethanol autothermal (ATR) reformer. Ethanol, water and air are fed to a preheater. In the ATR reformer, a consecutive reaction pathways of the steam reforming and the partial oxidation are carried out. The equilibrium composition of the synthesis gas from the ATR reformer is determined by using the total Gibbs free energy minimization method. Then, the reformate gas consisting of CH4, H2, H2O, CO, and CO2 is preheat to the SOFC operating temperature before it is fed to the SOFC-H+. At the anode side of SOFC-H+, the residual CH4 can further react with H2O via the steam reforming reaction and CO can convert to H2 via water gas-shift reaction within the cell. The SOFC-H+ dimension are: 0.4(L)x0.1(W)x0.03(H) m. Anode-supported SOFC-H+ has the thickness of anode/cathode/electrolyte as: 550/50/20 μm.

Fig. 1. Schematic of a proton-conducting SOFC with ethanol autothermal.

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SOFC stack. For the SOFC-H⁺, H₂ is oxidized to produce protons and electrons. The protons migrate through the electrolyte while the electrons flow to the cathode. At the same time, oxygen in air that is fed to the cathode side is reduced and here the water is produced. Simulations of the SOFC-H⁺ are performed based on a one-dimensional and steady-state fuel cell model coupled with detailed electrochemical models. The modeling of SOFC-H⁺ was reported in our previous work [2].

IV. RESULTS AND DISCUSSION

Under the standard conditions, the inlet molar flow rate of ethanol is 0.25 kmol/hr, steam to ethanol (STE) is 2 and oxygen to ethanol (OTE) ratio is 0.5. The reformer is operated at $T_r = 600^\circ$C while SOFC-H⁺ is run at $T_s = 750^\circ$C under atmospheric pressure. When the cell voltage is given as 0.7 V, the average current density can be computed. In order to obtain the net power output of 25 kW, the number of SOFC-H⁺ stack is determined both in parallel and series configurations. From the simulation results, it is found that the arrangement of the SOFC-H⁺ stack affects the required SOFC-H⁺ area. Table I presents the possible SOFC-H⁺ configuration. The fuel cell efficiency in all cases is ~31%.

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<thead>
<tr>
<th>Case</th>
<th>Number of SOFC-H⁺ stack</th>
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</tbody>
</table>

The simulation results also indicate that under these conditions, the integrated system can generate both electricity and high amount of synthesis gas (Fig. 2). Due to the use of a proton-conducting electrolyte, the high content of CO (> 20%) in the anode exhaust gas may cause the carbon deposition on the anode side and thus, this issue should be concerned in the operation.

V. CONCLUSION

This study presents the performance evaluation and design of an integrated system of SOFC-H⁺ and ethanol autothermal reformer. The effect of operating parameters (i.e., operating temperature and feed ratio) on SOFC-H⁺ stack configuration and CO content was examined. The simulation results indicated that the 25 kW SOFC-H⁺ system can be both the power generation and H₂ production units. Under the standard conditions ($T_r = 600^\circ$C, $T_s = 750^\circ$C, STE = 2 and OTE = 0.5), the required area of 25 kW SOFC-H⁺ system is 7-8 m² in which the number of cell in parallel and in series depends on an available installed area. In addition, it was found that SOFC temperature has strongly impact on the number of SOFC-H⁺ stack, whereas the steam to ethanol ratio affects the CO content.

TABLE I

**POSSIBLE SOFC-H⁺ CONFIGURATION FOR 25 kW**

<table>
<thead>
<tr>
<th>Case</th>
<th>Number of SOFC-H⁺ stack</th>
<th>Required area (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in parallel</td>
<td>in series</td>
</tr>
<tr>
<td>1</td>
<td>65</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>48</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>38</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>18</td>
<td>10</td>
</tr>
</tbody>
</table>

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PERFORMANCE MODELING OF AN ALKALINE ANION EXCHANGE MEMBRANE-BASED DIRECT GLUCOSE FUEL CELL

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Abstract – An AEM-based DGFC performance model is developed and compared against literature experimental results. Performance predictions for different anode and PtAg/C cathode catalysts, using the 1-D flux-based model, are reported.

Index Terms – Direct glucose fuel cell, anion-exchange membrane, performance model.

I. INTRODUCTION

Direct liquid fuel cells (DLFCs) employing methanol or ethanol as fuels have been widely studied in acidic, and recently in alkaline and alkaline-acid environment [1]. Glucose, which is abundant in nature and cheap, is a major biomass whose theoretical energy density (4.43 kWh kg⁻¹) is relatively less than that exhibited by methanol (6.10 kWh kg⁻¹) or ethanol (8.00 kWh kg⁻¹), and has recently shown a potential for powering medical implants [2], and small portable fuel cell applications [3-7]. A primary advantage of using glucose is the formation of non-toxic oxidation reaction products (water and CO₂; its total oxidation via a 24-electron transfer is written as: C₆H₁₂O₆ + 6O₂ → 6CO₂ + 6H₂O). However, in practice, the glucose oxidation reaction (GOR) is incomplete by the production of gluconic acid, which reduces the glucose-based fuel cell performance. The present study focus on mathematical modelling of the transport phenomena taking place in the alkaline, anion-exchange membrane (AEM) based direct glucose fuel cell (DGFC) to predict its performance.

II. THEORY

A. AEM-based direct glucose fuel cell mathematical model

The present work is based on our previous modelling studies for a direct ethanol PEM fuel cell [8, 9], appropriately modified to accommodate transport within an AEM.

Fig. 1 shows a schematic of the AEM-based DGFC with a mixture of glucose and aqueous potassium hydroxide (KOH) circulating in the anode, and oxygen in the cathode. Glucose electrooxidises at the anode and oxygen reduces at the cathode side. Electrons are transferred via the external circuit to the cathode, where they are utilized in the oxygen reduction reaction (ORR), forming OH⁻. These ions are now transported across the cell to the anode, where they are consumed together with glucose to form gluconic acid (C₆H₁₂O₇), as described by Eq. (1). The total fuel cell reaction is written in Eq. (3) in combination with the cathode reaction in Eq. (2):

Anode reaction
C₆H₁₂O₆ + 2OH⁻ → C₆H₁₂O₇ + H₂O + 2e⁻  \hspace{1cm} (1)

Cathode reaction
0.5O₂ + H₂O + 2e⁻ → 2OH⁻ \hspace{1cm} (2)

Overall reaction
C₆H₁₂O₆ + 0.5O₂ → C₆H₁₂O₇ \hspace{1cm} (3)

Fig. 1. Schematic of the AEM-based DGFC

1-D flux balance equations for glucose and oxygen transport are implemented in the anode, and cathode domains, respectively, of the diffusion and the catalyst layer. OH⁻ transport is implemented within the AEM. Experimentally-determined GOR kinetics data for PdRh/C electrocatalysts in alkaline medium [10], such as transfer coefficients and exchange current densities, determined from cyclic voltammetry (CV) analysis, are employed in activation overpotential estimation for different operating conditions. ORR kinetics data are obtained for a

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PtAg/C cathode catalyst [11]. The ohmic resistance is calculated from the specific conductance of KOH solution found from non-linear regression analysis given in literature. Water and glucose crossover (cf. fig. 1) through the AEM are also considered in the present study, although Fujiwara et al. [3] suggested that the crossover of glucose through AEM is more than 30 times smaller than that of methanol (cf. fig. 3 in [3]).

III. RESULTS

The trend of the polarisation V-I characteristic curve at different operating conditions, such as anode catalysts and loadings, glucose concentrations and temperature, is predicted by the proposed model and compared against experimental data from the literature (e.g. An et al.[6], Basu, Sood, Basu [7]; comparisons are not shown here).

Performance predictions are also reported hereafter for an AEM-type DGFC (28μm AEM A201-Tokuyama) with a PdRh/C anode and PtAg/C cathode catalyst (cf. fig. 2) with and without glucose crossover. Glucose crossover gives rise to a parasitic current (\(j_{\text{cross}}\) or \(j_{\text{leak}}\); see e.g. \([8, 9]\)). The net effect of this parasitic current loss is to offset the DGFC’s operating current by an amount given by \(j_{\text{cross}}\). This has a significant effect on the open circuit voltage (OCV) of the DGFC: OCV reduction below its thermodynamically-predicted value.

\[ \text{Fig. 2. Numerical predictions for an AEM DGFC (0.5M Glucose, 0.5M KOH, room temperature)} \]

The gross current produced at the DGFC electrodes then reads: \(j_{\text{gross}} = j + j_{\text{cross}}\). Here, \(j\) is the actual DGFC operating current that we can measure and use. \(j_{\text{leak}}\) and \(j_{\text{cross}}\) are based on \(j_{\text{gross}}\) since the reaction kinetics and species concentrations are affected by the crossover current. \(j_{\text{leak}}\) should be based, however, on \(j\) since only the operating current of the DGFC is actually conducted through the cell.

IV. CONCLUSION

An AEM-based DGFC performance model is developed and compared against literature experimental results. Performance predictions for different anode and PtAg/C cathode catalysts, using the 1-D flux-based model, are reported. Keeping in mind that a mathematical model is always a simplification of reality, the effect of different fuel cell operation and physico-chemical parameters on DGFC performance is investigated. Performance improvements are also discussed in view of potential polarisation losses reduction with the variation in either operating and/or physico-chemical conditions/parameters.

ACKNOWLEDGMENT

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REFERENCES

PERFORMANCE OF AN ALKALINE DIRECT GLYCEROL FUEL CELL WITH DIFFERENT ANODE CATALYSTS

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Abstract – Five different commercial catalysts, Pt/C, PtRu/C, Pt3Sn/C, Pt3Co/C and Pt3Ni/C, have been used for direct oxidation of glycerol in an alkaline fuel cell. KOH-doped polybenzimidazole was used as electrolyte membrane. The results show that the addition of a less noble secondary metal to platinum enhances the electrocatalytic activity, with an increase in the maximum power density, especially in the case of the PtRu/C and Pt3Sn/C. This result can be explained taking into account that, according to the XRD results, these two catalysts possess a large oxide fraction in its surface. As a consequence, the presence of oxygenated species coming from the second metal is crucial for promoting the glycerol electroxidation.

Index Terms - Alkaline Medium, Bimetallic catalysts, Direct Glycerol Fuel Cells, KOH doped polybenzimidazole.

I. INTRODUCTION

The large expansion of the biodiesel industry in the last decade demands for the search of alternatives for utilizing the glycerol byproduct. The traditional industries that absorbed this surplus (cosmetic, pharmaceutical and food and agriculture industries) are not able to handle any more the amount produced. One of the possible alternatives is the valorization of the glycerol in a fuel cell, where electricity and large added-value products can be obtained [1]. This system has demonstrated to be effective in alkaline medium, due to the enhanced glycerol electroxidation rates compared to acidic one [2]. The most extended, effective and robust electrocatalyst used for this process is platinum nanoparticles deposited on carbon, despite the existence of the possibility of using other noble metals, such as gold and palladium.

The glycerol oxidation process involves the participation of oxygenated species, whose origin, in principle, in monometallic platinum catalyst, are the oxygenated species available in the surface of the catalyst [3]. However, Pt-based bimetallic catalysts with secondary less noble metals, such as ruthenium and tin, have demonstrated to promote other alcohols oxidation processes by donating oxygenated species at lower potentials, or by an electronic effect that modifies the adsorption energies of the different reactive species formed on the catalyst surface.

Under these circumstances, the objective of this paper is to study the influence of the presence of a secondary less noble metal on the electrochemical performance of several Pt-based commercial catalysts in alkaline medium for glycerol oxidation. It focused on the electrochemical performance and the influence of one important operating variable, the temperature, on the cell performance. Physico-chemical characterization was carried out by the DRX spectra of the different catalysts in order to quantify the formation of a possible alloy between the platinum and the other metal, and to obtain information about the crystal sizes.

II. EXPERIMENTAL

Five different commercial catalysts were used in this study with a metal content of 20%: Pt/C, PtRu/C, Pt3Sn/C, Pt3Ni/C and Pt3Co/C from former ETEK-Inc (BASF Fuel Cells). The alloying degree and the average crystal size were determined by X-Ray Diffraction.

The electrodes with the different commercial catalysts were prepared by the painting procedure. A diffusion layer was made with carbon powder (Vulcan XC-72R) and 15wt.% Teflon TE-3893 (Dupont), and applied homogeneously over a carbon cloth (PWB-3, Stackpole) by vacuum filtration. Onto this layer, for the anode, a catalyst layer was applied with a platinum loading of 2 mg cm\(^{-2}\) (taking as base the actual composition obtained by EDS), and a Nafion\textsuperscript{®} one corresponding to a 10% in weight of the total catalyst weight. In the case of the cathode, the Pt loading was 1 mg cm\(^{-2}\). Electrodes were sandwiched between a commercial PBI membrane (Daposy, Denmark) immersed in 6 mol L\(^{-1}\) KOH for, at least, one week. Electrochemical measurements were performed potentiostatically at the different
operating temperatures with the aid of a power supply, monitoring the cell voltage with a multimeter. The reported values correspond to the average of three consecutive polarization curves, giving a resting time of 15 minutes between them. The fuel for all the measurements was 1 mol L$^{-1}$ glycerol and 4 mol L$^{-1}$ KOH, pumped with a Diaphragm Metering Pump (Prominent). The oxygen flow was controlled with the aid of a flowmeter RMS-11 (Digiflow), fixing a value of 20 mL min$^{-1}$.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the different commercial catalysts. As it can be seen, all the catalysts present the typical platinum fcc crystal structure. The main information obtained from the XRD patterns is summarized in Table 1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average crystal size (nm)</th>
<th>Lattice parameter (nm)</th>
<th>Degree of alloy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>3.4</td>
<td>0.3823</td>
<td>-</td>
</tr>
<tr>
<td>PtRu/C</td>
<td>2.4</td>
<td>0.3786</td>
<td>42.5</td>
</tr>
<tr>
<td>Pt3Sn/C</td>
<td>3.7</td>
<td>0.3893</td>
<td>39.1</td>
</tr>
<tr>
<td>Pt3Co/C</td>
<td>3.4</td>
<td>0.385</td>
<td>100</td>
</tr>
<tr>
<td>Pt3Ni/C</td>
<td>3.0</td>
<td>0.389</td>
<td>98.5</td>
</tr>
</tbody>
</table>

As it can be seen, all the catalysts are in the range of nanoparticle size, from 2.4 nm for the PtRu/C to 3.7 nm for the largest Pt3Sn/C catalyst. The degree of alloy shows that Ru and Sn partially insert in the Pt crystalline structure, with the remaining second metal in the form of oxide. In the case of Co and Ni, virtual complete alloying was achieved due to the proximity of the obtained lattice parameters to the ones corresponding to the Pt3Co and Pt3Ni intermetallic compounds.

Figure 2 shows the polarization curves obtained at 60ºC for the different catalysts.

As it can be seen, the presence of a secondary metal promotes the electroxidation of glycerol, reflected in the better electrochemical and the larger maximum power densities obtained. The presence of the less noble second metal is expected to provide the oxygenated species necessary for the glycerol electroxidation at lower potentials than platinum. The PtRu/C and Pt3Sn/C possess a large fraction of the second metal in the form of oxide, becoming sources for those -OH-like species. In the case of Pt3Co/C and Pt3Ni/C, the second metal is in the form of alloy, so that the expected oxidized fraction in the surface is lower than that of the others. This leads to a lower promotion of the electrochemical performance.

Furthermore, Pt3Co/C and Pt3Ni/C catalysts are known to reinforce the adsorption strength, so that glycerol intermediary species formed during the electrooxidation might “poison” the platinum surface, further depressing the effect of the second less noble metal.

Despite the curves are only displayed at the temperature of 60ºC, the same trends were observed at 30, 45 and 75ºC, confirming the beneficial effect of the secondary metal on the cell performance.

IV. CONCLUSION

The addition of a secondary less noble metal to a platinum-based anode catalyst for glycerol electroxidation in alkaline medium has displayed a beneficial effect on the electrochemical performance. Ru and Sn specially promote it, due to the presence of oxidized species on the surface that can provide oxygenated species to platinum at lower potentials. Co and Ni, in spite of showing a positive effect, increase the cell performance to a lower extent, primarily due to the massive formation of the corresponding alloys with Pt, which is expected to lower the fraction of oxidized species on the surface of the catalysts.

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ALGAL “LAGOON” EFFECT FOR OXYGENATING MFC CATHODES

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Abstract - This paper describes the active oxygenation performed by the photosynthetic organisms in the cathode of a two-chamber Microbial Fuel Cell system. The algal growth provided dissolved oxygen to the cathode oxygen reduction reaction in a sustainable manner through the recirculation of the catholyte connected to the photoreactors, which act as lagoons. Aiming towards self-sustainable applications, it has been demonstrated that catholyte recirculation can be facilitated by the MFC stack itself when a dc impeller pump was powered continuously for a short period of time by the electricity produced from these same 16 MFCs.

Index Terms – biomass, lagoon effect, microbial fuel cell, photosynthetic cathode.

I. INTRODUCTION

To successfully implement the Microbial Fuel Cell (MFC) technology as a viable power source for practical applications, power output and operational sustainability have to improve. This would exclude employment of noble metals (e.g. platinum) and chemicals (e.g. ferricyanide) as catalysts/reagents. The improvement of cathode oxygen reduction requires oxygen to be constantly supplied to the cathode electrode. Using active oxygenators such as photosynthetic organisms in situ to perform this task has the unavoidable downside of oxygen depletion during the dark phase, where photosynthesis stops and respiration occurs. An algal lagoon or photo-bioreactor connected to the cathodic side of MFCs can theoretically produce more biomass and also provide oxygenation for the cathodic chamber. Whilst the electroactive bacteria biodegrade organic matter in the anode, cations other than protons diffuse through the cation selective membrane into the cathode [1, 2] where they can be further assimilated by algal growth and locked into new biomass [3]. The development of new technologies could help utilise locked-in waste products for energy production in a carbon-neutral manner. This work is presenting the sustainable oxygenation of the MFC cathode by photosynthetic biocatalysts in a ‘lagoon’ kind of scenario and in addition the generated electricity by the stacked MFCs was used to power an impeller dc pump as a demonstration of an exemplar practical application. The produced algal biomass could furthermore be utilised as a carbon energy source in the same MFC anodes [4] – a direction that will be pursued as part of this study, in an attempt to develop a fully self-sustainable system.

II. MATERIALS AND METHODS

Fifteen MFCs (Fig 1) were tested in triplicate groups assembled with transparent 25mL continuous flow cathodes connected to 400mL photo-reactor flasks and 25mL batch mode anodes, which were inoculated with activated sludge. The anode and cathode half-cells contained carbon fibre veil electrodes (total surface area of 270cm²). MFCs connected to photo-reactor flasks were placed inside a thermostatic light incubator, controlled at 22°C.

figure 1 Microbial Fuel Cell scheme with photo-cathode.

III. RESULTS

Figure 2a presents the open circuit voltage (OCV) of algal-based cathode MFCs when the recirculating catholyte pump was switched OFF (batch mode). The voltage level exceeded 500mV during the light phase, but decreased to 100mV during the dark period. When the pump was switched ON (arrow on the graph) the open circuit voltage difference (between light and dark) almost vanished, suggesting that the algal growth in the photo-reactors...
compensated for the lack of oxygen generation (during the dark period) in the smaller cathodic chambers; this improved both stability and performance of the MFCs. In Figure 2b pumping was turned OFF once again, whilst the dark period was increased to 20h night over 4h day intervals. Voltage of the MFCs dropped into negative values and the short period of illumination was insufficient for the MFCs to fully recover. When the recirculation pump was switched ON, once again steady open circuit voltage levels were produced, with a lesser degree of fluctuation between the day/night cycles.

Despite the fact that photosynthesis stops inside both the MFC cathode and photoreactor flasks, the amount of oxygen concentration pooled inside the bioreactor compensates for the lack of oxygen production during the dark period inside the smaller MFC cathode chamber. This phenomenon is known as sewage lagoon [5] or photosynthetic pond and it is used in the wastewater treatment process. Furthermore, the fact that the amplitude of the OCV when the pump is switched ON is identical to the amplitude when operating in day/night batch mode (Fig 2a) may suggest that the output is a function of oxygen.

In order to demonstrate that this pumping can be facilitated by the MFC stack itself, aiming towards self-sustainable applications, a dc impeller pump (M200-S, 3V dc, RS, UK) was powered continuously for a short period of time, by the energy produced from these same 16 MFCs (15 described above +1 for balanced configuration). The energising of the pump was performed via a 5F super-capacitor (Figure 3), when the MFC stack was connected in a series/parallel configuration. Under this condition, 2 MFC units were connected in parallel, and the resulting 8 pairs, were connected in series. The super-capacitor was charged to the stack’s maximum voltage for this configuration (3-3.5V) for 24h, which allowed the running of the impeller pump for at least >1min (67secs operation has been recorded), until the capacitor voltage decreased to 1.0V, at which point the pump stopped.

**IV. CONCLUSION**

This study presents the sustainable oxygenation of the MFC cathode by photosynthetic biocatalysts in a ‘lagoon’ type scenario. This is the first time that the stack of completely biotic MFCs incorporating photosynthetic organisms in the cathode has been shown to power a practical application such as the impeller pump. Furthermore, it is allowing a route for energy abstraction from the biomass grown in the photo-assisted MFC.

**ACKNOWLEDGMENT**

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**REFERENCES**

PERFORMANCE OF DOUBLE PEROVSKITE AS SYMMETRIC ELECTRODES BASED ON IT-SOFC CONTAINING SULFUR IN FUEL

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Abstract - Double perovskite materials, Sr₂CoMoO₆ and Sr₂NiMoO₆ (denoted as SMMO, M=Co, Ni) were synthesized as symmetric electrodes in SOFC fed with H₂-H₂S. Ce₀.₈₅Sm₀.₁₅O₂₋δ as intermediate temperature solid electrolytes was adopted to fabricate single cell with structure of SMMO|SDC|SMMO. Electrochemical performances of two types of SOFCs as well as impedance tests were tested. Compatibility between electrodes and electrolytes was characterized by SEM-EDX. Temperature-programmed techniques, including H₂-TPR, O₂-TPD, were used to test catalytic activities of electrodes in different atmosphere, while thermogravimetry analysis was performed to evaluate their sulfur tolerance. Application of symmetric electrodes in SOFC, especially in IT-SOFC, simplifies the manufacture process of SOFC and reduces SOFC costs greatly.

Index Terms – symmetric electrode; SOFC; Sulfur tolerance

I. INTRODUCTION

One of major challenges posed for the SOFC commercialization is how to operate SOFC in crude fuel gas besides pure hydrogen, because of severe material demands for crude fuel gas containing sulfur, phosphorus etc. Electrodes deactivated by these impurities cause the rapid decline of SOFC performance[1]. Thus, electrode materials with both electrocatalytically active and tolerant to crude fuel gas become a crucial factor.

Fortunately, some materials with perovskite and double perovskite structure are proved to resist sulfur well and applied as anodes in SOFC. For example, Tao et al[2] verified anode La₀.₅Sr₀.₅Cr₀.₃Mn₀.₂O₃ (LSCMn) had good redox stability and performed well compared to traditional Ni-YSZ. Double perovskite Sr₂MnMoO₆ (M=Mg,Fe,Co,Ni) has also been regarded as a promising MIEC with an excellent tolerance to sulfur since Goodenough et al adopted Sr₂Mgₓ,MnₓMoO₆₋δ as anode during direct electrochemical oxidation of dry methane at 800 °C[3]. And, because of their redox stability both in reduced and oxidized atmosphere, these materials can be applied both as anode and cathode, as Ruiz-Morales, Chen[4] proposed. The innovation on symmetric configuration of SOFC reduces SOFC costs greatly and meanwhile introduces new understanding about sulfur tolerance.

At present, more attention is paid to the redox stability and symmetric SOFC (SFC) performance of electrodes materials fueled by H₂ or/and CH₄ without introducing H₂S[5,6]. To our best knowledge, few literatures deal with the symmetric electrodes against sulfur in SOFC conditions. In this paper, Co and Ni were respectively doped into B site of double-perovskites Sr₂MoO₆ to fabricate SFC based on Ce₀.₈₅ Sm₀.₁₅ O₂₋δ (SDC) as solid electrolytes [9]. The SOFC performances were presented when H₂ with 5% H₂S were used as fuel. Further, the catalytic activity of electrodes was verified by means of H₂-TPR and O₂-TPD while their sulfur tolerance was explored by thermogravimetry analysis.

II. EXPERIMENTAL

About 500 um dense SDC electrolytes were prepared by dry pressing method and then were sintered at 1300°C. Homemade electrodes gels were painted on both sides of electrolytes as symmetric electrodes. Single cells in the configuration of Sr₂MMoO₆ | SDC | Sr₂MMoO₆ (M=Co, Mo) were tested in H₂ with 1% H₂S as fuel and ambient air respectively. Single cell performances were evaluated by I-V or I-P measurements at 650-750°C. Fig. 1 shows cell currents density and power density increase as a function of elevated temperatures. At 750°C, the maximum power density Pₘₐₓ reaches 27 mW/cm².
for $\text{Sr}_2\text{CoMoO}_6$ and 23 mW/cm² for $\text{Sr}_2\text{NiMoO}_6$. $\text{Sr}_2\text{CoMoO}_6$ seems to be better than $\text{Sr}_2\text{NiMoO}_6$ when the performances of

Figure 1: I-V curves of symmetric SOFC with $\text{Sr}_2\text{CoMoO}_6$ and $\text{Sr}_2\text{NiMoO}_6$ as electrodes, respectively at 650-750°C

Figure 2: EIS for symmetric SOFC with $\text{Sr}_2\text{CoMoO}_6$ and $\text{Sr}_2\text{NiMoO}_6$ at 650-750°C

SFCs composed of two symmetric electrodes were compared in parallel. Electrochemical impedance spectroscopies (EIS) for these two SFCs were also investigated in Fig. 2 aiming to make certain the difference between two symmetric electrodes during SOFC operation. In H$_2$-1%H$_2$S atmosphere, ohmic resistance of SFC with $\text{Sr}_2\text{CoMoO}_6$ as electrode is less than that with $\text{Sr}_2\text{NiMoO}_6$, and differences in ohmic resistance of two SFCs are less than 1 Ωcm$^2$ from 650°C to 750°C. Compared to ohmic resistance, polarization resistances prevail in and vary greatly at different temperatures. It is more evident that $\text{Sr}_2\text{NiMoO}_6$ possesses much higher polarization resistance than $\text{Sr}_2\text{CoMoO}_6$. It has been concluded that SFCs applied in fuel containing higher concentration H$_2$S are feasible. Double perovskite materials, $\text{Sr}_2\text{CoMoO}_6$ and $\text{Sr}_2\text{NiMoO}_6$, are suitable for symmetric electrodes tolerant to H$_2$S, and $\text{Sr}_2\text{CoMoO}_6$ exhibits better electrocatalytic activity.

### III. Conclusion

Symmetric SOFC is one of solutions to sulfur impurities in fuel. SOFC with configuration of $\text{Sr}_2\text{MMoO}_6$ | SDC | $\text{Sr}_2\text{MMoO}_6$ (M=Co, Mo) were investigated within inter-temperature of 650-750°C. At 750°C, the maximum power density $P_{\text{max}}$ of 27 mW/cm² was achieved for $\text{Sr}_2\text{CoMoO}_6$, a little higher than that of $\text{Sr}_2\text{CoMoO}_6$. Double perovskite materials $\text{Sr}_2\text{CoMoO}_6$ as symmetric electrodes tolerant to H$_2$S, possesses better electrocatalytic activity.

### ACKNOWLEDGMENT

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DESIGN OF ENERGY RECUPERATION IN A SOLID OXIDE FUEL CELL-GAS TURBINE HYBRID SYSTEM WITH ETHANOL AS FUEL

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Abstract – An ethanol reforming and solid oxide fuel cell-gas turbine (SOFC-GT) hybrid system with anode and/or cathode recirculation is investigated in this study. The aim is to analyze the effect of the anode and cathode recirculation on the performance of SOFC-GT system. The results showed that the hybrid system with both the cathode and anode recirculation achieve the highest system efficiency.

Keywords – Solid oxide fuel cell, Gas turbine, Ethanol reforming, Combined heat and power.

I. INTRODUCTION

A solid oxide fuel cell-gas turbine (SOFC-GT) hybrid system is an interesting power generation technology due to its high efficiency. Most SOFC systems run on natural gas; however, natural gas is a limited and nonrenewable resource even it is a cost-effective feedstock. To date, ethanol is considered a promising fuel for SOFC as it can renewably produced from agricultural products. Since the direct feed of ethanol to SOFC leads to the degradation of anode catalysts caused by a carbon formation. To avoid this difficulty, an external reformer is integrated with the SOFC system for hydrogen production. However, the external reforming SOFC system requires higher air supply to SOFC than the direct internal reforming SOFC system[1].

Because the ethanol reformer and the air preheater need high external heat input, the efficient heat management of the SOFC system is necessary. Regarding the SOFC system, anode and cathode recirculation are employed to recover high-quality waste heat from the reformer and gas turbine, affecting the electrical and thermal efficiencies of the SOFC system. Thus, the objective of this study is to investigate the effects of the anode and cathode recirculation on the performance of SOFC-GT system.

II. SOFC-GT system

Fig. 1 shows the ethanol reformer and SOFC with gas turbine cycles integrated systems. Three SOFC system designs are consider: (1) SOFC-GT system with anode recirculation (AR), (2) SOFC-GT system with cathode recirculation (CR) and (3) SOFC-GT system with both the anode and cathode recirculation (ACR). Ethanol as a fuel is pumped, mixed with steam and reformed to synthesis gas in an external reformer. The synthesis gas with rich hydrogen is then sent to SOFC stack. Since an exhaust gas at the anode of SOFC is composed of residual fuel and steam, which can be used for the reforming of ethanol, a portion of the exhaust gas can be recycled to the external steam reformer. This is known as the SOFC system with the anode recirculation. The remaining anode exhaust gas is mixed with an outlet oxidant gas from the cathode in a combustor. The combustion gas goes through a high-temperature heat exchanger before it is fed to a turbine to produce electricity. The exiting gas from the turbine is sent to a recuperator to preheat a compressed air. For the hybrid SOFC system with the cathode recirculation, a portion of the cathode exhaust gas is recycled and mixed with a fresh air from the recuperator and then sent to the SOFC. The SOFC system with both the anode and cathode recirculation is similar to that with the cathode recirculation but includes the anode recirculation (dash line in Fig 1(b)). The performance of the SOFC-GT systems is analyzed based on the mathematical models of SOFC, gas turbine, and auxiliary units, which are derived from mass and energy balances under steady-state operation.
Fig. 1. The pressurized SOFC-GT hybrid system with (a) anode exhaust gas recirculation and (b) cathode exhaust gas recirculation.

III. RESULTS AND DISCUSSION

Table 1 show operating and design parameters used to evaluate the performance of the SOFC-GT hybrid system. All simulations of the system are run at an average current density of 0.4 A/cm$^2$ and fuel utilization of 0.65. The inlet molar flow rate of fuel is adjusted to the required current density and fuel utilization of the SOFC. The temperature across the fuel cell stack is limited to 100 K. To avoid the carbon formation in ethanol steam reformer, it is operated at the steam-to-carbon ratio of higher than one [1].

The cathode and anode recirculation in the hybrid system has direct effect on the SOFC and GT performance. Table 2 compares the simulation results of the AR, CR and ACR systems. The AR gives the lowest GT-to-SOFC power ratio due to the presence of lower residual fuel in the SOFC exhaust gas to the combustor. In the CR system, a part of the cathode outlet air recycled to the fuel cell results in an increase of the turbine inlet temperature. Thus, the GT-to-SOFC power ratio of the CR system shows the highest value. However, it is noted that the turbine inlet temperature should not be higher than 1223 K for design practice of small gas turbines. In this respect, the ACR system achieves the suitable inlet turbine temperature. When considering the external heat required for the hybrid system, the AR and ACR systems require lower external heat because steam required for the ethanol reformer is obtained from that generated by the SOFC stack through the anode gas circulation. The factor decreases the need of external heat for steam generator.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Cell operating temperature (K)</td>
<td>1073</td>
<td>Reformer temperature (K)</td>
<td>973</td>
</tr>
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<td>Number of cell</td>
<td>3098</td>
<td>Compressor isentropic efficiency (%)</td>
<td>78</td>
</tr>
<tr>
<td>Pressure ratio (bar)</td>
<td>3</td>
<td>Compressor isentropic efficiency (%)</td>
<td>82</td>
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</table>

From the results, the ACR system can be operated at the optimal inlet turbine temperature and GT-to-SOFC power ratio. Additionally, the external heat required for the ACR system is low. Therefore, the ACR system achieves the highest system efficiency, compared to other SOFC systems.

IV. CONCLUSIONS

The results indicate that the SOFC hybrid system with the anode recirculation can reduce the supplied heat for the external steam reformer; on the other hand, it degrades the gas turbine performance. When considering the hybrid system with the cathode recirculation, it is found that the turbine inlet temperature is extremely high, leading to a cooling problem of a micro turbine. The SOFC hybrid system with both the anode and cathode recirculation can achieve its high system performance.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support from the Faculty of Engineering, Burapha university.

REFERENCES

ELECTRICAL CHARACTERIZATION OF CO-PRECIPITATED YBaCo$_2$O$_{5+\delta}$ IN YBC-LSGM-YBC SYMMETRIC CELL

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Abstract – A co-precipitation technique in aqueous medium was used for the preparation of a model compound in the LnBaCo$_2$O$_{5+\delta}$ double perovskite series (namely YBaCo$_2$O$_{5+\delta}$). Some ion losses were detected in the mother liquors during the preparation; these are responsible of some deviations from the nominal stoichiometry of the powders. YBaCo$_2$O$_{5+\delta}$ (YBC) only shows a slight Ba understoichiometry and is obtained as nearly pure phase at 1150 °C. The co-precipitated YBC has comparable physicochemical characteristics with materials in the available literature, and shows an interesting improvement of the electrochemical performances, while benefiting for the simplicity and cost-effectiveness of the preparation route.

Index Terms - Co-precipitation; YBC; cathode; EIS.

I. INTRODUCTION

Layered perovskite oxide compounds of the series LnBaCo$_2$O$_{5+\delta}$. (Ln = lanthanide ions) have been recently investigated as potential SOFC cathodes [1]. Among their properties, high electronic (metallic) conductivity at intermediate to high temperatures, high oxygen vacancy concentration, ion transport properties and high oxygen surface exchange coefficients compared to disordered perovskites are well suited for SOFC cathode materials. Our group has recently applied a simple co-precipitation technique to the synthesis of mixed oxides with application in solid oxide fuel cells with the perovskite structure obtaining reasonably good materials, both for electrolyte [2] and electrode [3] applications with fair conduction properties and good stability, despite some deviations from the ideal stoichiometries. The same procedure is here proposed for the preparation of a compound in the layered perovskite series. As a model compound, YBaCo$_2$O$_{5+\delta}$ was chosen in the LnBaCo$_2$O$_{5+\delta}$ series.

II. EXPERIMENTAL

Nitrate salts were used as precursors; the precipitating agent was (NH$_4$)$_2$CO$_3$ and the solvent was distilled water. The co-precipitation procedure is reported in details elsewhere [2]; the precipitation pH was 7.4. The obtained powders were crushed in a mortar and fired up to 1150 °C with heating and cooling rates of 2 °C min$^{-1}$ and dwell time of 10 h. Powders were characterized by X-Ray Powder Diffraction (XRPD) and the XRPD data of samples fired at 1150 °C were refined with the Rietveld method using the software GSAS for the determination of the structural parameters.

The electrical conductivity and polarization resistance were determined as a function of temperature on the YBC sample fired at 1150 °C. A potentiostat/galvanostat (Amel 7050) equipped with a frequency response analyzer (510 V10, Materials and Mates) was used for the measurements. The electrical conductivity was measured with the four-electrode method on a sintered pellet. The relative density of the YBC pellet amounted to 96%. The electrodes were obtained by brushing Ag ink on each side of the pellet and applying Ag meshes as current collectors. The conductivity was determined in flowing air (100 Ncc/min) between 25 to 850 °C, by applying a constant current and measuring the output voltage. Electrochemical impedance spectroscopy (EIS) tests were performed using a symmetric cell configuration with LSGM as the electrolyte material. A pellet was fabricated from commercial LSGM powders (La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3-\delta}$, Fuel Cell Materials) calcined at 1450 °C for 5 h in air. A slurry of the YBC cathode was applied on each side of the electrolyte.
substrate as symmetrically as possible, and dried at 150 °C for 1 h in air. The cell was then calcined at 1050 °C for 4 h in air. SEM microscopy was used to verify the thickness of the layers (~30 µm, Fig. 1).

Fig. 1. SEM micrograph showing a part of the cross section of the YBC/LSGM/YBC cell.

The porosity (~68%) was estimated from the weight and the density values. The EIS tests were performed in flowing air (100 Ncc/min on each side of the cell) between 450 and 800 °C, in the frequency range 0.1 Hz – 1 kHz with 10 mV signal amplitude. Also in this case, Ag meshes and ink were applied on each side of the cell to form the electrodes.

III. RESULTS AND DISCUSSION

The precipitated powders were completely amorphous after desiccation at 110 °C. At 1150 °C just three weak reflections remained unidentified, while the rest of the pattern matches the one of YBaCoO_{5+δ} (PDF #047-0735). The XRD pattern was refined with the Rietveld method; it was indexed with a tetragonal primitive cell (space group P4/mmm) corresponding to that of YBaCoO_{5+δ} [4]. Refined cell parameters are \( a = 3.8769(1) \) Å, \( c = 7.5017(4) \) Å, and the cell volume is 112.75 Å³, slightly smaller than those found by Vogt [4].

The electrical conductivity increases from 10 S/cm at room temperature to a maximum of 40 S/cm, approximately at 300 °C, and then decreases to 20 S/cm when heating to 850 °C. This behavior is consistent with a transition from a semiconductor-type to metal-type of conductivity, and was previously reported for analogous YBC samples by other authors: specifically, the results obtained with the present material are in close agreement with Ref [5], in terms of temperature thresholds and conductivity values.

The dependence of the ASR on the temperature is summarized in the Arrhenius plot of Fig. 2 ( ■ this work, ▲ Ref. [5]). A comparison is also provided with the polarization values reported in the literature for a YBC/SDC/YBC cell tested under conditions analogous to those adopted in our work (▲, from Ref. [5]).

Interestingly, much lower polarization resistances are found in the case of the present material, which are also accompanied by a lower activation energy (0.92 eV vs. 1.44 eV).

IV. CONCLUSION

Although no definitive conclusions can be drawn concerning the main cause of this result, given that several factors can be responsible (for instance, different porosity and thickness of the layers may result in different impact of mass transfer resistances; the use of different electrolytes may have induced different interactions), the result shows that the co-precipitation synthesis route adopted in this work led to a very active material, with polarization resistances well comparable to those considered in the literature also in the case of other perovskite materials.

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EXPERIMENTAL ANALYSIS OF A HTPEM FUEL CELL SYSTEM FED WITH DIFFERENT TYPES OF FUELS

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Abstract - The introduction of the fuel cell technology within the small size power generators field may lead, with respect to the well-established internal combustion engines, to the improvement of electric efficiency and to the reduction of the environmental impact. Hydrogen availability, which represents one of the main limiting factors for the wider spreading of the fuel cells, may be solved by integrating into the system a fuel processor that is able to convert the available fuel into a hydrogen rich mixture. Simpler and cheaper fuel processors may be adopted if High Temperature PEM (HTPEM) fuel cells are used: operating at temperatures up to 180 °C, these cells allow to tolerate carbon monoxide concentrations up to 2% with limited performance losses. This paper presents the experimental activity carried out on a power generation system composed of a steam reforming unit and a HTPEM stack. The tests, carried out in start-up and steady state conditions, were aimed to assess the operation of the HTPEM system fed with different types of fuels, i.e. Liquefied Petroleum Gas (LPG) and biogas. Hydrogen and carbon monoxide concentration in the reformate were measured in different operating points using gas chromatography, while infrared spectroscopy was used to determine the temperature distribution on the stack.

Index Terms - Biogas, Fuel processor, HTPEM fuel cell, hydrogen

I. INTRODUCTION

This paper presents the experimental activity on a power generation system composed of a steam reforming unit and an HTPEM stack and all the necessary equipment dedicated to the data acquisition and stand-alone operation. The research was aimed to assess the operation of a HTPEM power generation system fed with different types of fuels, i.e. Liquefied Petroleum Gas (LPG) and biogas. The initial tests were carried out in laboratory with a single cell configuration in order to draw a baseline performance of the fuel processor, fed with LPG. The main research effort was concentrated on mid-term field tests, when the system was operated, both in single cell and stack configuration, into a mobile unit fed with biogas produced by an industrial size anaerobic digester, for more than 1200 hours [1].

II. EXPERIMENTAL SETUP

The experimental system presented in Fig. 1 consists of a fuel processor, a HTPEM fuel cell and a monitoring and control system [1]. When the system was fed with biogas, the hydrogen sulphide contained in the raw gas was removed by the means of a biotrickling filter. The fuel processor, described in [2], is composed of a steam reforming reactor and a single carbon monoxide water gas shift purification stage. The temperature of the system is maintained by a burner.

Fig. 1. Simplified schematic of the system fed with biogas (1 – biotrickling filter, 2 – fuel processor, 2a – burner, 2b – reformer and shift stages, 3 – HTPEM fuel cell stack, a – biogas, b – low H2S content biogas, c – combustion air, d – demi water, e – reformate, f – cathode air, g – anode-off gas)

At design conditions, when the fuel processor is fuelled with LPG or natural gas, the expected reformate flow rate is 2.0 Nm³/h, with a hydrogen percentage of 75-79% (vol. dry basis). In the same conditions, with a steam to carbon ratio of 3.5 the maximum content of carbon monoxide should be lower than 1%. The tests were carried out with a single cell and a 22 cells stack, both assembled with BASF Celtec P1000 MEA. The system engineering and the stack have been developed by the Italian company Cenergy.

For the sake of shortness, this abstract will present a comparison between two configurations only: the single cell system fed with LPG, which may be considered as a reference, and the stack system fed with biogas.
III. EXPERIMENTAL RESULTS

The fuel processor experiments concerned the operation with LPG and biogas, during startup and steady state conditions. As shown in Fig. 2, with the same air flow and air-fuel equivalence ratio, the burner reaches a stable temperature in 28 minutes with LPG and 50 minutes with biogas. When the shift reactor reached about 150 °C, the demi water was introduced into the system, causing a reduction of the reformer temperature. The fuel processor reached a stable condition in about 2 hour with LPG and 2.5 hours with biogas.

![Graph showing temperature variation during startup phase with LPG and biogas](image)

In order to calculate the fuel processor efficiency, the gas composition at the inlet and outlet was analyzed, using the Gas Chromatography technique. The reformate composition (dry basis) obtained with LPG and biogas with steam to carbon ratios of 3.8 and respectively 5, is presented in Fig. 3. The high concentration of CH4 was a problem during all the biogas tests. Several operating conditions were tested but it was not possible to reduce the concentration. The fuel processor efficiency with biogas, at the end of the field tests, considering the anode-off recirculation, was 60%. With LPG the efficiency was 75%.

Fig. 4. presents a comparison between the single cell (SC) and stack average cell (ST) polarization curves, when the system was fed with LPG, and biogas respectively.

The vertical bars show the cells voltage distribution in the stack for current densities of 111 and 220 mA/cm². The lower stack performance may be related to the lower operating temperature and to the higher cell voltage distribution.

The stack was operated for a total 417 hours, with current loads from 2.5 up to 10 A. Due to the necessity to test several thermal management options, the stack was operated more than 50% of the test time with low current. Based on the operation at 5 A, the average cell voltage degradation was about 66 µV/h.

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EFC13119

ENERGETIC ANALYSIS OF HYBRID M-HTFC/MGT SYSTEMS

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Abstract – The present work concerns the study of Hybrid Systems (HS) resulting from the integration of Medium and High Temperature Fuel Cell (M-HTFC) and Micro-Gas-Turbine (MGT). This work takes into account different typologies of M-HTFC/MGT hybrid systems. These systems differ from each other in their plant layouts. All the hybrid plants are considered in cogenerative arrangement. The purpose of this study is to carry out an energetic comparison among the hybrid systems analysed. This comparison is based on some indexes that allow evaluation of the plants performances. For this purpose, an energetic analysis is carried out, which is based on a “black box” depiction of the plant in which the components and the mutual interactions are highlighted. In fact, the energetic flows exchanged with each other and the lost powers are pointed out for each component of the plant. The fuel cell component of the plant is not analysed as a black box, but each element that constitute it (anode, electrolyte, cathode and possible internal reforming), is elaborated as a subsystem with the energetic and mass flows exchanged.

Keywords – Cogenerative Arrangement, Energetic Analysis, Hybrid Plants, M-HTFC.

I. NOMENCLATURE

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<tr>
<td>L</td>
<td>Non-dimensional losses</td>
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<tr>
<td>η, ε</td>
<td>Hybrid system and components efficiency</td>
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<td>P</td>
<td>Thermal Power associated to the flows of the plants</td>
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<td>electric, thermal, fuel, polarization, losses, anode, cathode, electrolyte</td>
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<td>COMB, CAT-OUT_IT, REC, AUX, HE, SPC(MGT), SPC(IT), SPC(HT)</td>
<td>Referred to combustor, IT-SOFC cathode flow rate output, anode recycle flow rate, auxiliary, heat exchanger, system power conditioning of MGT, IT-SOFC, HT-SOFC</td>
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<td>Referred to IT-SOFC, HT-SOFC, micro-gas-turbine, hybrid system</td>
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II. INTRODUCTION

The present work concerns the study of Hybrid Systems (HS) in a cogenerative arrangement. These systems are obtained from the coupling of Medium and High Temperature Fuel Cell (M-HTFC) with Micro-Gas-Turbine (MGT).

Hybrid Systems are mainly allocated to the field of centralized and distributed stationary power generation. They are characterized by a high electric efficiency and a good environmental impact. Some typologies of hybrid systems that differ from each other because of their layout are taken into account. The aspect that allows the layout of the plants object of this study to be distinguished, is the presence or the absence of the recycled internal flow rate, the way heat is recovered in addition to the presence of the external or the internal reforming. An energetic analysis to effect a comparison of the performances of the plant in a cogenerative arrangement is carried out for these systems. An analytical expression of electric efficiency for each plant considered in a cogenerative arrangement, is calculated according to its the thermal efficiency.

III. TECHNICAL DESCRIPTION OF THE HYBRID SYSTEMS CONSIDERED

Three typologies of hybrid systems both with Molten Carbonate Fuel Cell (MCFC) and with Solid Oxide Fuel Cell (SOFC) module are taken into account. In particular, the plants that are analysed are a 160 kW MCFC/MGT [1], a SOFC/MGT single staged and a SOFC/MGT combined staged [2] hybrid systems. For sake of brevity just the SOFC/MGT combined staged plant it is presented.
A. SOFC/MGT Combined Staged hybrid system

The hybrid system considered is obtained from the coupling of an IT-SOFC (Intermediate Temperature Solid Oxide Fuel Cell) module and a HT-SOFC (High Temperature Solid Oxide Fuel Cell) module with a MGT (Fig.1). In this system the anode flows of the IT-SOFC and HT-SOFC are connected in parallel while the cathode flows are connected serially. The plant in cogenerative arrangement is characterized by the presence of an Heat Recovery system (HR) for the generation of the thermal power by the exhaust flows.

![Fig. 1: SOFC/MGT Combined Staged hybrid system layout](image)

The analysis that is carried out is based on a black box depiction of the systems taken into account. This approach allows pointing out the interactions among the components of the plants by the exchanged mass and energetic flows. Different loss factors and their influence on the electric efficiency trend are highlighted. The effects and the power lost but is considered to made up of the elements that compose it are taken into account in terms of non dimensional factors, and the energetic comparison of the systems taken into account. This approach allows the elaboration of an analytical expression of electric efficiency (equation 1). An equation that system that is constituted for the hybrid plant analyzed. That allows the elaboration of an analytical expression of electric efficiency according to its thermal efficiency (equation 1). The coefficients of equation (1) are listed in TABLE 1.

\[
\eta_{el} = \frac{1}{d} \left[ \frac{P_{f, HE2}}{P_f} + a \left( \frac{P_{f, HT}}{P_f} + \frac{1}{d} \frac{P_{rec}}{P_f} + b \frac{P_{comb}}{P_f} - \frac{e}{d} \left( \frac{P_{comb}}{P_{f}} - \frac{P_{f, HT}}{P_f} \right) \right) \right]
\]

\[
\eta_{el}^{Norm} = \frac{1}{a} \left[ \frac{\eta_{el}^{Norm}}{\eta_{el}} \right] + b \left( \frac{\eta_{el}^{Norm}}{\eta_{el}} \right) + \frac{1}{d} \left( \frac{\eta_{el}^{Norm}}{\eta_{el}} \right) - \frac{c}{d} \left( \frac{\eta_{el}^{Norm}}{\eta_{el}} \right) + \frac{d}{e} \left( \frac{\eta_{el}^{Norm}}{\eta_{el}} \right) - \frac{e}{f} \left( \frac{\eta_{el}^{Norm}}{\eta_{el}} \right) + \frac{1}{g} \left( \frac{\eta_{el}^{Norm}}{\eta_{el}} \right) - \frac{h}{i} \left( \frac{\eta_{el}^{Norm}}{\eta_{el}} \right)
\]

\[
\eta_{el}^{Norm} = \frac{1}{a} \left[ \frac{\eta_{el}^{Norm}}{\eta_{el}} \right] + b \left( \frac{\eta_{el}^{Norm}}{\eta_{el}} \right) + \frac{1}{d} \left( \frac{\eta_{el}^{Norm}}{\eta_{el}} \right) - \frac{c}{d} \left( \frac{\eta_{el}^{Norm}}{\eta_{el}} \right) + \frac{d}{e} \left( \frac{\eta_{el}^{Norm}}{\eta_{el}} \right) - \frac{e}{f} \left( \frac{\eta_{el}^{Norm}}{\eta_{el}} \right) + \frac{1}{g} \left( \frac{\eta_{el}^{Norm}}{\eta_{el}} \right) - \frac{h}{i} \left( \frac{\eta_{el}^{Norm}}{\eta_{el}} \right)
\]

Therefore the electric efficiency of the hybrid system is also determined by the polarization losses of the fuel cell, the anodic recycle flow rate, the cathodic exhaust flow rate, etc.

CONCLUSION

The methodology elaborated provides a simple instrument for the energetic evaluation of hybrid systems in a cogenerative arrangement. The mathematical relationships that are obtained, after simplifying assumptions, allow a useful graphical representation of the systems analysed besides offering an instrument for comparison of the plants in cogenerative arrangement. Through some indexes such as the Primary Energy Saving (PES) etc., an energetic comparison of the considered hybrid plants in a cogenerative arrangement is carried out. The plants that realize best performances are those that achieve a better recovery of the energetic content of the flows that the components of the plants exchange to each other.

REFERENCES


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SYNCHROTRON SAXS AND GISAXS CHARACTERIZATION OF HIGH TEMPERATURE PEM FUEL CELLS CATALYST DEGRADATION

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Abstract – In this communication the application of Small-Angle X-ray Scattering on PEM fuel cells will be presented. The presentation will be focused on the investigation of the catalyst NPs.

Index Terms – CATALYST, GISAXS, HT-PEMFC, SAXS.

I. NOMENCALATURE
PEM Proton Exchange Membrane
MEA Membrane Electrode Assembly
NPs Nano-Particles
SAXS Small Angle X-ray Scattering
GISAXS Grazing Incidence SAXS

II. INTRODUCTION
Catalyst degradation in High Temperature PEM fuel cells is one of the main issues related to the durability of the MEA. The catalyst has a central role in the chemical conversion process and its behavior is directly linked with the performance of the fuel cell. The catalyst deteriorates during operation through aggregation, dissolution and isolation of the NPs, with the result of a lower catalytic activity [1]. The degradation state of the catalyst can be analyzed by means of synchrotron Small-Angle X-ray Scattering (SAXS) and Grazing Incidence Small-Angle X-ray Scattering (GISAXS).

III. SMALL ANGLE X-RAY SCATTERING
SAXS is a standard scattering technique often used to investigate colloids and it is based on the detection of electron density inhomogeneities within the sample. The data that can be obtained regard geometry and size distribution of objects between 1 nm and 100 nm [3].

As the catalyst usually employed in PEM fuel cells is in the form of Pt NPs of 3-5 nm [1] SAXS is suitable for characterizing the catalyst and its evolution.

![SAXS setup in transmission geometry (top), GISAXS setup: the beam is reflected by the sample surface (bottom)](image)

In SAXS the x-ray beam is transmitted through the sample and the resulting scattering caused by the interaction between X-rays and the electrons of the sample is detected. The obtainable information is an average on all the volume exposed to the beam. Grazing Incidence SAXS is used to analyze the surface of the samples, which is inclined from grazing conditions up to a few degrees from the beam direction. The beam is reflected by the sample after the penetration, which is depending on the grazing angle and material parameters. The scattering produced during this path is detected. The advantage...
of GISAXS is the possibility to obtain only the superficial information. In PEM fuel cells this feature is very important in order to focus on the catalyst layer and avoid the scattering provoked by the other layers of the MEA. Another advantage of using GISAXS on MEAs is the possibility to separate the information coming from anode and cathode. These techniques can be performed both in a synchrotron and with laboratory devices: the advantage of using synchrotron radiation is that the radiation brightness is $10^{12}$ times higher and thus a higher precision and versatility of setups can be achieved. In particular, both in situ and time resolved experiments are possible.

IV. APPLICATIONS IN PEM FUEL CELLS

SAXS has been used several times in PEM fuel cells to determine the catalyst particles size and distribution. Stevens et al. [6] used SAXS to determine the average Pt particle size in samples of carbon with different Pt loadings and compared the results with those obtained from wide-angle X-ray diffraction studies. Tsao et al. [7] used SAXS to investigate the structure of Pt NPs for fuel cells at various hot pressures. Smith et al. [8] studied the Pt particles growth during potential cycling by means of in situ SAXS measurements. Yavuz et al. [9] carried out an in-situ and real-time monitoring of size and morphology dependent activity of Pt coated single crystalline VO$_2$ nanowires in methanol oxidation reaction using GISAXS. The research activity carried out by the authors at the Elettra SAXS beamline [4] was focused on SAXS and GISAXS on HT-PEM MEAs. In a submitted work [5] a new MEA has been compared with two samples subjected to 100,000 load cycles. The result was an increased size (from 4.52 nm up to 7.66 nm) and polydispersity of the catalyst NPs. A wide area of the MEA has also been mapped with SAXS. The comparison between the result of a degraded MEA (Figure 3) and a new one can give useful information on the distribution of the catalyst evolution on the surface. Figure 3 shows the area of the MEA exposed to the beam (left) and the plot of the correlation length from 3200 single exposures (right). The correlation length derived from the SAXS pattern is a parameter proportional to the mean radius of the NPs, thus its plot shows the variation of the mean size of the catalyst NPs on the entire examined area. A trace of the bipolar plates channels seems to be present. The spatial distribution of catalyst NPs sizes, obtained after data elaboration, could confirm a link between channels geometry and catalyst evolution.

GISAXS has been used to differentiate the information of anode and cathode, as shown in Figure 4. First results seem to show a different size distribution of the catalyst NPs already in a virgin MEA.

REFERENCES

EFFECT OF Nb OR Cr DOPING ON THE ELECTROCHEMICAL PROPERTIES OF Sr$_2$MgX$_{0.2}$Mo$_{0.8}$O$_{6-\delta}$, DOUBLE PEROVSKITE

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Abstract – The influence of Nb or Cr doping on the electrochemical properties of Sr$_2$MgMoO$_{6-\delta}$ (SMM) for oxidation of hydrogen, methane and CH$_4$/CO$_2$/H$_2$ simulated biogas mixtures were investigated by impedance spectroscopy (IS) and compared with those obtained for SMM. The results revealed that the substitution of Nb for Mo in SMM had a negative effect on the electrochemical properties, caused by the increase of area specific resistance (ASR) values in all studied gas compositions, while the substitution of Cr for Mo in SMM reduced the ASR values in methane. Therefore, small substitution levels of Cr in SMM can improve the electrocatalytic activity of anode material for direct methane oxidation.

Index Terms – Anode, double perovskite, impedance spectroscopy, SOFC.

I. INTRODUCTION

Many ceramics have been investigated as potential anode materials for SOFC, most of them based on perovskite-type structure, such as chromium manganites, doped strontium titanium oxides and double perovskites based on SrMgMoO$_{6-\delta}$. These anodes exhibit the ability to directly operate on hydrocarbon fuels without external reforming. Nevertheless, chromium manganites show a low performance for direct hydrocarbon oxidation while activated titanates present limitations as low reduction kinetics and low electronic conductivity. On the other hand, SrMgMoO$_{6-\delta}$ appears as a good candidate due to get high power densities when using methane as a fuel and to have good tolerance to sulphur. Though, in a recent work was observed that Sr$_2$MgMoO$_{6-\delta}$ possessed very poor intrinsic catalytic activity for oxidation of both H$_2$ and CH$_4$, in absence of Pt paste/mesh as anodic current collector [1]. In this context, the incorporation of Nb or Cr could enhance the electrocatalytic activity for methane oxidation.

In previous studies performed by our group, Sr$_2$Mg(Mo$_{0.8}$Nb$_{0.2}$)O$_{6-\delta}$ (SMMNb) and Sr$_2$Mg(Mo$_{0.8}$Cr$_{0.2}$)O$_{6-\delta}$ (SMMCr) were studied in terms of structural properties as SOFC anode materials and exhibited acceptable electrical conductivity and good thermal and chemical compatibility with LSGM electrolyte [2]. In this work, the influence of Nb or Cr partial substitution for Mo on the electrochemical properties of Sr$_2$MgMoO$_{6-\delta}$ (SMM) for oxidation of H$_2$, CH$_4$ and CH$_4$/CO$_2$/H$_2$ simulated biogas mixtures has been investigated by impedance spectroscopy (IS) and compared with those for SMM.

II. EXPERIMENTAL

SMM, SMMNb and SMMCr were synthesized by solid state reaction and calcined in air during 50 h at 1673, 1773 and 1623 K, respectively. Reduced phases were obtained by further reduction at 1173 K in 10% H$_2$/N$_2$ for 50 h. Samples were characterized by XRD, XPS and SEM-EDAX.

The electrochemical characterization was carried out on symmetrical cell configuration using LSGM as electrolyte with a porous layer of La$_{0.4}$Ce$_{0.6}$O$_{2-\delta}$ (LDC) to prevent interdiffusion of ionic species between anode materials and electrolyte. Fabrication of the cell can be found in a previous report [2].

The activity of the anode materials on the electrolyte was evaluated by the interfacial area specific resistance (ASR) by impedance spectroscopy in H$_2$ and CH$_4$ as temperature function (873-1073 K) and three simulated biogas mixtures (CH$_4$/CO/H$_2$ 70/25/5, 60/35/5 and 50/45/5) at 1073 K. The fuels were supplied to the cell after passing through a saturator at room temperature. The impedance spectra were collected by an AUTOLAB system, from 100 KHz to 10 mHz at open circuit with a signal amplitude of 5 mV. Zview software was used to fit the experimental data to the equivalent circuits.

III. RESULTS AND DISCUSSION

Initially, SMM and SMMCr exhibit a main double perovskite phase with trace impurities of SrMoO$_4$ and Sr$_{2.67}$Cr$_2$O$_{6}$, respectively. After reduction, the impurities disappeared and only a single phase is presented in both samples. While, SMMNb shows a single double perovskite phase in both oxidized and reduced states. XPS revealed the coexistence of Nb$^{5+}$ and Nb$^{6+}$ for SMMNb and Cr$^{6+}$ and Cr$^{3+}$ for SMMCr in their oxidized states, and only Nb$^{5+}$ or Cr$^{3+}$ was detected after their reduction. In the three compounds, the Mo valence (Mo$^{5+}$) did not change significantly after reduction.
SEM micrographs show that the incorporation of Nb or Cr in the structure does not produce notably morphological changes in both oxidation and reduced states. Samples exhibit an inhomogeneous particle size distribution ranging between 0.2-2 µm. EDX microanalysis indicated that the experimental values are in good agreement with the nominal ones and kept the composition after reduction.

Impedance spectra for symmetrical cells prepared with SMM, SMMNb, SMMCr and LSGM as electrolyte were measured in wet H₂ and CH₄ as a function of temperature (873-1073 K). Fig. 1 shows the impedance spectra obtained for these three interfaces studied at 1073 K in H₂ and CH₄. The overall electrolyte resistance of the symmetrical cell was obtained from the high-frequency intercept and it has been deducted from the spectra. The lowest impedance values were obtained in wet H₂. However, the results revealed modifications of the electrochemical behaviour with the atmosphere. The lowest values of impedance were obtained in the interface with SMM and SMMCr in H₂ and CH₄, respectively; and the highest one corresponds to SMMNb.

![Fig 1](image-url)

**Fig 1.** Electrochemical studies of SMM, SMMNb and SMMCr on LSGM in wet H₂ (a) and CH₄ (b) at 1073 K.

All experimental data were analysed, using an equivalent circuit fitting with a series of three parallel combinations of resistance and a constant phase element. The process of electrochemical fuel oxidation in anode/electrolyte interface usually possesses three different contributions. The high frequency arc (HF), attributed to the transfer of species charges trough the anode/electrolyte interface, the intermediate frequency arc (MF), associated to the charge transfer reaction and the low frequency arc (LF) ascribed to diffusion process or/and adsorption of charged species [3]. In all cases, the highest resistance values were ascribed at the LF arc that could be indicate the diffusion process or/and adsorption of charged species [3]. In all cases, the highest resistance values were ascribed at the LF arc that could be indicate the diffusion process or/and adsorption of charged species as limiting step for the oxidation of H₂ or CH₄ reactions. The area specific resistance (ASR) was obtained by the sum of the individual resistances of the three arcs and is directly depending on the rate limiting step of the electrochemical process involved in the fuel oxidation reaction at the anode. The ASR values at 1073 K are collected in Table 1.

<table>
<thead>
<tr>
<th>Gas composition</th>
<th>SMM</th>
<th>SMMNb</th>
<th>SMMCr</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.72</td>
<td>1.55</td>
<td>1.44</td>
</tr>
<tr>
<td>CH₄:CO₂:H₂ 70:25:5</td>
<td>6.62</td>
<td>9.93</td>
<td>4.73</td>
</tr>
<tr>
<td>CH₄:CO₂:H₂ 60:35:5</td>
<td>6.10</td>
<td>6.21</td>
<td>6.46</td>
</tr>
<tr>
<td>CH₄:CO₂:H₂ 50:45:5</td>
<td>4.68</td>
<td>5.20</td>
<td>6.56</td>
</tr>
</tbody>
</table>

Biogas is a potential source fuel for the SOFC by direct internal reforming (DIR) at the SOFC anode. Its composition usually lies within the following ranges: CH₄= 50-70 %, CO₂= 25-50 %, H₂=1-5 %, N₂=0.3-3 % with various minor impurities, notably NH₃, H₂S and halides. In this study, the three studied systems were tested at 1073 K in different simulated biogas compositions (CH₄/CO₂:H₂ 50/45/5, 60/35/5 and 70/25/5). The Nyquist plots revealed a decrease of impedance values with the increase of methane content in the biogas composition for the systems with SMM and SMMNb. While the system with Cr shows similar impedance in the three simulated biogases mixtures. All impedance spectra were fitting using an equivalent circuit with three arcs. The ASR values obtained are also presented in Table 1. It can see that the presence of CO₂ in the fuel favoured the reforming methane in the systems with SMM and SMMNb, while the system with Cr is not affected by the variation in the CH₄/CO₂ ratio.

### IV. CONCLUSION

Results revealed that the substitution of Nb or Cr by Mo in Sr₂MgMoO₆-δ structure affected in the electrochemical properties depending on the gas compositions, H₂, CH₄ or three simulated biogas mixtures. The ASR, obtained in symmetrical cell configuration, highlights that niobium has a negative effect in all studied atmospheres, with less significant differences in the simulated biogas mixtures. While the incorporation of Cr in the lattice reduces the ASR values in CH₄ and similar values were found in biogas mixtures with high content of methane.

### ACKNOWLEDGMENT

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PEMFC BIPOLAR PLATES MADE FROM PVDF/PET BASED COMPOSITES:
CRYSTALLIZATION, STRUCTURE AND THROUGH-PLANE RESISTIVITY

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Abstract – Polyvinylidene fluoride/poly(ethylene terephthalate) (PVDF/PET) based composites for PEMFC bipolar plates (BPs) were prepared at different crystallization temperatures and characterized by XRD, DSC, and resistivity setup. Composite conductivity was obtained by adding a mixture of carbon black (CB) and graphite (GR). To improve composite processability, its viscosity was reduced by using a small amount of cyclic oligomers of butylene terephthalate (c-BT) and TPO elastomer. It has been proved that the resistivity was mainly governed by the network of CB/GR developed inside the PET phase, and decreasing the crystallinity of PET led to a decrease of through-plane resistivity, which is desirable for BPs.

Index Terms – Bipolar plate, Resistivity, Crystallinity, PEMFC.

I. INTRODUCTION

To date, three types of materials are used in PEMFC BPs [1]: metals, graphite and polymer composites. Metal BPs could offer good electrical conductivity but they are unable to resist corrosion. Although graphite BPs have high electrical conductivity, they are heavy, brittle and require machining, leading to higher costs. Some polymers are deemed to be good materials for BPs because they have corrosion resistance and ease of processing. However, their resistivity is so high that conductive additives, such as CB and GR, have to be added in order to ensure electrical conductivity. For the sake of decreasing the resistivity, an excess of conductive additives is generally added to the polymer matrix leading to a decrease of BP mechanical properties. We recently developed BP materials based on a co-continuous PVDF/PET mixture in which a mixture of CB/GR was incorporated [2]. These conductive materials allowed us to develop a BPs having a through-plane resistivity of around 0.3 Ω·cm. In this work, we based our research on previously developed PVDF/PET composites [2] to further investigate the relation between polymer crystallization temperature/degree of crystallinity and BP resistivity.

II. EXPERIMENTAL

PVDF (Kynar®720) from Arkema, USA, and PET (PET 9921w) from Eastman, USA, were used. CB and GR additives were Printex XE-2 (Degussa-Hüls, Germany) and Timrex KS-75 (Timcal, USA), respectively. c-BT oligomer (160 Resin) was from Cyclic Corp., USA. Compared to the PVDF/PET based composites developed in our previous work, a small quantity of c-BT oligomer (3.7 wt.%) and TPO (4.9 wt.%) were added to decrease composite viscosity and to facilitate the demolding of BPs. The PVDF/PET based blend composition is detailed in Table 1. After blending (10 min @ 280°C) using a HaakeBuchler internal mixer (50 rpm), the prepared composite was taken out then placed into a BP mould with serpentine flow channels and 2 mm in cavity thickness. BP compression molding was done at 280°C for 15 min under a force of 2 tons using a CARVER compression machine. The mold was then cooled down to the desired crystallization temperatures (200°C, 180°C, 160°C, 140°C and 20 °C) at 40°C/min then maintained at these temperatures for 3 h. After crystallization, the mold was quickly cooled to room temperature in order to maintain the developed crystallinity of the BP sample.

III. RESULTS AND DISCUSSION

The effect of the cooling rate on composite crystallization was investigated by DSC (Fig. 1). The increase of the crystallization temperature, T1, of the PET phase indicates that the ability to nucleate for PET inside the composite was enhanced compared with pure PET. The T2 peaks correspond to the crystallization of PVDF phase, which decreased from 139.6 to 126.1°C when cooling rate was increased from 5 to 40°C/min. Those values were lower than those of pure PVDF at the same cooling rates [3]. So the nucleation ability of PVDF phase was weakened compared with pure PVDF. The
crystallization peaks T3 are attributed to the crystallization of the small c-BT molecules. The melting behavior of PVDF/PET based composites crystallized at different temperatures is depicted in Fig. 2 and Table 2. As shown, the composite sample crystallized at 20°C showed four melting temperatures: 133°C (for c-BT phase), 160.5°C and 166.4°C (for PVDF phase) and 224.2°C (for PET phase). The two melting peaks of PVDF phase are lower than that of pure PVDF (170°C), which is an indication of the presence of non-perfect PVDF crystals. For crystallization at 180 or 200°C, only PET phase crystallizes, and when the composite was rapidly cooled to room temperature, the PVDF phase did not have enough time to crystallize properly leading to many defective crystals, which decreased the melting temperature of PVDF phase. Table 2 shows the degree of crystallinity Xc, Xc,(PVDF phase) and Xc,(PET phase) at five different crystallization temperatures (Tc). Results show that Xc, (PET phase) decreased with decreasing the Tc. The two temperatures 180 and 200°C were not the appropriate Tc for PVDF phase since they were above PVDF melting temperature. So after treatment at these temperatures, composite samples were rapidly cooled down to room temperature leading to PVDF crystals with many defects. Table 3 shows that Xc,(PVDF phase) was higher than Xc, (PET phase), respectively at lower Tc. So the degree of crystallinity of the whole PVDF/PET based composite exhibited the similar trend as that of PVDF phase. In the present work, we measured the through-plane resistivity of PVDF/PET based composites crystallized at different temperatures and the corresponding results are presented in Table 3. It was found that composite through-plane resistivity decreased with decreasing Tc, except for composites crystallized at 180°C where the resistivity was the lowest (0.63 Ω.cm). For Tc between 170 and 200°C, the resistivity decreases with decreasing Tc. For Tc lower than 170°C (i.e., below the melting temperature of PVDF), Table 3 shows that the resistivity of the PVDF/PET based blends decreases as Tc decreases. In this temperature range, PVDF and PET phases crystallize separately when the composite is cooled from melt. Since PVDF chain flexibility is higher than that of PET [2], PVDF will crystallize first and more easily than PET at the same temperature below 170°C. As a consequence, the stronger crystallization ability of PVDF phase leads to its volume shrinkage in the PVDF/PET based composite and the more amorphous and CB/GR filled PET phase becomes a more continuous phase, leading to lower resistivity values. Since below 170°C the degree of crystallinity of the PET phase decreases as Tc decreases, the through-plane electrical resistivity is consequently decreased.

REFERENCES

Table 1. Composition of PVDF/PET based composites

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight % (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>39.7</td>
</tr>
<tr>
<td>PET</td>
<td>31.2</td>
</tr>
<tr>
<td>CB</td>
<td>14.9</td>
</tr>
<tr>
<td>GR</td>
<td>5.6</td>
</tr>
<tr>
<td>c-BT</td>
<td>3.7</td>
</tr>
<tr>
<td>TPO-RP</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Table 2. Melting temperature and degree of crystallinity for PVDF/PET based composites crystallized at 20, 140, 160, 180, and 200°C.

<table>
<thead>
<tr>
<th>Tc (°C)</th>
<th>Tm,c (°C)</th>
<th>Tm,p (°C)</th>
<th>Xc,c (PVDF phase)</th>
<th>Xc,p (PET phase)</th>
<th>Through-plane resistivity (Ω.cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>161.5</td>
<td>228.4</td>
<td>45.1</td>
<td>50.1</td>
<td>0.69</td>
</tr>
<tr>
<td>180</td>
<td>161.2</td>
<td>228.3</td>
<td>45.9</td>
<td>50.1</td>
<td>0.63</td>
</tr>
<tr>
<td>160</td>
<td>164.9</td>
<td>228.4</td>
<td>45.9</td>
<td>50.1</td>
<td>0.75</td>
</tr>
<tr>
<td>140</td>
<td>151.7</td>
<td>231.7</td>
<td>45.9</td>
<td>50.1</td>
<td>0.70</td>
</tr>
<tr>
<td>20</td>
<td>161.5</td>
<td>228.4</td>
<td>45.9</td>
<td>50.1</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Fig. 1. Cooling DSC curves of PVDF/PET based composites

Fig. 2. Heating DSC curves (Tc= 20, 140, 160, 180 and 200°C)
Abstract – Perovskites and spinel oxides coatings were applied on the surface of a ferritic steel used as interconnects for solid oxide electrolyser cell (SOEC) working at 800°C. This work presents new results obtained in the H₂/H₂O side. The experiments were performed for 3000h on uncoated K41X (AISI 441) steels. The application of perovskite (La₁₋ₓSrₓMnO₃₋δ) or spinel oxide (Co₃O₄) coatings improved the behavior of the steels and consists in interesting opportunities to use the K41X steel as interconnect for hydrogen production via high temperature steam electrolysis.

Index Terms – High temperature electrolysis, hydrogen, interconnects, ferritic steels, perovskite and spinel coatings.

I. INTRODUCTION

High temperature steam electrolysis (HTE) represents a clean way to produce hydrogen. It works as an inverse fuel cell, using air at the anode side and water vapour at the cathode side. As for SOFCs technology, a major technical difficulty related to the high temperature steam electrolysis is the development of interconnects working efficiently for a long period (around 25000 hours). Ferritic stainless steels are among the most promising materials, due to their good high temperature corrosion resistance and their quite good electrical conductivity. A commercial alloy containing 18 wt. % of chromium, K41X (AISI 441), was tested as interconnect at 800°C in Ar/1%H₂/9%H₂O atmosphere (cathode side of HTE) for 3000 hours. The electrical conductivity was evaluated in the same atmosphere for 100 hours. The tests evidenced that uncoated K41X steel is not suitable for HTE interconnect application in H₂/H₂O atmosphere. As a consequence, coatings, composed of spinel (Co₃O₄) or perovskite (La₁₋ₓSrₓMnO₃₋δ) phases, were tested. These coatings showed in a previous paper beneficial effect in the anode side [1]. The study allows understanding interconnects degradation process and the beneficial role played by the surface coatings.

II. EXPERIMENTAL CONDITIONS

The material selected for this study, K41X (AISI 441), is a commercial stainless steel containing 18 wt. % of chromium (Fe - 18%Cr - 0.58%Si - 0.52%Nb - 0.25%Mn - 0.14%Ti). The as-received samples were cut into squares of 10 mm x 10 mm and 1 mm thick.

The perovskite coatings, LSM (La₁₋ₓSrₓMnO₃₋δ), were prepared by screen-printing process, followed by 5 hours at 850°C in air, in order to improve the compacity of the coating and its adhesion to the substrate. The spinel coatings (Co₃O₄) were applied on the K41X surface by physical vapour deposition (PVD) technique, followed by a crystallisation treatment performed during 10 hours at 800°C in air.

All the experimental tests were performed at 800°C for 3000 hours in a flux of controlled Ar/1%H₂/9%H₂O gas, representing the SOEC cathode side. Area specific resistance (ASR) measurements were performed in-situ for 100 hours by using a 4-point set up [2]. The voltage value is measured by applying a constant current of 150 mA. According to the Ohm’s law (R=V/I), the electrical resistance is estimated. ASR parameter is then obtained by multiplying this resistance by the sample
surface (ASR = R x S).

The morphologies and the chemical composition of the corrosion products were characterized by scanning electron microscope (FEG-SEM) coupled with an energy dispersive X-ray (EDX) spectrometer. Phase composition of the oxide scales was determined by X-ray diffraction (XRD).

III. RESULTS

After 3000h ageing in Ar-1%H2-9%H2O, the oxide scale formed on uncoated K41X is around 5 µm thick and composed of small crystallites rich in Cr, Mn with a little Fe. XRD indicates the presence of (Cr,Mn,Fe)3O4, Cr2O3 et (Mn,Fe)O phases (Fig. 1). The ASR parameter is 0.44 Ω.cm²; it is too high to use interconnect without conductive coatings.

The oxide morphology of the Co3O4 coated sample is totally different and the surface of the sample is covered with large crystals of metallic Co (Fig. 2). Below this metallic layer, the oxide scale (around 3 µm thick) is composed of (Cr,Mn)3O4 (external part) and Cr2O3 (internal part). The presence of a metallic layer is due to the reduction of the spinel phase into Co during the exposure in H2/H2O atmosphere. It explains why the ASR parameter is excellent when the spinel oxide coating is applied (ASR=0.038 Ω.cm²).

The LSM coated alloy presents the same oxide mainly composed of (Cr,Mn)3O4 (external part) and Cr2O3 (internal part), but it is thinner (1 µm thick) compare to the previous samples. The LSM coating is still present and does not show any modification after 3000h in Ar/1%H2/9%H2O. The ASR is 0.06 Ω.cm²; this very low value allows a possible application of LSM coatings on interconnects.

A crack parallel to the LSM coating/thermally grown oxide layer is visible in Fig. 3. This crack probably formed during the polish cross-section preparation, as no detachment was observed on the surface observations.

IV. CONCLUSION

The application of a spinel oxide, Co3O4, and a perovskite oxide, La1-xSrxMnO3-δ, improved the behavior of a ferritic steel used as interconnect for high temperature electrolysis. The ageing after 3000h in H2/H2O atmosphere evidenced a better behaviour of the coated samples. ASR measurements showed a beneficial effect of the coatings, leading these two coatings as very promising for interconnects protection.

ACKNOWLEDGMENT

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PERFORMANCE DEGRADATION STUDY ON POLYBENZIMIDAZOLE FUEL CELLS SUBJECTED TO DIFFERENT AGEING TESTS

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Abstract - Polybenzimidazole (PBI) based High Temperature Polymer Electrolyte Membrane (HTPEM) fuel cells represent a possible alternative to Nafion based PEM (LTPEM), especially for micro Combined Heat and Power (CHP) applications: due to their high CO tolerance HTPEMs allow fuels other than pure hydrogen to be used by means of a simplified fuel processing unit. Nevertheless, costs, performance and performance degradation issues still have to be overcome to achieve widespread commercialization. The research presented aims to evaluate the performance degradation of PBI based HTPEM fuel cells subjected to different operating conditions.

Index Terms – HTPEM, Polybenzimidazole, Degradation, Fuel Cells.

I. INTRODUCTION

Polybenzimidazole (PBI) based High Temperature Polymer Electrolyte Membrane (HTPEM) fuel cells demonstrated a good lifetime under steady state operations [1]. However higher performance degradation rates are expected when HTPEM operate under realistic conditions, such as load and start/stop cycling [1, 2, 3]. The presented research aims to compare the performance degradation of HTPEM fuel cells subjected to different performance ageing procedures which simulate realistic fuel cell operating conditions. Three different performance ageing procedures have been considered and applied on three HTPEM fuel cells. Collected data can support the identification of optimal operating strategies. The aged MEAs will be also subjected to a catalyst nanomorphological analysis using Small Angle X-ray Scattering techniques (SAXS) [3].

II. METHODOLOGY

A. Ageing procedures

Three different ageing procedures have been considered and applied on three HTPEM Membrane Electrode Assemblies (MEAs) operated with hydrogen and air. The MEAs have been labeled as MEA (a), MEA (b) and MEA (c). MEA (a) has been subjected to 100,000 triangular sweep cycles between 0.01 A/cm² and 0.5 A/cm². MEA (b) has been subjected to 100,000 triangular sweep cycle between Open Circuit Voltage (OCV) and 0.5 A/cm². During load cycling, MEA temperatures were kept constant at 160 °C. MEA (c) has been subjected to 650 start/stop cycles. Start/stop procedures consist of temperature cycles from 40 °C to 160 °C. A 10 A load is imposed from 120 °C to 160 °C.

Figure 1. Imposed current variation for MEA (a), MEA (b) and start/stop procedure implemented for MEA (c).
During cool down phase, from 120 °C to 80 °C both anode and cathode sides have been purged with nitrogen. Figure 1 describes more in detail the current profile for MEA (a), MEA (b) and start/stop procedure for MEA (c). In order to measure cell performance degradation, fuel cell potential variation with time and polarization curves have been recorded for all MEAs.

III. EXPERIMENTAL RESULTS

Figure 2 shows the polarization curves for MEA (a), (b) and (c), measured at the beginning and at the end of the ageing procedures.

A. Load cycling - MEA (a) and MEA (b)

The performance loss, in terms of potential reduction, between the start and the end of the 100,000 load cycling procedure is less than 6% for both MEAs. However, it is possible to observe that the cell potential decreases as current density increases: at 200 mA/cm², cell potential loss is respectively 2% and 3% for MEA (a) and MEA (b); at 600 mA/cm² performance degradation is respectively 4% and 5% for MEA (a) and MEA (b). A higher performance loss for MEA (b) can be related to OCV operation.

B. Start/stop cycling - MEA (c)

For MEA (c), the performance loss after 650 start/stop is 9% at 200 mA/cm². However it has to be observed that a significantly performance degradations occurs only after 450 cycles. Before 450 cycles the performance loss is 1% at 200 mA/cm² and 6% when the cell is operated at 600 mA/cm². Between 450 and 650 a high performance loss is measured: 8% at 200 mA/cm² and 12% at 500 mA/cm². In contrast with load cycling procedure, start/stop operation influences OCV: at the beginning of the test, OCV is equal to 0.9 V while is 0.7 V at the end the test.

IV. CONCLUSION

The investigated load cycling procedures cause a performance loss, in terms of cell potential, of less than 3% when the cell is operated at 200 mA/cm². The measured degradation rate is about 0.20 µV/cycle or 40 µV/h considering 450h of operations. In [1] a smaller performance degradation rate, 5 µV/h, is found for a fuel cell operated at constant load condition for 6000h. It can be concluded that the applied load cycling procedures significantly affects performance degradation. It can be also observed that operating the cell at OCV increases the degradation rate: higher degradation rates are calculated for both load cycling with OCV operations (MEA (b)) and start/stop cycling (MEA (c)). Higher degradation rates can be related to Pt catalyst crystallite size increase which is associated to high cell potential [4]. Furthermore, electrolyte redistribution due to volume expansions/contractions is believed to influence MEA durability during start/stop cycling [1]. In particular, for start/stop cycling, the performance loss is about 12 µV/cycle for the first 450 cycles. Between 450 and 650 start/stop cycles degradation rate increases to 0.27 mV/cycle. In [1], 240 start/stop cycles have been made on the same type of MEA without considering purging operations. A cell potential loss of 0.20 mV/cycle has been measured which is higher than the performance loss measured in this work for the first 450 cycles. As expected, purging the cell with nitrogen appears to increase fuel cell life.

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ESD – EFFICIENT SYNERGY DRIVE FOR ELECTRIC VEHICLES REGARDING AN INTEGRATED COMPRESSOR FOR FUEL CELL CHARGING IN COMBINATION WITH A POWERSHIFTABLE DUAL-SPEED TRANSMISSION

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Abstract - High expectations are set in electromobility, especially in Germany, linked with the political aim of bringing more than a million licensed electric vehicles on the streets by 2020. According to the official statistics, however, only 4,541 electric vehicles and 47,642 hybrid vehicles were registered in Germany by January 2012, which also includes any other type, such as range extender and plug-in hybrid systems. A major reason for the low market shares of electric vehicles are the currently huge costs for customers, more than a third of which are caused by the traction battery and the fuel cell system. Local emission-free driving furthermore often involves mobility restrictions, e.g. limited energy capacities, environmental conditions reducing the cruising range or potential problems during a battery recharge. One key-approach to increase efficiency and reducing costs is the principle of integrated design and optimization of powertrain components in order to integrate sub-systems like the fuel cell charging compressor into the vehicle powertrain.

Index Terms – fuel cell compressor, integrated efficient powersplit drivetrain, twin motor powertrain, seamless 2-speed (dual speed) transmission

I. INTRODUCTION
The new integrated system drive for electric vehicles, which was developed at Chemnitz University of Technology (CUT), combines the electric traction motor, which has a high power capacity, with today’s separately driven fuel cell charging systems. The electric motor for the fuel cell air compressor will thus be expanded and integrated into the transmission system to utilize said drive specifically for driving at partial load. In this way the required driving power can be distributed between both electric drives with an operation strategy, which reduces particularly the losses in many driving situations due to the efficient map utilization. The integration of both system drives into a compact gearbox design also reduces the required installation space and the system weight to its minimum.

II. ESD – EFFICIENT SYNERGY DRIVE

A. System Functionality
The ESD-powertrain concept allows the utilization of all degrees of freedom in order to reduce energy losses in the powertrain. The main feature of this integrated powertrain concept is the dual use of an electric motor with a low power capacity for fuel cell charging and driving the vehicle at partial load. Simultaneously the concept also includes a typical traction motor with a higher power capacity. Thus the mechanical power consumed by the vehicle and the fuel cell air compressor can be efficiently distributed among both motors in every operation scenario with an operating strategy. The specific design process for the electric powertrain components allows for an efficient utilization of the loss maps.

Figure 1 shows an exemplary powertrain structure of the ESD concept for a central drive architecture. Both electric motors enable the continuous torque transfer, which allows, in combination with said transmission structure, the seamless changing of two modes in many driving situations. Similar to the function of a DCT, one electric motor powers the vehicle, while the other one synchronizes itself to the speed of the respective mode. According to the ESD-concept, each power path is used independently in every mode, because the output torque is often provided by both electric machines.

Another advantage of the concept is the low kinetic requirements on the shifting actuator system. Because of the torque transfer and the active synchronization with both electric motors, no friction work needs to perform by the actuator system. Aside from the application of a highly efficient electromotive actuator, the drag losses can be reduced due to the elimination of friction based shifting elements.

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The remaining transmission elements, such as spur gears, dog clutches and bearings require only a simple and efficient oil mist lubrication, which reduces the hydraulic system effort and the costs to a minimum.

**B. Operating Modes**

**TABLE I**

<table>
<thead>
<tr>
<th>Mode</th>
<th>Operating modes for ESD-Hybrid strategy</th>
<th>Speed</th>
<th>Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>High torque launching and high gradeability, 100% battery power, 0% fuel cell power</td>
<td>&lt; 40 kph</td>
<td>All</td>
</tr>
<tr>
<td>2</td>
<td>Main mode for usual driving situations, 100% fuel cell power with high efficiency, Efficient power split between EM1 and EM2, Battery used for dynamic load peaks</td>
<td>&lt; 70 kph</td>
<td>&lt; 10 kW</td>
</tr>
<tr>
<td>3</td>
<td>Overdrive mode for higher speeds, Mixed powerflow from Fuel Cell and Battery, Fuel Cell compressor with EM2 decoupled from the powertrain, EM1 with low speeds for driving</td>
<td>&lt; 70 kph</td>
<td>&gt; 10 kW</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 70 kph</td>
<td>&gt; 10 kW</td>
</tr>
<tr>
<td>4</td>
<td>Economy mode for constant speed driving and low output power, 100% fuel cell power with high efficiency, Only EM2 powering the Fuel Cell compressor and the vehicle with highest system efficiency</td>
<td>&lt; 50 kph</td>
<td>&lt; 10 kW</td>
</tr>
<tr>
<td>5, 6</td>
<td>Safety modes for mechanical decoupling between road and the electric machines</td>
<td>All</td>
<td>All</td>
</tr>
</tbody>
</table>

Mode 2 is the most important mode for high system efficiencies, which is used for low and medium speeds and low output power. This case represents more than 65% of a typical vehicle load cycle and enables the highest energy consumption benefit by the utilization of three main effects at ESD. Firstly the power demand of the fuel cell air compressor, which can be coupled on the powertrain, increases the load level of the overall system. This leads to higher efficiencies and lower losses in the electric machines and the power inverter compared with a separately driven air compressor and a single traction motor for driving. Secondly the whole power demand can now be distributed on both electric motors EM1 and EM2 via the mechanical coupling in the transmission. This dynamic torque distribution allows the loss-optimal controlling of the electric machines, the AC/DC inverter and the DC/DC converter. This effect is furthermore gained by the mechanical twin-speed transmission which enables a lower speed for the high torque machine EM1. This additionally reduces the iron losses in the electric machine. With these synergistic effects the energy consumption benefit can be estimated between 7% and 14% for real driving cycles.

**III. CONCLUSION**

The ESD-concept (Efficient-Synergy-Drive) allows the utilization of all degrees of freedom to reduce losses in the powertrain of electric vehicles. The main feature of the integrated powertrain concept is the dual use of an electric motor with a low power capacity for fuel cell charging and driving at partial load. As before the powertrain also consists of a traction motor with a high power capacity. Thus the mechanical power consumed by the vehicle and the fuel cell air compressor can be efficiently distributed among both motors in every operation scenario with an operating strategy.

The specific electrical design and the transmission structure leads to an efficient utilization of the loss maps. The investigations shown that the widely known consumption advantage of two-speed transmissions (see [1] and [2]) can also be achieved by applying two electric machines with different power capacities and different speeds. With ESD it is rarely necessary to shift gears only to fulfill efficiency requirements, which also enables the prevention of frequent speed synchronizations.

Furthermore the electric motors enable the continuous torque transfer, which allows the seamless shifting process of two modes in many driving situations.

One central issue of the concept is the intelligent integration of the power intensive fuel cell air compressor into the drivetrain system. The power demand of the fuel cell air compressor increases the load level of the electric machines and the power inverter. This leads to higher efficiencies and lower losses compared with a separately driven air compressor and a single driving motor. With these synergistic effects the energy consumption benefit can be estimated between 7% and 14% for real driving cycles.

**REFERENCES**


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CHARACTERIZATION OF GDL TREATED WITH PERFLUOROPOLYETHERS FOR PEMFC BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

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Abstract - Two different gas diffusion layers (GDLs) having the same textile properties (i.e. density, warp, weft and weight), produced by an Italian Company (Saati), but coated with two different fluoro polymers, were investigated. Particularly one of them was coated with a conventional fluoropolymers such as PTFE and was used as reference, the other was treated with a linear perfluoropolyether (PFPE) peroxide. The thermal decomposition of a linear PFPE peroxide produced linear PFPE radicals that covalently bonded the unsaturated moieties on the surface of GDL. Perfluorinated radicals can directly bond to the carbonaceous structure without any spacer that could decrease both thermal and chemical stability of the resulting materials [1]. Resulting material hydrophobicity has been verified by contact angle measurements. In order to evaluate electrochemical properties, the samples were tested in a cell assembly and Electrochemical Impedance Spectroscopy (EIS) was employed to assess ohmic resistances and the different nature of voltage losses [2].

Index Terms – Gas Diffusion Layers, PEM, Perfluoropolyethers, EIS

I. INTRODUCTION
A gas diffusion layer (GDL) is inserted between the BP and the MEA. The GDLs in a PEM is a critical component because it must transport reactant gases, electrons and heats and also remove reaction products (liquid and gas). As such, the GDL is a critical link between the electrochemical reaction and the system engineering needed to construct a fuel cell [3], and it is the focal point of this work.

An innovative perfluoropolymer was used to coat the surface and its properties were investigated and compared with a reference sample prepared with PTFE.

II. EXPERIMENTAL

Sample preparation
The Gas Diffusion Layer used in this study was a commercial carbon cloth (S5 purchased by SAATI S.P.A. Italy). The PFPE peroxide was a high molecular weight FOMBLIN® Z PFPE (Solvay Specialty Polymers). For sake of comparison a GDL was coated with a conventional fluoropolymers such as PTFE (Algodlon® D 1214X Solvay Solexys) and was used as reference.

The GDL sample was dipped for 1 min in the solution of PFPE peroxide in a glass vessel, using Galden® HT55 as fluorinated solvent. The solvent was evaporated at 60°C. After that the peroxide was thermally decomposed starting from a temperature of 150 °C to 195 °C, by increasing it stepwise at the rate of 15 °C/h, and then heated at 200 °C for four hours. Thereafter the sample was washed with the perfluorinated fluid in order to remove the unlinked PFPE and with water to hydrolyze perfluoroacetyl end groups [1]. The sample was finally dried at 200°C in high vacuum for 24h. The final amount of PFPE was about 0.24 %C wt.

The reference sample, coated with PTFE, by dip-coating. After drying, the sample was sintered (350°C) to obtain the solidification and cross link of the PTFE in the surface of the carbon cloth. The final amount of PTFE was about 10%wt.

Contact angle
In order to evaluate the hydrophobicity of the samples prepared, a contact angle measurement was assessed. The contact angle instrument was a Data Physics OCA 150 and the software was SCA20 version 2.3.9. build 46. The contact angles were measured directly on the carbon cloth surface, putting above water droplets of 4µl. Usually superhydrophobic surfaces are characterized by a contact angle above 150°. Contact angles of water droplets deposited directly on the surface of unmodified carbon cloth are not stable and quickly absorbed by its porous structure. Taking in consideration the sample coated with PFPE (0.24% wt), the measured contact angle is 172°. The reference sample coated with PTFE (10% wt) is about 150°.

**Electrochemical performances**

A single cell (Fuel Cell Technologies) was used for the steady state polarization measurements. The cell used in the present work has a single serpentine at the anode and a triple one at the cathode. The employed membrane electrode assembly (MEA) was a catalyst coated membrane (CCM) consisting of Nafton® 212 with a thickness of 50 µm and the catalyst layers coated directly onto such membrane. The active area was 25 cm² and two different platinum loadings were used: 0.3 mg·cm⁻² for the anode and 0.6 mg·cm⁻² for the cathode. Hydrogen and air were used as the anodic and the cathodic feedings, respectively. The flow rates were controlled and detected by a calibrated flow meter; the degree of humidity and the gas temperature were controlled by humidifiers and temperature controllers. One temperature (60°C) and two cathodic relative humidities (60 and 100%) were adopted; while, the hydrogen relative humidity was fixed at 80%. An electronic load (RBL488-50-150-800) measured and controlled voltage, current and electric power produced; to obtain a polarization curve the cell voltage was changed from OCV to 0.15 V with steps of 0.05 V, keeping it constant for 400 seconds for each value and at each step the resulting average current was recorded (potentiostatic mode). The polarization phenomena during the running of the FC were investigated via Impedance Spectroscopy in Galvanostatic mode at different current densities. The EIS spectra were recorded at OCV and from low to high current density (0.1 – 1.0 A/cm²).

The steady state current density-potential and current density-power density curves of the cell assembled with the PFPE-based GDL are reported and compared to those obtained with a traditional GDL treated with PTFE in figure 1. Firstly, it can be noticed that the presence of PFPE allowed to improve the electrical performance of the cell for both the operating condition here tested. In particular PFPE sample shows the performance, in terms of maximum power density reached and slope of the polarization curve. Thus, the novel GDLs seem to be able to reduce the ohmic resistance of the whole system as confirmed by EIS. Moreover the PFPE-GDL shows lower values of polarization and diffusion resistance in all the experimental conditions investigated.

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STRUCTURAL AND ELECTROCHEMICAL PROPERTIES OF NANOSTRUCTURED PD-PROMOTED \( \text{La}_{(1-x)}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta} \) CATHODES FOR IT-SOFCs

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Abstract - Nanostructured \( \text{La}_{(1-x)}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta} \) perovskites and \( \text{Ce}_0.8\text{Gd}_{0.2}\text{O}_{2-\delta} \) fluorite powders were successfully prepared by citrate sol-gel method starting from nitrates of the metal cations. Calcined powders were characterized by XRD and Rietveld refinement, EXAFS and XPS analyses. Electrochemical impedance spectroscopy (EIS) measurements on symmetric cells were performed to evaluate the use of \( \text{La}_{(1-x)}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta} \), as a cathode material for intermediate temperature solid oxide fuel cells based on gadolinium doped ceria electrolytes. Moreover, to improve the performance of LSCF, the effect of Pd doping was investigated. Our results demonstrate that LSCF with 20\% mol Fe content (LSCF0.2) has lower ohmic resistance (\( R_{\text{ohmic}} \)) compared to LSCF with Fe 80\% mol (LSCF0.8). In addition, Pd doping decreased both, ohmic (\( R_{\text{ohmic}} \)) as well as polarization (\( R_p \)), resistances for LSCF samples. The best characteristics as cathode at intermediate operating temperatures were found for LSCF0.2-Pd at 690 °C with area specific resistance of 0.07 \( \Omega \) cm\(^2\).

Index Terms - IT-SOFC, Cathode, LSCF, EIS.

I. NOMENCLATURE

LSCF - \( \text{La}_{(1-x)}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta} \).

LSCF0.2 - \( \text{La}_0.6\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta} \).

LSCF0.2-Pd - \( \text{La}_0.6\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.17}\text{Pd}_{0.03}\text{O}_{3-\delta} \).

LSCF0.8 - \( \text{La}_0.6\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta} \).

LSCF0.8-Pd - \( \text{La}_0.6\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.77}\text{Pd}_{0.03}\text{O}_{3-\delta} \).

GDC - \( \text{Ce}_0.8\text{Gd}_{0.2}\text{O}_{2-\delta} \).

II. INTRODUCTION

In recent years great efforts have been devoted to develop intermediate temperature SOFCs (IT-SOFCs), operating at 500-800 °C, in order to reduce the high cost and materials degradation typical of standard high-temperature devices. Lowering the operating temperature, however, decreases the electrode kinetics, in particular the oxygen reduction at the cathode. To overcome these drawbacks new composition for cathode materials and a tight control of the cathode properties through new syntheses are required.

Lanthanum cobaltite doped with strontium and iron (LSCF) is a promising candidate for cathode for IT-SOFCs due to high electronic and ionic conductivity. Moreover, it has been reported that the performance of a LSCF cathode can be further enhanced by dispersing into the lattice a small amount of noble metals, such as Ag, Pt, Pd.

In the present work electrochemical characterizations of LSCF cathode materials with fixed La-Sr composition (x=0.4) and two different Fe content (y= 0.2 and 0.8, respectively named as LSCF0.2 and LSCF0.8) were carried out. Promotion of LSCF0.2 and LSCF0.8 by incorporation of palladium 3 mol\% was also investigated.

The synthesized LSCF and Pd-promoted LSCF cathodes were characterized by XRD and XPS techniques. Detailed structural investigations of Pd-promoted LSCF oxides were carried out by Rietveld analysis of XRD data and by EXAFS experiments.

III. EXPERIMENTAL

All LSCF perovskites were synthesized by sol-gel citrate method starting from La(NO\(_3\))\(_2\)·6H\(_2\)O, Sr(NO\(_3\))\(_2\), Co(NO\(_3\))\(_2\)·6H\(_2\)O, Fe(NO\(_3\))\(_2\)·9H\(_2\)O as precursors. The obtained gel was calcined at 350 °C 1 h, to promote citrate decomposition, and then at 800 °C 4 h (temperature rate 5 °C/min). LSCF0.2-Pd and LSCF0.8-Pd were also prepared, in the same conditions as described above, using Pd(NO\(_3\))\(_2\)·xH\(_2\)O as palladium precursor. The synthesis of the GDC electrolyte was performed starting from Ce(NO\(_3\))\(_3\)·6H\(_2\)O and Gd(NO\(_3\))\(_3\)·6H\(_2\)O as metals precursors in presence of citric acid. The final fluorite phase was obtained after calcination at 700 °C 4 h (temperature rate 5 °C/min).
Symmetric cell fabrication
Dense electrolyte pellets for impedance measurements were prepared by weighing 0.8 g of GDC powder into a 20 mm diameter pellet press and compacting by uniaxial pressing with 2 tons for 10 minutes. Pellets were sintered at 1300 °C for 4h.

The pellet surfaces were carefully polished before the electrode deposition. LSCF powders, previously calcined at 800 °C, were mixed with PEG (Mw 400) and ethanol to form a slurry and subsequently used to coat the GDC electrolyte sintered pellets. After coating one side of the pellet, it was left for 30 minutes at 160 °C for drying. Then the procedure was repeated on the other side. The resulting coated LSCF pellet was sintered at 900 °C for 1h.

IV. RESULTS AND DISCUSSIONS
XRD patterns with Rietveld refinements of all LSCF and LSCF-Pd, prepared and subsequently sintered at 1300 °C, revealed the presence of a single phase with rhombohedral distorted perovskite-type structure and space group R-3CH. Fig.1 shows fitted EXAFS spectrum of the sample LSCF0.8-Pd, which describes the Pd local environment from the sum of contributions taking into account the fcc and Pd-O distances. Comparison of the fourier transforms of the data and the calculated structure in Fig.1 it is evident that a signal around 3.86 Å is missing. Furthermore, coordination number of the first shell involving the Pd-O distance is greater than four, suggesting that the Pd cation is not present as PdO phase. It should be noted that the Pd-Pd distances in the oxide structure are 3.03 and 3.34 Å, respectively.

Figure 1. EXAFS fitting of LSCF0.8-Pd sample.

These results suggest palladium dispersion into the LSCF perovskite structure.

Electrical conductivity investigations of LSCF samples by means of Four-Point probe using the Van der Pauw method were compared with results obtained by Electrochemical Impedance Spectroscopy (EIS) measurements. EIS tests were carried out in the range of temperature 600-700 °C on symmetric cells of LSCF electrodes deposited on GDC electrolyte.

Pd-doping improved the performance of both LSCF0.8 and LSCF0.2 by decreasing the ohmic and the polarization resistance of the symmetric cell. In particular, as shown in Fig. 2, GDC symmetric cell with LSCF0.8-Pd gave ASR values of 3.36 Ω cm² to 0.70 Ω cm² from 610 up to 690 °C, which are lower than previously observed for LSCF0.8 in the same temperature range (6.91 Ω cm² to 1.53 Ω cm²). The best characteristics as cathode at intermediate operating temperatures were found for LSCF0.2-Pd at 690 °C with area specific resistance of 0.07 Ω cm².

V. CONCLUSION
LSCF and GDC powders prepared by sol-gel citrate method are porous and consist of a single perovskite phase, whereas on LSCF-Pd doped samples, palladium was incorporated into the LSCF perovskite structure. Porous cathodes and dense electrolyte pellets were therefore obtained.

Our results show that area specific resistance of LSCF/SDC/LSCF is beneficially influenced by Pd-doping and iron has a slightly negative effect on the ASR, so the best characteristics as cathode at intermediate operating temperatures were found for LSCF0.2-Pd at 690 °C with area specific resistance of 0.07 Ω cm² and R_ohmic of 5.51 Ω cm².
BATTERY AND FUEL CELL VEHICLES – A CONCEPT TO INCREASE EFFICIENCY AND RANGE

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Abstract - The presentation highlights the differences between battery and fuel cell powered e-mobility and which concept is more or less useful for short and long travel distances. Furthermore, to achieve higher efficiencies and to reduce system complexity – respectively costs – for both concepts, at Chemnitz University of Technology (CUT) a new drivetrain layout, called ESD (Efficient Synergy Drive) was developed. It combines two electric drives nested in one package, one for lower power demands during driving situations at constant speed, one for high power demands at high acceleration conditions. Both are linked by a gearbox that enables efficient power distribution.

Index Terms – battery and fuel cell electric vehicles, system layout, efficient synergy drive, driving range

I. INTRODUCTION

Electromobility nowadays is seen as one of the key technologies towards sustainable mobility. Therefore two options are focused. One is the battery electric vehicle with its high overall efficiency, directly storing electric energy and converting it via an electric drive on a very short way into kinetic energy, propelling a vehicle. The other is the fuel cell electric vehicle, usually storing the energy with a chemical energy carrier and converting it with a fuel cell to electricity which then is used to power the electric drive for propulsion. Specific differences between these concepts amongst others are [1]:
- energy density for on board storage,
- filling/charging duration,
- types and costs of infrastructure,
- method for energy distribution and labeling
- achievable range allowing vehicle comfort features.

Nevertheless both concepts have in common that several auxiliary units are necessary, some for operating the system, some for driving comfort, e.g. an air conditioning compressor or an air compressor to charge the fuel cell. These units have to be driven by an extra electric motor due to the absence of a rotating drive section like the crank shaft in a typical internal combustion engine (ICE).

These additional, independently assessable components on the one hand side lead to a higher flexibility in system control. But on the other side they lead to an increase of system weight, volume, costs and in most cases to an efficiency drop.

Based on these insights and considering the fact, that the power output from some of the auxiliary devices’ drives could be suitable to propel a vehicle under certain driving conditions, some new driving concepts for battery and fuel cell powered vehicles were developed.

II. OPTIMIZATION OF DRIVE SYSTEM LAYOUT

Below an overview of conventional drivetrain layouts for battery and fuel cell powered vehicles is given and then a possible optimization concerning the coupling of an auxiliary device is explained.

A. Battery vehicle system layout

A typical battery vehicle system consists of a battery, an inverter and an electric drive. For comfort issues an air conditioning compressor is added, see Fig. 1.

![Fig. 1: Simplified battery vehicle system layout](image)

An obvious optimization can be obtained by combining the
two electric drives and inverters to one drive unit, see Fig. 2.

![Fig. 2: Optimized battery vehicle system layout](image)

For this kind of optimization a special gear box unit is needed which allows the machine E1 as well as the machine E2 (or combined) to propel the vehicle. This development, called “Efficient synergy drive” (ESD) is described in detail in [2].

B. Fuel cell vehicle system layout

A typical fuel cell vehicle system consists of a fuel cell system, a hybrid battery, a power distribution unit (PDU), a DC/DC converter, an inverter and an electric drive. For charging the fuel cell an air compressor is needed, see Fig. 3.

![Fig. 3: Simplified fuel cell vehicle system layout](image)

In this case an optimization can be found by combining the air compressor drive and the main drive into one assembly, also together with the newly developed gearbox, see Fig. 4.

![Fig. 4: Optimized FC vehicle layout](image)

In difference to the air conditioning compressor described under A. with its own built-in volume control, e.g. established by a swash plate, the usual screw-type compressor for charging a fuel cell has a fixed built in volume ratio. So the compressor drive speed needs to be controllable independently to match the fuel cell’s mass flow requirements. A solution is then either designing the fuel cell as a range-extender wherein the load point is adaptable to each driving condition. Or another solution is mounting a continuous variable transmission to give the compressor the needed speed.

First estimations for overall efficiency and range increase for battery and fuel cell powered vehicles with the optimized system layouts show a considerable increase, although exact computations to confirm results are still to be completed.

III. CONCLUSION

The main issue of both optimized concepts is the use of the auxiliary drive for propelling the car during phases with only relative low power output needed, e.g. under driving conditions with constant speed. Because of a high percentage of these driving conditions included in most standard driving cycles, the use of the smaller electric drive with high efficiencies at full load instead of the bigger drive with lower part-load efficiencies, leads to increase of overall efficiency and range for battery and fuel cell electric vehicles.

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ADSORPTIVE REMOVAL OF H2S IN BIOGAS CONDITIONS FOR HIGH TEMPERATURE FUEL CELL SYSTEMS

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Abstract – Desulphurization represents a crucial step in fuel processing for high temperature fuel cell applications, because of the stringent requirements of fuel cell catalysts. Moreover, when fuel cell stacks are used in a micro-CHP system, the necessity to reduce the amount of H2S present in the fuel is paramount. The possibility to use a renewable energy source, as biogas from anaerobic digestion instead of natural gas, to feed a fuel cell stack, could have a significant impact in terms of fossil fuels saving and environmental conservation. In this work, desulphurization tests for H2S removal are carried out in biogas conditions, using commercial adsorbents, like activated carbons (AC), activated alumina, zeolite and sepiolite. The first part of the test campaign was focused on the definition of the material characterized by the best performance in terms of H2S adsorption capacity. Then, the influence on adsorption capacity of operating parameters, such as gas hourly space velocity (GHSV), humidity (Relative Humidity 50%) and gas matrix composition (N2, CH4, CO2 and a mixture of CH4 and CO2) was investigated, in order to obtain a compact filter with high removal activity.

Index Terms – Desulphurization, adsorption, biogas, activated carbons.

I. INTRODUCTION

One of the solutions that could contribute to decrease dependence from fossil fuels is represented by the exploitation of fuels from biomass through anaerobic digestion. The use of this renewable source determines a very low environmental impact, but the resulting biogas is generally poor in energy content [1]. For this reason, biogas can be exploited using a high efficiency conversion system, such as high temperature fuel cells, enhanced in a micro-cogeneration plant.

Biogas, depending on its source (landfill, agricultural waste, industrial wastewater, sewage sludge) can have different compositions, but, in general, it is mainly constituted by CH4 (45-75%) and CO2 (25-55%) [2]. Unfortunately, halogenated hydrocarbons, siloxanes and sulphur compounds can often be found in biogas. The main sulphur compounds present in biogas are hydrogen sulphide (100-1000 ppm), mercaptanes (0-100 ppm) and traces of COS and CS2. H2S represents one of the most harmful compounds for environment and working equipment. In fuel cell applications, H2S poisons both the reformer and the electrochemical gas sensor (MECCOS eTr, detection limit 0-1 ppm), able to perform an immediate and continuous reading. The concentration values were also verified, by gas chromatographic analysis, using a DANI GC 1000 equipped with a Restek Rxi-1ms column and a Flame Photometric Detector (FPD). All the pipelines and the fittings in the test bench are made of Teflon or stainless steel treated with Sulfinet® to prevent the adsorption of H2S on the working surfaces of the system and, therefore, to preserve ppm levels of active sulphur compounds.

For the test campaign, seven commercial materials were been selected, in particular four steam activated carbons (Norit RB1, RBAA1, RGM1 and Desotec Airpel Ultra DS), an impregnated activated alumina (Galipur S), a natural zeolite (ATZ) and a natural sepiolite. The adsorbent materials, originally pellet-shaped (activated carbons and activated alumina) or in granular form (zeolite and sepiolite), were ground and sieved, obtaining homogeneous powder with particle size in the range 250-355 μm. The H2S adsorption capacity (C_{tot} in mg/g) is calculated using the following equation:

\[ C_{\text{ads}} = \frac{Q_{\text{tot}} \cdot MW \cdot [C_{\text{in}} \cdot t_{1} - (t_{1} - t_{0}) \cdot 0.5]}{V_{m} \cdot m \cdot 10^{3}} \]

where:
- \( Q_{\text{tot}} \) = total gas flow rate (nl/h);
- \( MW \) = molecular weight (H2S=34 g/mol);
- \( C_{\text{in}} \) = inlet H2S concentration (ppmv);
- \( t_{1} \) = breakthrough time at 1 ppmv of outlet H2S concentration (h);
- \( t_{0} \) = breakthrough time at 0 ppmv of outlet H2S concentration (h);
- \( V_{m} \) = molar volume (24.414 nl/mol);
- \( m \) = mass of adsorbent material (g).

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III. RESULTS AND DISCUSSION

The first part of the experimental activity was focused on the definition of the best performed material in terms of \( \text{H}_2\text{S} \) adsorption. The used operating parameters were: \( \text{H}_2\text{S} \) inlet concentration 200 ppm, gas matrix \( \text{N}_2 \), GHSV 10,000 h\(^{-1}\), h/d (height of the filter; d=filter diameter) 0.32 and temperature 30°C. The results showed that the best performed material was the steam activated carbon Norit RGM1 impregnated with Cu-Cr salts (Fig.1 and Tab.1). Moreover, the other impregnated materials (Airpel Ultra DS, Norit RBA1A, treated with KOH, and Galipur S, impregnated with KMnO\(_4\)) exhibited significant values of \( \text{H}_2\text{S} \) adsorption capacity. Zeolite and sepiolite presented very low activity in terms of \( \text{H}_2\text{S} \) adsorption and, therefore, they are not suitable for this type of application, even if they present good selectivity for natural gas odorants, in particular for mercaptans.

The effect of space velocity was investigated for AC Norit RGM1 and AC Airpel Ultra DS in the range 1,000-20,000 h\(^{-1}\). The results showed that \( \text{H}_2\text{S} \) adsorption capacity is strongly influenced by GHSV in the range 1,000-5,000 h\(^{-1}\). The two activated carbons present the same behavior in terms of GHSV variation; for all the tested values, the sorption capacity of Ultra DS is 18-75% lower than RGM1 (Fig.2).

The activated carbons Norit RGM1 and Airpel Ultra DS were also studied in wet conditions, using 100 ppm of \( \text{H}_2\text{S} \), GHSV 10,000 h\(^{-1}\) and \( T=30\)°C. The results showed that the use of \( \text{N}_2 \) as carrier gas led to the highest adsorption capacity (Tab.3). The adsorption capacity decreases using \( \text{CO}_2 \), \( \text{CH}_4 \) (simulating a natural gas) and a mixture composed of 70% \( \text{CH}_4 \) and 30% \( \text{CO}_2 \) (simulating a biogas) respectively. This behavior can be explained considering a competitive adsorption between \( \text{H}_2\text{S} \) and \( \text{CO}_2 \), that is enhanced by the simultaneous presence of \( \text{CH}_4 \).

The influence of gas matrix on \( \text{H}_2\text{S} \) adsorption capacity of AC RGM1 was evaluated. The inlet \( \text{H}_2\text{S} \) concentration was 100 ppm, GHSV 10,000 h\(^{-1}\) and \( T=30\)°C. The results showed that the use of \( \text{N}_2 \) as carrier gas led to the highest adsorption capacity (Tab.3). The co-presence of \( \text{CH}_4 \) and \( \text{CO}_2 \), simulating a biogas, led to a significant reduction of \( \text{H}_2\text{S} \) adsorption capacity: therefore, the use of an inert gas as \( \text{N}_2 \) can lead to overestimate the adsorption capacity of the filter. In dry conditions, for low values of space velocity (1,000 h\(^{-1}\)) and when the gas matrix is \( \text{N}_2 \), the achieved \( \text{H}_2\text{S} \) adsorption capacity is 93.6 mg/g. Other tests will be performed to evaluate the influence of temperature and \( \text{H}_2\text{S} \) inlet concentration and also to estimate the effects of other pollutants, in order to determine the minimum volume needed for one year-activity of the filter in a fuel cell micro-CHP system.

IV. CONCLUSIONS

The impregnated AC Norit RGM1 presents high \( \text{H}_2\text{S} \) removal activity. The results highlighted a marked influence of GHSV in the range 1,000-5,000 h\(^{-1}\), where the \( \text{H}_2\text{S} \) adsorption capacity rapidly decreases at the increasing of GHSV. The presence of humidity can enhance the performance of RGM1 and, in particular, of Ultra DS. Gas matrix composition is able to influence the adsorption capacity of \( \text{H}_2\text{S} \) using AC RGM1. The co-presence of \( \text{CH}_4 \) and \( \text{CO}_2 \), simulating a biogas, led to a significant reduction of \( \text{H}_2\text{S} \) adsorption capacity: therefore, the use of an inert gas as \( \text{N}_2 \) can lead to overestimate the adsorption capacity of the filter. In dry conditions, for low values of space velocity (1,000 h\(^{-1}\)) and when the gas matrix is \( \text{N}_2 \), the achieved \( \text{H}_2\text{S} \) adsorption capacity is 93.6 mg/g. Other tests will be performed to evaluate the influence of temperature and \( \text{H}_2\text{S} \) inlet concentration and also to estimate the effects of other pollutants, in order to determine the minimum volume needed for one year-activity of the filter in a fuel cell micro-CHP system.

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ELECTRIC FIELD ASSISTED SINTERING OF LSCF AND LSCF/GDC COMPOSITES

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Abstract—The possibility of flash-sintering \((\text{La}_{0.6}\text{Sr}_{0.4})(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_3\) (LSCF) and its composites is investigated in the present work. Pure LSCF and three different composites containing \(\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_2\) (GDC) in dog-bone shaped samples are sintered under electric field within a furnace, where temperature is raised at a constant rate. Flash-effect of increased conductivity and subsequent rapid sintering in LSCF is observed at 25-210°C under 5.0-12.5V/cm. Specimen temperature in such sintering is measured by pyrometer and is observed to be in 900-1360°C range. The extent of sintering is confirmed through SEM where a dense morphology is observed for well sintered samples. In composites containing GDC flash-effect is recorded under slightly higher electric field which increases with second phase content. Addition of GDC to LSCF is found to increase the homogeneity and isotropy in the sintering. By using flash-sintering, LSCF and LSCF/GDC composites can be produced at sufficiently low temperatures in 1 min.

Index Terms – Flash-sintering, LSCF, GDC

I. INTRODUCTION

Electric field assisted sintering has been recently shown to allow the production of high density ceramic materials in a very short time, sometime in few second, thus being named as flash-sintering. Such new sintering technique could be a promising technique for the processing of solid oxide fuel cell materials for its very short time that can reduce sintering stresses between different layers at high temperature. In addition, it could be useful to control undesirable reactions, occurring at high temperature. Materials used in SOFC technology such as YSZ electrolyte, NiO/YSZ composite anode, conducting Mn-Co spinel for interconnect coating have been reported to be treated by flash-sintering and consolidated in few minutes [1]. In the present work, the possibility of flash-sintering conducting LSCF-(\(\text{La}_{0.6}\text{Sr}_{0.4})(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_3\)) cathode material and its composites containing GDC - \(\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_2\) is investigated.

II. EXPERIMENTAL PROCEDURE

Electric field-assisted sintering was performed on dog-bone shaped samples produced by uni-axial pressing LSCF powder containing different amounts of GDC (100:0, 60:40, 50:50, 40:60, LSCF: GDC weight ratio) in a furnace where temperature was raised at a constant rate; the electric field was applied, current and voltage were constantly recorded. The phase stability and microstructure of sintered samples were analyzed by XRD and SEM.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the power dissipation vs. furnace temperature of LSCF sample subjected to different electric fields. The sudden rise in power dissipation observed for fields > 2.5V/cm is due to the abrupt increase in conductivity, which is a sign of flash-sintering (FS). LSCF is shown to be flash-sintered under 5.0-12.5V/cm at temperatures of 25-210°C using current density of 1.18-1.50 A/mm². Such flash-sintering effect is associated to the semiconducting nature and high conductivity of LSCF [2]. In order to compare the level of sintering, specimen temperature (Ts) was measured during FS which is presented in Table 1. Under the employed E-fields and current densities, Ts in the range of 900-1360°C are observed. Microstructure of LSCF samples subjected to different E-fields is given in Fig. 1(b). The microstructure of samples, FS990 and FS1150 are observed to be porous and affected homogeneously by E-field. The well sintered sample FS1280, produced with 1280°C and within a short time (~2 min) are observed to show relatively higher degree of sintering with fully connected grains compared to CS sample produced at the same temperature. It shows the superiority of FS technique over CS in terms of processing-cost and time savings. Under the same current density, change of field from 7.5 to 10V/cm causes a significant change in the microstructure. From SEM images the sintering effects of different E-fields is always found to be homogeneous. XRD pattern of FS sample (FS1280) are found congruent with that of raw powder as like CS sample which suggest that E-field assisted flash-sintering does not produce any structural change in LSCF.
The power dissipation vs. furnace temperature plot of flash-sintering performed on LSCF/GDC composites under 15V/cm is shown in Fig. 2(a). Addition of GDC content results in an increase shift of flash parameters (threshold electric field and temperature). The curves show a significant and systematic increase in the onset temperature with GDC additions. Compared to LSCF, composites are flash-sintered at higher electric fields (10-20V/cm) and higher furnace temperatures which is associated with the flash-sintering requirement of low conductive GDC phase. Dominance of GDC in composites is reflected in gradual increase in power dissipation before the flash-onset which is observed for higher GDC content. Also for the composites, as shown in Fig. 2(b), dense microstructure can be produced by the application of an E-field at much lower temperatures with respect to CS. Well grown and homogeneous microstructures of composites under E-field suggest that the two phases are good compatible under the FS which firstly comes with increase in conductivity and then leads to sintering. The choice of the current density is pointed out to be another important parameter. Under the same field, compositions containing more LSCF require higher current to guarantee the same dense microstructure. 50/50 LSCF/GDC composite is slightly more porous than 40/60 one under 0.57 A/mm² and 15V/cm, whereas with higher current density (0.9 A/mm²) 60/40 LSCF/GDC composite is dense. The microstructure of the composites appears sintered to larger areas with respect to pure LSCF; this can be related to the higher green density of the composites which provides more homogeneously distributed conductive environment around LSCF grains.

**IV. CONCLUSIONS**

It has been shown that it is possible to flash-sinter LSCF in 1-2 min of time at temperature (close to ambient) which is 1100-1200°C lower than CS temperatures using fields of 10-12.5V/cm. The sintering effect on grain morphology is found to be homogenous, which is a good observation for optimization of porosity under flash-effect. The measurement of specimen temperature clarifies the role of local temperature and can be an important consideration for the development of cathode on YSZ electrolyte. Moreover, 1 min of independent or co-sintering with YSZ electrolyte may result into improved interface. LSCF-GDC composite flash sinters at relatively higher temperature and under higher E-field. The addition of GDC to LSCF increases homogeneity, isotropy in sintering.

**REFERENCES**


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ENERGY MANAGEMENT SYSTEM FOR
A FCHV BASED ON LINEAR
PROGRAMMING

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Abstract - The current transportation system is mainly based on fossil fuels, which are depleting by nature and causing environmental problems. Fuel cells with proton exchange membranes represent a promising alternative to replace the internal combustion engines used in the transportation sector. This paper develops an energy management system for fuel cell hybrid vehicles based on a linear programming technique; the energy management system aims to achieve an optimal coordination among power units for the purpose of reducing hydrogen fuel consumption and lowering operational cost. The formulation considers the lifecycle cost, limits and ramp rates of the system components, hydrogen tank capacity and battery state of charge. Comparison against a rule based energy management system indicates a 6% to 15% reduction in system cost and up to 23% reduction in hydrogen fuel consumption.


I. NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{FC}, P_{BT}$</td>
<td>FC and BT output power, kW</td>
</tr>
<tr>
<td>$P_{br}, P_L$</td>
<td>Brake Power and Load power, kW</td>
</tr>
<tr>
<td>$SOC_{BT}, E_{BT}$</td>
<td>Battery SOC and Energy Capacity, kWh</td>
</tr>
<tr>
<td>$R_{down-fc}, R_{up-fc}$</td>
<td>FC Ramp down and Ramp up rates, kW</td>
</tr>
<tr>
<td>$R_{down-bt}, R_{up-bt}$</td>
<td>Battery Ramp down and Ramp up rates, kW</td>
</tr>
<tr>
<td>$γ_{FC}$</td>
<td>Cost of hydrogen consumption, $$/kWh</td>
</tr>
<tr>
<td>$γ_{SL-FC}, γ_{BT}$</td>
<td>Initial Cost of FC and BT system, $$/kWh</td>
</tr>
<tr>
<td>$M_{H2}$</td>
<td>Initial mass of hydrogen tank, grams</td>
</tr>
<tr>
<td>$V$</td>
<td>The volume of the fuel tank, m$^3$</td>
</tr>
<tr>
<td>$T_{amb}$</td>
<td>Ambient Temperature, °C</td>
</tr>
<tr>
<td>$C_{H2}$</td>
<td>Cost of Hydrogen Fuel, $</td>
</tr>
<tr>
<td>$P_{atm}, P$</td>
<td>The initial pressure and Pressure at step k, Pa</td>
</tr>
<tr>
<td>$λ$</td>
<td>Consumed rate of H$_2$ per kW of energy</td>
</tr>
<tr>
<td>$d(k)$</td>
<td>Time duration factor between each step k</td>
</tr>
</tbody>
</table>

II. INTRODUCTION

Fuel cell hybrid vehicles (FCHV) combining fuel cells (FC) and batteries attract the attention of engineers and researchers due to their promising future as alternatives to the internal combustion engine vehicles [1]. There is a wealth of papers that address the design of the energy management systems (EMS) in FCHV. Two kinds of controllers are addressed [2], offline controllers using linear and dynamic programming techniques [3][4] and online controllers using fuzzy logic [5].

This paper formulates the system as an optimization problem with an objective to lower hydrogen consumption and achieve an optimal split of power between sources. The life-cycle cost of system components, as well as the limits and ramp rates of FC and battery are accounted for in the objective function and constraints. Linear programming is used to find the optimal trajectory for known driving cycles. It will be shown that with the same driving cycle, the proposed technique will result in lower fuel consumption and lower cost as compared to a rule-based controller.

III. PROBLEM FORMULATION

The vehicle considered in this paper is a light duty sprinter with a 70kW induction motor, a 70kW FC system and a 1.9 kWh battery. The problem is formulated as a constrained optimization problem with linear constraints.

$$\min \left[ \sum_k \left( \gamma_{FC} P_{FC}(k) + \gamma_{SL-FC} P_{BT}(k) + \gamma_{SL-FC} P_{H2}(k) \right) d(k) \right]$$ (1)

The cost minimization function in Eq. (1) calculates the cost of energy from the FC as well as the lifecycle cost of FC and BT. It also considers the braking energy cost as equivalent.
to the FC energy. This is due to the fact that this dissipated energy originally came from the FC.

The system constraints include an SOC period coupling constraint that calculates the available state of charge of the battery after each discharge in a given time step d(k). The power balance constraint which ensures that the load is served at each step k. The system dumps any available extra power via $P_{br}$. Limitation and ramp rate constraints for the power sources is also accounted for. The storage capacity constraint ensures that the hydrogen tank is able to cover the entire desired trip.

IV. SIMULATION RESULTS

The parameters used to run the linear program are:

- Initial SOC = 0.8
- $\gamma_{FC}$ ($/kWh) = 0.161$
- $\gamma_{BT}$ ($/kWh) = 0.39$
- $\lambda$ (Sg/kWh) = 54
- $\gamma_{SL-FC}$ ($/kWh) = 1$
- $MO_{H_2}$ (g) = 1970

The system simulation is performed under the MatLab environment. NEDC driving cycle which represents a typical European driving cycle is considered. Fig. 1 scans a certain episode of the driving cycle when the FC and battery are optimally supplying the load according to the LP results. During the trip when the battery is fully charged and the load is generative, power is being dissipated through brake. At other instances, the battery is gradually discharged to help the FC in meeting the power demand.

This linear programming method is compared against the rule based (RB) method proposed in [6]. The RB method sets the split of power between the FC and the battery according to the demanded load, the FC power limits and ramp rates, and the battery power limits and SOC ranges. Results indicate that the method proposed in this paper yields lower hydrogen consumption levels as well as reduced cost values. This is revealed in Table I. The hydrogen fuel consumed during the NEDC driving cycle is reduced by 23 % using LP based EMS and that for the highway driving cycle is lowered by 8 %. The cost for the NEDC and highway driving cycles is reduced by 15 % and 6 % respectively using the LP based EMS as opposed to the rule based EMS.

V. CONCLUSION

This paper presented a methodology to optimize the controller of FCHV based on linear programming. The problem formulation which takes into account the life-cycle cost of the system components considered minimizing hydrogen usage along with operational cost. The life-cycle cost of the battery is modeled by imposing a cost on the number of discharging cycles, while the life-cycle cost of the FC is represented as a penalty factor which is a fraction of the FC initial cost. Test simulations were performed on two driving cycles. The objective was to develop a conceptual approach for an energy optimization approach which is able to consider a wide range of constraints and targets. The simulations in this article serve to explain and to prove the process. Comparison against a rule based EMS indicates that the system cost can be reduced by 6 % to 15 % depending on the driving cycle. Moreover, up to 23 % reduction in hydrogen fuel consumption is noted. Future work is headed towards transforming the LP formulation into a dynamic programming formulation which is easier to implement on real time controller chips.

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CONSIDERATION ABOUT THE LCOE OF HYDROGEN FUEL CELL POWERTRAIN IN THE ITALIAN CONTEXT

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Today Fuel Cells are present in a wide range of products: portable applications, micro Combined Heat and Power CHP system, recreation products, niche and professional application, military items and prototype vehicles.

In presence of such a wide context of application, I chose to consider only the vehicle power generation system hydrogen fuel cell based (H2FC powertrain) because, if the current US Hydrogen and Fuel Cell Vehicle Program is able to meet all the 2017 technological targets, in the subsequent year, the high volume associated with the H2FC vehicles mass production will permit to reduce dramatically the Fuel Cell (PEM) system manufacturing costs, in order to be competitive with current gasoline ICE systems.

In my opinion, in mass production perspective, “H2FC Powertrain” will be so cost competitive to be useful adopted also for stationary power generation application. In this perspective the “H2FC Powertrain Power Generation Plant” investments cost will be one of the lowest compared to other current power generation technologies [1, 2, 3 and 4].

In this article, the H2FC powertrain was considered as power generation plant and, based only on public data it was compared with the traditional power generation technologies.

The notion of Levelized Costs of Generating Electricity (LCOE) is a handy tool for comparing the unit costs of different power generation technologies. In LCOE financial model, different cost components are taken into account: capital costs, fuel costs, operations and maintenance costs (O&M). These costs are an average over the life of a project and for a specific technology, based on a specific and particular set of assumptions. The costs cash-flow is discounted to the present (date of commissioning) using assumed specific discount rates. The resultant LCOE values, one for each generation option, are the main driver for choice technology.

In this article the fuel cell powertrain module was considered as a black-box and not changed or optimized for generation purposes. Obviously we have in mind that a longest life is technical feasible. Also in a conservative perspective, we do not take in consideration the possibility to recover the heat co-produced during the electricity generation (like in a CHP power plant).

Using the U.S. DOE “H2FC Powertrain” data (referred to high projected production volume) the 2012 LCOE would be USD 173 for MWh. Using the 2017 U.S. DOE data target the H2FC powertrain cost range moves to USD 107-207 for MWh and, for the lower value of this range, it appears competitive with many of the power generation technologies analyzed in the U.S. context [5, 6, 7, 8 and 9].

In this article the U.S. DOE “H2FC Powertrain” data were analyzed with reference to the Italian context and, using a cross rate of 1.3 USD for EUR, these U.S. data in Italy were: LCOE of 133 EUR/MWh today, and a range of 82-159 in 2017; Overnight cost of EUR/kW 36 today, and 23 in 2017.

For the lower value of this range we found that, in 2017 this technology appears competitive with almost all current Italian renewable technologies LCOE data (with exclusion of large hydro) and, in the 2030 scenarios, it is comparable with many of the power generation technologies considerate [10, 11, 12, 13 and 14].

REFERENCES


CHEMICAL EXPANSION OF PEROVSKITE-TYPE SOFC CATHODE MATERIALS

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Abstract – Mixed ionic and electronic conducting (MIEC) oxides can undergo both thermal expansion and that induced by the defects of oxygen nonstoichiometry in the oxide lattice. The latter is chemical or defect-induced expansion. This property is extremely sensitive to the defect structure of the oxide material. This paper shows theoretical approach which allows quantitative prediction of chemical expansion of MIEC oxides on the basis of a relative change of the mean ionic radius. In order to enable such computation modeling analysis of the defect structure of the La$_{1-x}$Sr$_x$Fe$_{1-y}$B$_y$O$_{3-\delta}$ (B=Co or Ni) oxide materials was carried out. The experimental data on chemical expansion and those calculated on the basis of the model proposed were shown to be in good agreement for all oxides investigated.

Index Terms – chemical expansion, MIEC, SOFC, oxygen nonstoichiometry

I. INTRODUCTION

The unique feature of oxides is their ability to undergo both thermal expansion and that induced by oxygen vacancies formation in the oxide lattice at high temperature and low oxygen partial pressure ($p_{O_2}$) [1,2]. The latter measured at constant temperature relative to selected reference state is called isothermal, or chemical, or, in other words, defect-induced expansion.

Recently [1,2] we have evolved the chemical expansion model based on the relative change of the mean ionic radius and showed that the chemical expansion of undoped LaCoO$_{3-\delta}$ and LaMnO$_{3-\delta}$ observed on oxygen deficiency growth is solely caused by this reason. However, the question on the nature of chemical expansion in other MIEC oxides with wider oxygen nonstoichiometry domains still remains open.

It is worth to note that chemical expansion is extremely sensitive to the defect structure of the oxide material. Therefore reliable data on the defect structure of oxide materials is of key importance for understanding the origin of their chemically induced lattice strain. On the other hand, chemical expansion of oxide crystal cell precisely measured with ppm-resolution allows better understanding its local electronic and defect structure.

The refinement of defect structure of the selected La$_{1-x}$Sr$_x$Fe$_{1-y}$B$_y$O$_{3-\delta}$ (B=Co or Ni) oxides by means of the quantitative modeling on the basis of the available data on oxygen nonstoichiometry was, therefore, the first priority purpose of the present study. The second one was to explain the chemical expansion of MIEC oxides studied on the basis of relative change of the mean ionic radius.

II. EXPERIMENTAL

Powder samples of La$_{0.7}$Sr$_{0.3}$Co$_{0.9}$Fe$_{0.1}$O$_{3-\delta}$ and LaFe$_{0.6}$Ni$_{0.4}$O$_{3-\delta}$ were synthesized by glycerol-nitrate technique described elsewhere [1,2].

The phase composition of the powder samples prepared accordingly was studied by means of X-ray diffraction (XRD) with an Equinox 3000 diffractometer using Cu K$_α$ radiation. XRD showed no indication for the presence of a second phase.

Chemical expansion of La$_{0.5}$Sr$_{0.5}$Co$_{0.9}$Fe$_{0.1}$O$_{3-\delta}$ and LaFe$_{0.9}$Ni$_{0.1}$O$_{3-\delta}$ was measured as a function of $p_{O_2}$ at temperature between 600 and 1050 °C using a home-made dilatometer supplied by $p_{O_2}$ control and adjustment system.

III. RESULTS AND DISCUSSION

A. Defect structure analysis

It is generally recognized that the defect structure of the oxygen deficient LaBO$_{3-\delta}$ (B=Mn, Fe, and Co) is based on the simultaneous presence of B-species in different oxidation states such as B$^{3+}$, B$^{4+}$, and B$^{2+}$ cations in its structure. The following defect equilibria may, therefore, be written

\[ O_6^{\circ} + 2B_8^{\ast} \leftrightarrow V_{O}^{\ast\ast} + 1/2O_2 + 2B_8^{\ast} \quad K_1 = \frac{[V_{O}^{\ast\ast}][B_8^{\ast}]^2}{[O_6^{\circ}][B_8^{\ast}]^2} \]  \hspace{1cm} (1)

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and
\[ 2B^+_g \Leftrightarrow B^+_g + B^+_g, \quad K_2 = \frac{[B^+_g]^2}{[B^+_g]^2} \tag{2} \]
where \([B^+_g], [B^+_g]_0\), and \([B^+_g]_0\) correspond to concentration of \(B^{3+}, B^{4+},\) and \(B^{2+}\), respectively.

For oxides with partial substitution of other 3d-metal for a host metal on B–site the defect structure can be more complicated due to an electron exchange between this metal and a host metal. However, different simplifications are acceptable depending on the nature of a dopant and a host metal. For instance, we can treat iron as cation \(\text{Fe}^{4+}\) in \(\text{La}_0.7\text{Sr}_0.3\text{Co}_0.9\text{Fe}_{0.1}O_{3-\delta}\) since that is less electronegative element as compared to cobalt.

Oxygen nonstoichiometry of \(\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}\) measured in Ref. [3] is given, as an example, in Fig. 1 as a simultaneous function of \(p_{O_2}\) and temperature. The result of nonlinear surface fitting for this cobaltite using the model described by Eqs. (1) and (2) is also shown in Fig. 1. As seen the model proposed fits the experimental data on oxygen nonstoichiometry really good over the complete \(p_{O_2}\) and temperature ranges investigated.

\[ [c_i]_0 \quad \text{and} \quad [r_i]_0 \in \text{ABO}_{3-\delta}\text{ perovskite containing oxygen vacancies. The subscript, 0, in} \ c_i \ \text{and} \ L_0 \ \text{denotes in} \ Eq. (3) \ \text{that these properties belong to the perovskite in a reference state.} \]

Appropriate concentrations were calculated on the basis of the defect structure model and substituted in general expression Eq. (3) yielding the model equation of oxide chemical expansion which enabled its value calculation. The results of such calculations are shown in Fig. 2.

IV. CONCLUSION

Theoretical approach which allows quantitative prediction of chemical expansion of MIEC oxides on the basis of a relative change of the mean ionic radius was proposed and successfully verified. Cobalt spin state was shown to significantly influence the chemical expansion of perovskite-type oxides.

ACKNOWLEDGMENT

This work was financially supported by the Russian Foundation for Basic Research grant No. 12-03-31317.

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Fig. 1. Oxygen nonstoichiometry of \(\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}\) vs. \(\delta\). Points – experimental results [3], surface – calculation according to defect model

B. Chemical expansion

Recently we have explained the chemical expansion of the perovskites \(\text{LaCoO}_{3-\delta}\) [1] and \(\text{LaMnO}_{3-\delta}\) [2] using the model developed on the basis of the relative change of the mean ionic radius. According to this model isothermal defect-induced expansion can be computed by using the following equation

\[ \Delta L = \frac{\sum c_i r_i - c_i_0 r_i}{\sum c_i_0 r_i} L_0, \tag{3} \]

where \(c_i\) and \(r_i\) are the concentration and ionic radius, respectively, of an ion \(i\) of \(\text{ABO}_{3-\delta}\) perovskite containing oxygen vacancies. The subscript, 0, in \(c_i\) and \(L_0\) denotes in

Fig. 2. Chemical expansion of \(\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}\) vs. \(\delta\). Points – experimental results, lines – calculation according to model proposed with different fractions of \(\text{Co}^{3+}\) in high spin state.

Fig. 2 shows that \(\text{Co}\) spin state significantly influences chemical expansion and model proposed fits experimental data really good.

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PERFORMANCE OF MCFC FED WITH SIMULATED FLUE GAS

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Abstract – The effect on MCFC performance with CO₂ lean oxidant gas, simulating combustion flue gas was evaluated. Furthermore, measurements to test the effect of SO₂ in the oxidant gas stream in concentrations up to 24ppm and during 90 min exposure, followed by regeneration with clean gas, was performed.

Results show that the performance of the button cell with CO₂ lean oxidant gas is acceptable at a base load of 100mA/cm². The effect on fuel cell performance of short term exposure to SO₂ is only clear in the higher range of contaminant concentration (>12ppm). Studying the performance degradation of the fuel cell caused by SO₂ in flue gas is important for the use of MCFC as a CCS application.

Index Terms - CCS, flue gas, MCFC

I. INTRODUCTION

The MCFC is a high temperature fuel cell with a molten carbonate electrolyte. Advantages of MCFC include fuel flexibility, the use of cheap non-noble catalysts, high efficiency and CHP operation. Lately, the MCFC has come of interest for use in CCS (Carbon Capture and Sequestration) applications in combination with conventional combustion power plants as a method to reduce CO₂ emissions from energy production.

In the MCFC, carbonate ions are transported from cathode to anode side as a part of the cell reaction. By feeding the cathode with combustion flue gas the MCFC can be used to concentrate CO₂ to the anode exhaust while also producing electricity, which makes it an attractive alternative to conventional CCS technologies. The possibility to retrofit existing power plants also creates a potential additional market for MCFC. Flue gas from combustion plants differ in composition from the standard oxidant gas used for MCFC, with significantly lower concentrations of oxygen and carbon dioxide, and which affect the fuel cell performance negatively. Flue gas also often contains high concentrations of sulfur contaminants which has a detrimental effect on fuel cell performance and lifetime. The effect on fuel cell performance and degradation of using flue gas is a concern for the use of MCFC as a CCS application. The objective of this work is to analyze the sensitivity of button cell performance to CO₂ lean flue gas, and to evaluate the performance degradation caused by sulfur contaminants in flue gas, to find suitable operational conditions for MCFC as a CCS application.

II. EXPERIMENTAL

Fuel cell performance was evaluated with polarization measurements and Electrochemical Impedance Spectroscopy (EIS). Measurements were performed on a button cell with 3cm² electrode area, equipped with separate reference electrodes for measurement on individual electrodes. Contaminants were added to the gas stream in N₂ carrier gas after humidification to avoid scrubbing of sulfur contaminant. The total flow rate for anode and cathode was 200mL/min. All experiments were performed with electrode material delivered from Ansaldo. Electrolyte is (Li/K)₂CO₃ (62/38). The cell was operated at 650°C.

III. RESULTS AND DISCUSSION

To simulate combustion flue gas, the MCFC was fed with CO₂ lean oxidant gas in the range of 6-12%. This is in the lower range of operation for MCFC with maintained minimum performance, although a combination of CO₂ concentration and oxidant utilization has been reported to determine the performance limit [1]. The button cell is operated with a stoichiometric surplus of reactants to maintain homogeneous conditions throughout the cell, and the tolerance for operating under CO₂ lean conditions must be evaluated specifically for the button cell. Measurements with CO₂ lean oxidant gas (Fig. 1) show that the MCFC button cell can be operated with
simulated flue gas, although the CO₂ concentration is a critical factor. The cell voltage at a base load of 100mA/cm² was observed to be stable during 100h at each concentration. The IV-curve with CO₂ lean oxidant gas experiences a second, steeper, slope with increasing current density. The breaking point is shifted to higher current densities with increasing CO₂ concentration. This is potentially related to the utilization factor of CO₂, which has been calculated to 15-20%.

SO₂ in flue gas is known to cause corrosion, but may also transfer as sulphate or sulphide from cathode to anode side. Sulphur contaminant at the anode is known to form NiS which can cause poisoning of the anode side catalyst [2]. In button cell testing studying the effect of H₂S on the anode side catalyst [2], an exposure time of 90min was found to be sufficient to detect poisoning effects [3]. The exposure time of low levels (1-24ppm) of SO₂ and anode gas composition for contaminant testing was selected to be the same in this set of experiments.

The effect of short term exposure to SO₂ in the oxidant gas is clear only at concentrations higher than 12ppm (Fig. 2). Even at 24ppm SO₂ the cell voltage is fully recuperated after 24h with clean gas. The cell impedance under load shows an increase in the mass transfer region with higher SO₂ concentration, visible despite disturbance due to water content (Fig. 3). Analysis of the individual electrode performance indicates that the anode performance is affected negatively, although post test analysis of electrode material is necessary to identify any remaining sulfur in the fuel cell.

IV. CONCLUSION
The results of operating the button cell with CO₂ lean oxidant gas show that the fuel cell can be operated with as low CO₂ concentration as 6% with stable performance at current densities below 100mA/cm². Short term exposure of SO₂ in oxidant gas is a feasible method to study the degradation effects on fuel cell performance only for high concentrations of contaminant. This result can be used as selection criteria when considering a suitable target concentration for further contaminant testing with simulated flue gas conditions at the cathode side.

ACKNOWLEDGMENT
This work was performed within the MCFC-CONTEX project (FCH-JU).

REFERENCES

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**Abstract** - A lumped parameter dynamic model is developed for predicting the stack performance, temperatures of the exit reactant gases and coolant liquid outlet in a proton-exchange membrane fuel cell (PEMFC) system. The air compressor, humidifier and cooling heat exchanger models are integrated to study the fuel cell system. A PID temperature control is implemented to study the effect of stack temperature on settling times of other variables such as stack voltage, air flow rate, oxygen excess ratio and net power of the stack.

The model allows an assessment of the effect of operating parameters (stack power output, cooling water flow rate, air flow rate, and environmental temperature) and parameter interactions on the system thermal performance. The model represents a useful tool to determine the operating temperatures of the various components of the thermal system, and thus to fully assess the performance of the thermal system, especially when investigating applications that have highly dynamic operating conditions.

**Index Terms** – PEM fuel cell; System dynamic model; Thermal cooling of fuel cell stack

I. INTRODUCTION

An analytical dynamic model and a general framework for the control design of a PEM fuel cell system temperature is proposed. The model presented below considers only the thermodynamic cooling of the fuel cell for the sake of brevity. We refer to previous work which has been focus mainly on system component modeling and cell electrochemistry [1], [2].

II. MODEL DESCRIPTION

The net heat generated by the chemical reaction inside the fuel cell, which causes its temperature to rise or fall, can be written as:

\[
Q = (E_{\text{reverse}} - V_{\text{cell}}) \times I
\]  

(1)

where \(E_{\text{reverse}}\) is the reversible cell voltage calculated by the hydrogen lower heating value if the generated water is in vapor form (1.254 V). To maintain the operating temperature of the stack within the desired range this heat should be removed from the stack. The heat dissipation may be done by convection, conduction, radiation or phase change.

With reference to figure 1, the coolant, is circulated through the stack by a pump and its temperature, at the stack inlet, is controlled by keeping the temperature of the fuel cell at a desired mean value. This goal is reached by an external circuit which dissipates the heat by means of a radiator-fan. The temperature of the coolant, leaving the PEMFC stack is considered constant whereas the heat exchanger cooling fan has a variable speed.

![Fig. 1. Fuel cell thermal model](image-url)

**Fig. 1. Fuel cell thermal model**

The energy balance can be written as follows:

\[
MC_{\text{stack}} \frac{dT_{\text{stack}}}{dt} = E_{\text{net}} - E_{\text{elec}} - \Theta_{\text{heat}} - \Theta_{\text{cond}} - \Theta_{\text{conv}} - \Theta_{\text{ph}}
\]  

(2)

where \(M\) is the total mass of the fuel cell stack, \(C_{\text{stack}}\) the average specific heat of the stack, and \(dT_{\text{stack}}/dt\) the temperature change with respect to time. Each component of the energy balance is presented below.
\[ \Delta H = \frac{nF}{2} \Delta H \]
\[ \Delta H_{\text{elec}} = V_{\text{stack}} I \]
\[ \Delta H_{\text{liquidcool}} = \Delta H_{\text{liquidcool}} \times C_{p,\text{liquidcool}} \times (T_{\text{liquidcool, out}} - T_{\text{liquidcool, in}}) \]
\[ \Delta H_{\text{aircool}} = \omega_{\text{fan}} \times \text{Air displacement} \times C_{p,\text{air}} \]
\[ \Delta H_{\text{Conv}} = k \times A \times (T_{\text{stack}} - T_{\text{Amb}}) \]

where \( \Delta H_{\text{liquidcool}} \) is the heat dissipated through the liquid coolant, \( \Delta H_{\text{aircool}} \) is the heat dissipated through the air fan and is adjusted by means of the PID control, \( \Delta H_{\text{Conv}} \) is the heat loss from the surface of the stack to the ambient is the sum of the convective and radiative fluxes, \( T_{\text{stack}} \) (°C) is the stack temperature, \( T_{\text{Amb}} \) (°C) is the ambient temperature.

Finally, the water coolant, needed to assure the operating temperature in the stack, is calculated according to the following equation:

\[ \Delta T_{\text{MTD}} = \frac{kA_{\text{liquidcool}} \times \Delta T_{\text{MTD}}}{c_{p,w}(T_{\text{liquidcool, out}} - T_{\text{liquidcool, in}})} \]

where \( c_{p,w} \) is the specific heat of water (kJ/kg °C), \( T_{\text{liquidcool, out}} \) and \( T_{\text{liquidcool, in}} \) (°C) are the coolant temperatures at the inlet and outlet of the stack. \( T_{\text{liquidcool, in}} \) is determined experimentally whereas \( T_{\text{liquidcool, out}} \) is fixed to 60°C. Heat exchanger AU value is determined experimentally as a function of mass flow rate.

The stack is kept at constant temperature by means of a PID controller which determines the heat exchanger fan speed.

\[ T_{fc, ref} \]
\[ \text{Err} \]
\[ T_{fc} \]

Fig. 2. Fuel cell temperature control via coolant mass flow rate

III. RESULTS

The open circuit voltage is function of temperature. It was observed that at temperature increasing by 20°C the voltage increasing by about 0.1.5V.

The dynamic property of PEM fuel cell depends mainly on three aspects: double-layer charging effects, fuel and oxidant flow delays, and fuel cell thermal mass. The double-layer charging effect has a time constant normally small (less than 1 s). The main contributors to the temperature change delays are mass flow rate and the fuel cell thermal mass (Time constant \( \tau = MC_{f}/k_{RC} \)). The fuel and oxidant flows cannot follow the load current changes instantaneously. The delays can be in the range several seconds. Also, the temperature of fuel-cell stack cannot change instantaneously. The temperature change PEM fuel cell stack is in the order of minutes. Thus, the fuel and oxidant flow delays and the thermodynamic characteristics will normally dominate the transient responses in the long time operation. The Matlab Simulink model responses are given in figure 3.

The employed coolant is a mix of water and ethylene glycol. The control objective is to guarantee that the stack temperature stays in an acceptable range.

The fuel cell electrical and thermal performance is shown in the next figure. Parasitic losses are shown to be larger increasing the load. A higher coolant and air mass flow rate is required to keep temperature constant at 65°C.

Fig. 3. Fuel cell stack performance thermal cooling

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MATHEMATICAL MODELING AND PERFORMANCE ANALYSIS OF A RESIDENTIAL MICRO COGENERATION PLANT BASED ON A HIGH TEMPERATURE PEM FUEL CELL STACK

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Abstract - In the present study, new configurations for a PEM fuel cell based residential micro-cogeneration system have been proposed in which the conventional low temperature PEM fuel cell is replaced by a high temperature one. The configuration of the plant is accordingly modified and detailed mathematical models for HT PEM fuel cell stack and all other components of the plant have been developed. In the next step, the thermal and electrical performance and the primary energy saving of the plant in the design condition for two different configurations is obtained. Finally, the performance of the system for other designed fuel utilization factors and current densities has been evaluated and the corresponding effects have been discussed.

Index Terms: cogeneration, fuel processor, high temperature PEM fuel cell, fuel processor, residential.

I. INTRODUCTION

PBI based high temperature PEM fuel cells operate in the range of 120-200 °C; Operating at higher temperature than conventional low temperature PEM fuel cell stack, aside from higher efficiency, leads to other significant advantages. The HT PEM fuel cell have less CO poisoning problems and can operate at higher inlet CO concentration. Further, owing to the fact that the water is always in the gas phase and the membrane does not need to be hydrated, this type of fuel cells do not deal with the flooding and drying of membrane issues which is one of the main problems of conventional LT PEM fuel cells. [1-2]

Accordingly, application of high temperature PEM fuel cells in residential micro cogeneration system can be an interesting alternative as no humidification or air quenching unit will be needed and a simpler syngas purification unit can be utilized.

Accordingly, in the present article, new configurations for an already operating residential micro cogeneration system based on a PEM fuel cell (Sidera30) which had been designed for meeting the electrical demand of a building with 12-15 conventional flats has been proposed. In the proposed configurations, the low pressure PEM fuel cell stack has been replaced by a high temperature one and the configuration of the plant is also accordingly modified. Detailed models for the components are developed and the performance of the system for two different proposed configurations in the design condition has been investigated. Finally, the systems performance in other design current densities and fuel utilization factors is also evaluated and discussed.

II. PLANT DESCRIPTION

Figure 1 demonstrates a schematic representation of the first proposed configuration (configuration I). The plant is composed of a fuel processor, an HT PEM fuel cell stack, low pressure and high temperature water circuits and other auxiliary components. In the first step, the mixture of natural gas and superheated steam enters the steam reformer where they undergo the steam methane reforming reaction producing hydrogen and CO.
hydrogen is consumed through the electrochemical reaction generating electricity. The anodic outlet, which still includes unconsumed amounts of hydrogen and methane, is directed to the burner to burn together with the auxiliary methane generating combustion products which will provide the required energy of the SMR reactor and subsequently produce the steam and warm water in the super heater and economizer respectively. In the other side, the compressed air is fed to the cathodic side providing the required oxygen. Two recuperators are also employed for warming up the fuel cell inlet streams.

### III. MODEL DESCRIPTION

#### A. HT PEM fuel cell stack

A quasi 2D model has been developed in order to simulate the diffusion of reactants through the MEA and also the concentration distribution through the channel. One stack with 440 cells has been considered in the model. The approach proposed in [2] is employed for developing the model and the data given in the same paper has been employed for validating the developed model; the details of the model are given in [1].

#### B. Fuel Processor

Detailed models have been developed to simulate the kinetic behavior of the fuel processor components, where the proposed model and the kinetic coefficients, given in [3], have been employed. Experimental data received from "Sidera30" already operating plant have been employed for validating the fuel processor model. The detailed model is illustrated in [1].

### IV. RESULTS AND DISCUSSION

Considering the fact that the considered system is an upgrade of an already operating LT-PEMFC based plant (Sidera30), two different configurations have been considered. In configuration I, major modifications have been applied including employing a larger WGS and eliminating all of the proxes and adding a water removal system before the anode inlet and two recuperators for warming up fuel cell inlet streams. While, in the configuration II (not shown in the paper) the same WGS reactor size is used, 1 prox reactor is still utilized, no anodic water removal device is employed and recovery heat exchangers for anodic and cathodic heat recovery are added. The details of configuration II are given in [1]. The temperature and composition of syngas through the fuel processor for configuration I in the design condition (case A) is given in Table I, while the performance analysis results of the system in this case is next shown in Table II. In the next step, performance of the system for case B with higher utilization factor has been investigated demonstrating the fact that increasing $\lambda_{H_2}$ has a negative effect on the electrical and overall performance of the system. Afterwards, in order to investigate the effect of changing the size of the stack, the performance of the system for the design current density of 0.4 (A.cm$^{-2}$) (Case C) has also been evaluated. It is demonstrated that operating at higher current densities results in an increment in the voltage losses and consequently a decrease in electrical efficiency. Finally, the performance of the plant in the second configuration for two different utilization factors (Case D and Case E) have been investigated. It is observed, owing to the fact that water at the anodic outlet in the second configuration is not removed, due to the transport of water to the cathodic side, the partial pressure of oxygen in the cathode decreases resulting in lower fuel cell efficiency. The mentioned effect is observed since water transport has been considered in the model.

Table I Dry molar fractions and temperature of syngas

<table>
<thead>
<tr>
<th>Stream</th>
<th>CH4(%)</th>
<th>H2(%)</th>
<th>CO(%)</th>
<th>CO2(%)</th>
<th>T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR Outlet</td>
<td>5.7</td>
<td>74.4</td>
<td>4.7</td>
<td>15.1</td>
<td>585</td>
</tr>
<tr>
<td>WGS Outlet</td>
<td>5.6</td>
<td>75.3</td>
<td>4.7</td>
<td>18.1</td>
<td>335</td>
</tr>
</tbody>
</table>

Table II Performance of the considered systems

<table>
<thead>
<tr>
<th>Case</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Configuration</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>$\lambda_{H_2}$</td>
<td>1.2</td>
<td>1.2</td>
<td>1.4</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>Stack Voltage (V)</td>
<td>267.3</td>
<td>268.4</td>
<td>234.7</td>
<td>260.7</td>
<td>261.6</td>
</tr>
<tr>
<td>Stack Current (A)</td>
<td>119</td>
<td>103.7</td>
<td>115.5</td>
<td>114.3</td>
<td>106.8</td>
</tr>
<tr>
<td>Stack Electrical power (kW)</td>
<td>31.8</td>
<td>28.3</td>
<td>27.1</td>
<td>26.80</td>
<td>25.1</td>
</tr>
<tr>
<td>Overall Elec. efficiency %</td>
<td>29.6</td>
<td>26.3</td>
<td>25.1</td>
<td>23.7</td>
<td>22.9</td>
</tr>
<tr>
<td>Thermal power (kW)</td>
<td>52.9</td>
<td>55.6</td>
<td>58.0</td>
<td>63.5</td>
<td>61.1</td>
</tr>
<tr>
<td>Thermal Efficiency %</td>
<td>53.2</td>
<td>55.4</td>
<td>57.7</td>
<td>58.6</td>
<td>58.1</td>
</tr>
<tr>
<td>Overall 1st law efficiency%</td>
<td>82.5</td>
<td>81.7</td>
<td>82.8</td>
<td>82.3</td>
<td>81.0</td>
</tr>
<tr>
<td>Primary Energy Savings %</td>
<td>23.62</td>
<td>20.5</td>
<td>20.2</td>
<td>23.7</td>
<td>17.0</td>
</tr>
</tbody>
</table>

### V. CONCLUSION

It was demonstrated that employing an HT PEM fuel cell instead of an LT one can result in considerable simplification of the plant configuration beside leading to higher efficiency. Since the cost of this new generation of PEM fuel cells is decreasing, it can be a promising substitute for LT types in small scale cogeneration systems in the near future. It was also demonstrated that increasing the fuel utilization factor has an adverse effect on the performance of the system and also operating at higher current density leads to a decrement in the electrical efficiency and PES, however operating at this condition, the required capital cost of the stack can be reduced.

### VI. ACKNOWLEDGMENT

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### REFERENCES


INTEGRATION OF MCFC IN A CEMENT PLANT FOR HIGH EFFICIENCY CARBON CAPTURE

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Abstract – In this study, the application of Molten Carbonate Fuel Cell (MCFC) in cement plant with CO₂ capture is performed under technical prospective. MCFC represents one of the most promising option for reducing carbon dioxide emissions by post combustion capture. The application of this technology, has been already investigated in Natural Gas Combined Cycle (NGCC), PC fired steam cycle and Integrated Gasification Combine Cycle (IGCC). The application on cement plant flue gas is assessed in this work.

Index Terms – Cement Plant, Clinker, Fuel Cell, CO₂ Capture

I. INTRODUCTION

Carbon dioxide concentration in atmosphere and the consequent effect on climate change have pushed research activity in “CO₂ free” technologies for power plants and industries.

After power generation, the main industrial emitter worldwide is the cement industry, which is based on an energy intensive process. During cement production a large amount of CO₂ is emitted, because of the double emission connected to the decomposition of limestone (calcination: CaCO₃→CaO+CO₂) and to the combustion of fuels, necessary for the sustainment of the endothermic calcination process and the formation of clinker.

A modern cement plant is composed by a 4-5-stage preheating tower, a bottom precalciner, a rotating kiln and a clinker cooler. Exhaust gases from the kiln and the precalciner go through the raw-meal preheating tower, where they preheat the solid mixture entering the process while they are cooled down from the calcination temperature (850-880°C) to 300-350°C. Afterwards, they are sent to the raw meal drier before leaving the plant with a high CO₂ concentration (>30%).

At the state of the art, the conventional technology for post combustion capture of CO₂ is based on chemical solvents, which are very expensive and require a substantial energy consumption for regeneration.

One way to reduce the emission of CO₂ while maintaining high thermodynamic performance could be the use of MCFC. High efficiency and high carbon capture rate using this concept have been verified through plant simulations in combined cycles [1], coal fired steam cycles [2] and IGCC [3]. The aim of the work is to assess the application of this CO₂ separation process in cement plants.

Cement plant flue gases are fed to the cathode of an MCFC, in order to separate CO₂ and produce electric power for both the self-sustainment of the cement plant and additional energy export. Gases from the fuel cell are cooled down, recovering heat and after purification CO₂ is compressed for storage [4].

II. METHODOLOGY

Mass and energy balances have been estimated by a proprietary computer code (GS) [5]. A detailed simulation of CO₂ purification unit has been performed in Aspen Plus®[4].

III. PLANT LAYOUT AND MAIN RESULTS

A simplified plant layout is shown in Fig.1, while the main operational parameters of power plant and the energy balance of the process are reported in Tab.1 Gas fed to the MCFC is extracted from the outlet of the preheating tower of the cement plant at 315°C. This choice is non-invasive for the cement plant and suitable for application on existing plants. Before
entering MCFC flue gases are cooled down and sent to the filtering and sulphur removal section. Further investigations on flue gas composition have to be carried out to check the presence of other possible contaminants (Cl, Hg or other heavy metals) that could be dangerous for the fuel cell. Flue gases are then reheated to 580°C after mixing with an exchanger (up to 400°C) and then by burning residual CO and water preheating. Finally this rich CO₂ stream is directed to the purification section[4], where high-purity CO₂ is separated from a H₂/CO-rich stream. The latter is partly burned for air heating and partly recycled as MCFC fuel.

Gas exiting the cathode side of the cell (84% O₂, vol) is sent to the hot side of heat recovery section 1 and then released to ambient, while the stream leaving the anode side is cooled down in a second heat recovery section and used for natural gas and water preheating. Finally this rich CO₂ stream is directed to the purification section[4], where high-purity CO₂ is separated from a H₂/CO-rich stream. The latter is partly burned for air heating and partly recycled as MCFC fuel.

CO₂ captured from cement flue gases (Eq.1), obtaining negative emission of up to -1250 g/kWh.

\[ E_{\text{eq}} = \frac{3600 \times \left( m_{\text{CO₂, emitted}} - m_{\text{CO₂, captured}} \right)}{P_e} \]  

Moreover, the specific primary energy consumption corresponding to the CO₂ avoided (SPECCA index [1]) shows very low values.

### Energy & CO₂ balance

<table>
<thead>
<tr>
<th>Number of MCFC stacks</th>
<th>2 stacks</th>
<th>3 stacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q, LHV, in [MW_LHV]</td>
<td>134.84</td>
<td>177.57</td>
</tr>
<tr>
<td>Fuel cell power [MW_e]</td>
<td>68.63</td>
<td>95.32</td>
</tr>
<tr>
<td>ORC Power [MW_e]</td>
<td>9.09</td>
<td>9.61</td>
</tr>
<tr>
<td>Auxiliaries [MW_e]</td>
<td>-14.79</td>
<td>-20.86</td>
</tr>
<tr>
<td>Overall net power [MW_e]</td>
<td>62.94</td>
<td>84.07</td>
</tr>
<tr>
<td>Net electric LHV efficiency</td>
<td>46.7%</td>
<td>47.3%</td>
</tr>
<tr>
<td>CO₂ from cement plant flue gas [kg/s]</td>
<td>41.63</td>
<td>41.63</td>
</tr>
<tr>
<td>CO₂ from natural - captured [kg/s]</td>
<td>6.17</td>
<td>9.04</td>
</tr>
<tr>
<td>CO₂ from natural gas - emitted [kg/s]</td>
<td>1.18</td>
<td>0.69</td>
</tr>
<tr>
<td>CO₂ captured [kg/s]</td>
<td>27.29</td>
<td>38.86</td>
</tr>
<tr>
<td>CO₂ released in ambient [kg/s]</td>
<td>21.78</td>
<td>12.54</td>
</tr>
<tr>
<td>Equivalent CO₂ emissions [g/kWh]</td>
<td>-1135.3</td>
<td>-1245.7</td>
</tr>
<tr>
<td>CO₂ capture efficiency</td>
<td>55.5%</td>
<td>75.6%</td>
</tr>
<tr>
<td>CO₂ Avoided, cement plant</td>
<td>47.7%</td>
<td>69.9%</td>
</tr>
<tr>
<td>SPECCA-Specific Primary Energy Consumption for CO₂ Avoided [MJ/kgCO₂]</td>
<td>1.03</td>
<td>0.89</td>
</tr>
</tbody>
</table>

Tab. 1. Results of the two cases of cement plant integrated with MCFC.

### IV. Conclusions

A detailed study of MCFC integration in a cement plant has been performed. Results show that the proposed power plant guarantees a strong reduction of CO₂ emission with a very promising electric efficiency, supported by the additional electricity produced by an ORC unit. The solution permits to avoid about 48% and 70% of CO₂ emission in cement plant, with a “negative-emission” electric power output of about 63 and 84 MWₑ respectively.

### References


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HYBRID CFD AND EQUIVALENT-CIRCUIT IMPEDANCE MODELING OF SOLID OXIDE ELECTROCHEMICAL CELLS

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Abstract - Electrochemical impedance spectroscopy (EIS) analysis of solid oxide fuel and electrolytic cells (SOFC and SOEC) is extensively used for understanding the influence of many process (kinetic activation, gas transport, gas conversion…) and degradation phenomena. Two main drawbacks characterize classical equivalent circuit based EIS models: a) they are usually zero dimensional and use bulk condition for setting the parameters and b) they don’t fit well experimental data under load conditions mainly because mass transport processes are not well modeled. In the present work impedance due to mass transfer is obtained from fully three dimensional CFD simulations. Multispecies mass transport and Navier Stokes transient equations are solved both for the fuel and oxidant sides. Impedance is finally computed as a function of frequency using an open source tool based on OpenFOAM®. The code is reversible and allows to simulate both SOFC and SOEC operation mode. These improvements show in a more clear way how mass transfer processes influence the SOC performances, low frequency processes and high frequency processes dependent on species concentrations.

Index Terms - CFD modeling, Electrochemical impedance spectroscopy (EIS), open source tool OpenFOAM®, numerical results validation.

I. INTRODUCTION

Classical SOC EIS models based on equivalent-circuit approach are essentially made by a series of black boxes that take into account the different processes [1]. The implicit hypothesis consists in the linearity of the model so each process doesn’t affect other processes. Each black box contains a simple or detailed model that describes a particular phenomenon. Usually this sub-models are based on nonlinear functions respect to the temperature or species molar fractions. The typical not detailed mass transfer description can significantly affect the results when species diffusion become important, i.e. in complex geometries or under load.

II. MODEL DESCRIPTION

A. Hybrid approach

Hybrid model aims to couple the main advantages of two different approaches, the frequency domain based models characterized by:

- a good results for high frequency processes;
- a very detailed electrochemical description;
- a not trivial mass transport process evaluation;

and time domain based models characterized by:

- a detailed mass transport description;
- a three dimensional domain;
- a complete set of partial differential equations;
- a relatively slow characteristic time.

The hybrid model consist in a series of high frequency processes sub-models overlapped on a three dimensional framework where transient partial differential equations are solved as shown in Fig. 1. The model inputs are the geometry and the main parameters, while the outputs are the local variables distribution (temperature, species molar fractions, etc…) and the overall impedance spectrum.
B. Processes description

For low frequency processes a complete transient Navier-Stokes equations set with arbitrary species fluxes diffusion description is implemented. Equations are solved in time domain and the impedance value is derived computing the difference in modulus and the shift between current and voltage signals.

For high frequency processes the electrochemical phenomena are supposed collapsed in a very thin region close to the electrolyte. This reduce the computational domain in a two dimensional plane where a distributed grid of high frequency sub-models is solved. Ohmic processes are based on a pure temperature dependent resistive element while activation processes are modeled using different equivalent circuits combining resistive effects (derived from Butler Volmer equation) and capacitive effects.

III. THE TOOL

All the equations are solved using an open source tool (OpenFOAM®). The basic classes designed for solving standard non isothermal compressible flows are coupled with an in-house developed multispecies mass transport library as described in [2] and with an ad hoc routine to couple frequency domain with time domain data.

After some preliminary tuning operations, the simulation start from open circuit voltage (OCV) and proceeds with a full polarization. For the desired voltage points a complete impedance analysis is performed.

The open source solution guarantees an high versatility in the model definition and a good and low cost scalability in term of high performance computing for large computational domains. For the present work parallel computing from 2 up to 64 processors was used.

IV. NUMERICAL RESULTS AND VALIDATION

The main results consist in the evaluation of the sensitivity of the low frequency part of the spectrum respect to the inflow condition and water content. The non-linearity effects become evident between parts of the cell directly fed by fresh flow (i.e. near the inlet) and the parts where stagnant flow is predominant. This lets to predict effects induced by different flow fields and plates geometries.

The second important result is the good prediction of the mass transfer arcs under load as shown in Fig. 2. A quantitative comparison between experimental data and complete domain numerical results was also performed.

V. CONCLUSION

An hybrid CFD and equivalent-circuit impedance model for solid oxide cells was developed. It is based on a distributed high frequency processes over a three dimensional CFD framework. Exact solution of mass transfer processes provide a model that can fit and predict SOFC performances under load without re-tune any parameter. Furthermore each high frequency sub-model can use correct local bulk temperature and species molar fractions values to better simulate high frequency parts of the spectrum.

The main advantages of this approach are a) the improvement in performance prediction at high fuel utilization and current density and b) the capability to predict different operating conditions without retuning model’s parameters. The model is fully scalable from single electrode level up to complete stack level.

Numerical results are validated using in house experimental data (Risø DTU).

REFERENCES


SMART MINIATURE MICROBIAL FUEL CELL DESIGN FOR INCREASED ELECTRICITY GENERATION AND WASTE WATER TREATMENT

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Abstract - Microbial Fuel Cells (MFCs) are a green sustainable energy with minimal carbon footprint, suitable for wastewater remediation and generation of useful amounts of electricity. This study focuses on the architecture and rapid prototyping materials used for building MFCs that are likely to affect the overall performance. Three MFC versions of the same design were made out of three different polymers and compared with a different MFC design under different electrical configurations in terms of power production and COD reduction. Power densities of individual units, connected in parallel and in series configuration reached up to 2.1 mA/m², 4.9 mA/m² and 9.5 mA/m² respectively.

Index Terms – COD reduction & Energy harvesting, small size Microbial Fuel Cells, stacking of MFCs, Twist n’ Play MFC design.

I. INTRODUCTION

A microbial fuel cell (MFC) is a bioelectrochemical device that is capable of converting biomass into electrical energy for as long as feedstock is supplied to it. Even though the technology has existed for over century [1], it has only been during the last decade that MFCs have shown their energy harvesting potential and their ability to power real-world applications [2]. To date, various types of MFC reactors have been developed from MFC research groups, including miniature, cylindrical, up flow, and stacked reactors using different materials in an effort to optimise the architecture for further scale-up and real-time implementation [3]. Small size MFCs benefit from lower activation losses, higher substrate utilisation (mass transfer) due to decreased diffusion resistance, and optimised volume-to-surface-area ratio resulting in higher power densities [4].

II. METHODS

For the needs of this study, 3 different commercially available thermoplastic polymers; PC (Polycarbonate), ABS (Acrylonitrile Butadiene Styrene) and RC25 Nanocure (ceramic-filled photo curable resin) were investigated as the structural material for 3 versions (triplicates) of a 6.25 mL cylindrical screw cap single chamber MFC (twist and play). This new design was compared to an existing MFC configuration [3] of the same volume (control) (Fig. 1). All MFCs used non-modified anode/cathode carbon fibre veil electrodes with a surface area of 154.8 cm².

Fig. 1. CAD drawing of the new screw cap MFC design. A) anode, B) cathode and C) control MFC design.

The MFCs were initially inoculated in batch-mode with activated sewage sludge and were replenished every 24h with 1 mL of TYE (1% Tryprone, 0.5% Yeast extract) for the first 14 days of the experiment. A 2.7kOhm resistor was connected to each MFC during this period. Following 15 days from the beginning of the experiment the feedstock was replaced with fresh non-treated human urine. At the same time, MFCs constructed from the same material formed hydraulically connected triplets, each connected to a continuous flow system. (22.4 mL/day) and tested under different electrical configurations. An HP Agilent 34970A
(Hewllet Packard, UK) unit was used for real time monitoring and for graphical analysis GraphPad Prism 5.01 (GraphPad Software Inc.).

III. RESULTS

A. Individual MFC units

Polarisation sweeps on individual units constructed from PC showed an increase in power by 10%, RC25 performed similarly with the control Nanocure, however ABS underperformed compared with the control by 22% (Table 1). Furthermore, the new design MFCs were tested for their ability to reduce chemical oxygen demand (COD). It is important to point out, that the twist and play MFC was primarily designed to be watertight and minimize oxygen presence when stacked in continuous flow mode, but allow air to penetrate when in batch mode. On the other hand, the control MFC was primarily designed to be permeable to atmospheric oxygen either in stack or in batch mode. Results suggested that COD removal from individual units from all 3 materials, exceeded the control values reaching up to a 15% improvement in urine utilisation (Table 2).

B. MFCs in parallel and in series connection (n=3)

Performance was also examined when MFCs, of the same material, were stacked in triplets and connected in parallel and in series configuration. The MFC triplet made out of ABS, produced 35% and 38 % more power when connected in parallel and in series, respectively, when compared to the control triplet. Similarly, the RC25 triplet exhibited a 28% increase equally when in parallel and in series connection. Interestingly, the PC triplet underperformed by 10% when connected in parallel, but produced 30% higher power than the control MFC when connected in series (Table 1). The large variations in performance between parallel and series connection for all materials may be attributed to the time taken between the measurements, hence the maturity of the biofilm. It is important to mention that in all cases the maximum power transfer (MPT) load from the polarization curves was similar for all MFCs.

<table>
<thead>
<tr>
<th>Power mW/m²</th>
<th>MFC unit</th>
<th>3 In parallel</th>
<th>3 In series</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>2.1</td>
<td>2.9</td>
<td>8.5</td>
</tr>
<tr>
<td>RC25</td>
<td>1.9</td>
<td>4.4</td>
<td>8.2</td>
</tr>
<tr>
<td>ABS</td>
<td>1.5</td>
<td>4.9</td>
<td>9.5</td>
</tr>
<tr>
<td>Control RC25</td>
<td>1.9</td>
<td>3.2</td>
<td>5.9</td>
</tr>
</tbody>
</table>

Table 1. Maximum power points from all three scenarios

The results from COD removal in parallel and in series show an increase in COD treatment from the control MFC. This can be attributed to the fact that when the control MFCs were connected in series and in parallel, the additional utilisation occurred due to the presence of atmospheric oxygen in the anode chamber. Therefore, the initial results from COD removal and power generation from individual units, suggest that even in the presence of oxygen, the new MFC design allowed the anaerobic biofilm to utilise more efficiently the available organic substrate.

Analysis of individual cells indicated that PC was the best performing material, which concurs with previous findings [5], however in more complex electrical configurations ABS proved to be the better material in terms of power generation.

<table>
<thead>
<tr>
<th>COD removal</th>
<th>MFC unit</th>
<th>3 In parallel 1k load</th>
<th>3 In parallel 105Ω load</th>
<th>3 In series 300Ω load</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>44%</td>
<td>24%</td>
<td>15%</td>
<td></td>
</tr>
<tr>
<td>RC25</td>
<td>37%</td>
<td>34%</td>
<td>16%</td>
<td></td>
</tr>
<tr>
<td>ABS</td>
<td>36%</td>
<td>25%</td>
<td>14%</td>
<td></td>
</tr>
<tr>
<td>Control RC25</td>
<td>29%</td>
<td>38%</td>
<td>25%</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. COD removal from all different materials in different electrical configurations.

IV. CONCLUSIONS

This study introduced a novel MFC design (twist and play), which outperformed the previous RC25 design in terms of power and COD treatment. Furthermore, a range of structural materials was tested using the new design and it was found that ABS and PC were superior. These results demonstrate that the RP technology is critical to advancing the MFC technology, particularly for miniaturisation, stacking and powering real-world applications.

ACKNOWLEDGMENTS

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REFERENCES


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THE EXPERIMENTAL STUDY ON THE DYNAMIC BEHAVIOR OF COUPLED REACTOR WITH CATALYTIC COMBUSTOR AND STEAM REFORMER

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ABSTRACT
The coupled reactor with catalytic combustor and steam reformer has been regarded as external reformer for the solid oxide fuel cell (SOFC) system. The methane conversion rate of a steam reformer can be increased by thermal integration with a catalytic combustor. When the SOFC is operated during transients of instant load changes such as start-up and stop, the amount of SOFC anode-off gas used as a fuel for catalytic combustor and the amount of methane should be converted into hydrogen can be changed, which can make the SOFC system unstable. The objective of the study is to investigate the dynamic correlation between catalytic combustor and steam reformer during transient. The 1 kW coupled reactor is fabricated and used to investigate its dynamic behavior experimentally. In order to determine the experimental condition, the system analysis for the coupled reactor and SOFC has been conducted with ASPEN PLUS®. The study can provide the basic insight to establish the optimal design for the coupled reactor during transient.

EXPERIMENTAL SETUP
Figure 1 shows the schematic diagram of the experimental apparatus used to estimate the coupled reactor performance. The mass flow rate of the reactant gas was controlled by the mass flow controller (Brooks Instrument® 5853S). Pure CH4 (>99.95 %) mixed with steam was used as the reactant gas for the steam reformer. In order to simulate the SOFC anode-off gas, H2, CO, CO2, CH4, and steam was uniformly mixed by passing it through the static mixer and supplying it to the catalytic combustor. The gas compositions at the outlet of the steam reformer and catalytic combustor were measured by gas chromatography (Agilent 7890A).

EXPERIMENTAL CONDITIONS
The gas compositions of the coupled reactor are represented by the gas temperature. In order to investigate the dynamic correlations between catalytic combustor and steam reformer, the variations of the
temperature distribution in the coupled reactor along the gas flow direction were captured. Table 1 presented the variations of the operating parameters of excess air ratio. Since the catalytic combustion is drastically degraded at a temperature higher than 950 °C, the range of operating conditions were set to be values that make the temperature of the catalytic combustor lower than 950 °C. Consequently, the coupled reactor was operated at the instant changes of excess air ratio from 2.5 to 4.5.

Table 1. The variations of the operating parameters for the coupled reactor

<table>
<thead>
<tr>
<th>Inlet temperature</th>
<th>Excess air ratio</th>
<th>Fuel utilization</th>
<th>SCR</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 °C</td>
<td>350%</td>
<td>60%</td>
<td>2.5, 3.0, 3.5, 4.0, 4.5</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSIONS

Figure 2 shows the variations of the temperature distribution in the coupled reactor at the instant change of the excess air ratio from 2.5 to 4.5. As the excess air ratio is increased from 2.5 to 4.5, the maximum temperature of the catalytic combustor is increased from 760 °C to 930 °C during 72 sec. In the catalytic combustor, most of the fuel was combusted at the inlet of the combustor and the heat generated from the catalytic combustion is gradually transferred to the steam reformer along the gas flow direction. This resulted in the highest variation of the temperature at the inlet section of the catalytic combustor during transient. Since the heat is transferred from the catalytic combustor to the steam reformer, the temperature in the outlet section of the steam reformer is increased from 577 °C to 596 °C during 120 sec. The difference of characteristic time for the temperature increase between catalytic combustor and steam reformer was resulted from the time discrepancy of reaction kinetics and thermal capacity between catalytic combustor and steam reformer, and the thermal resistance through the catalytic combustor and steam reformer. Since the temperature variation in the catalytic combustor during transient is decreased along the gas flow direction, the temperature of the steam reformer is not changed from the fourth section to the outlet.

CONCLUSIONS

The dynamic correlation between the catalytic combustor and steam reformer was experimentally investigated at the instant changes of excess air ratio. This work suggests the basic insight for optimal design of the coupled reactor during transient.

REFERENCES

EXPERIMENTAL STUDY OF A FIXED BED MEMBRANE REACTOR FOR HYDROGEN PRODUCTION

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Abstract - The integration of palladium based membrane reactor in PEM fuel cell based heat and power cogeneration systems allows to feed fuel cells with a pure hydrogen flux. The characteristics of a thin (4.5 μm) Pd-23%Ag alloy membrane supported on porous Inconel substrates on a fixed membrane reactor test bench have been investigated. The hydrogen fluxes under controlled conditions of temperature (673-873 K) and trans-membrane differential pressure (200–700 kPa) were measured. An hydrogen permeability value of 9,18×10⁻¹³ mol/(m²·s·Pa) at 773 K have been founded and this is consistent with available literature data. The infinite hydrogen selectivity has been demonstrated by the tests.

Keywords - Hydrogen, Palladium membrane, Membrane reactor, Permeability

I. INTRODUCTION

In the field of pure hydrogen production from reforming of hydrocarbons, a large number of studies have revealed the performance enhancement of catalytic membrane reactors (CMR) compared to conventional systems. In particular, in Combined Heat and Power (CHP) applications based on PEM fuel cells, greater attention has been given to the use of dense metallic membranes thanks to the very high purity achievable (>99.99 % H₂) which is very favorable for PEM lifetime.

Compared to a conventional fuel processor that produces in 4 stages (steam reforming reactor, two water gas shift reactors and a preferential oxidation reactor) a flow of H₂ diluted with CO₂ and other inert, the CMR solution allows the fuel cell to operate at a higher voltage (for a given specific current) and fuel utilization factor, but strongly reduces degradation rates due to CO poisoning.

II. EXPERIMENTAL SETUP

A. Membrane reactor test bench

Performances of a membrane reactor strictly depend on the membrane characteristics as permeation flux and perm-selectivity. The reactor tested has 10 commercial dead-end membrane tubes of 3.18 mm outside diameter and 200 mm length and it is filled with a CPO catalyst Ni-Al₂O₃ (supplied by REB [1]). The membrane consists of a porous metal support reinforced with Inconel, having two Pd₀.⁷₇-Ag₀.²₃ layer: one of thickness 3.0 μm on the outer surface and one of thickness 1.5 μm on the inner surface. The 10 tubes are welded by their open ends to a plate manifold.

The reactor is capable of producing 3 Nl/min of hydrogen from steam reforming. The maximum operating temperature (to maintain membrane stability) is 973 K. The membrane reactors can be fed with three different gases, CH₄, N₂ and H₂, controlled by mass flow controllers and steam supplied by means of a pump. The reactor pressure is controlled by using pressure transmitters and a modulating valve located in the retentate outlet pipeline. The maximum working pressure of the reactor is 10 bar, while on the permeate side pressure it is ambient. The gas analysis section consists of mass flow meters both on the retentate and the permeate sides.

Fig. 1 Membrane reactor setup
A scheme of the fixed bed membrane reactor is shown in Fig. 1. The reactor has an internal diameter of 21.2 mm and 510 mm height and it is externally heated by an 850 W electric furnace. The temperature inside the bed is measured at three different heights (at the top, bottom and middle of the membrane tube), and controlled modulating the furnaces power output. Permeate from each tube is collected at the bottom of the reactor.

**B. Hydrogen permeation test**

Starting from the flowrate measurement of the permeated hydrogen, the general expression of the hydrogen flux (Eq. 1) was considered to determine the permeance with three parameters to be calculated: \(E_a\), \(P_0\) and \(n\).

\[
J_{H_2} = \frac{P_0 e^{-\frac{E_a}{RT}}}{t} \left( P_P^n - P_F^n \right)
\]  

The main parameters of a membrane affecting on overall permeation performance are the temperature and the membrane permeance. Permeance expression typically depends on temperature, showing higher values for higher temperatures.

Different reactor operating conditions were investigated by varying the hydrogen partial pressure, feeding pure hydrogen or \(H_2/N_2-H_2O\) mix, and gas temperatures. In particular, the behavior of the membrane has been investigated in the range of operating conditions where processes for producing hydrogen from hydrocarbons take place: temperatures from 673 to 873 K and pressures from 200 to 700 kPa.

**III. RESULTS**

**A. Hydrogen permeation behavior**

In the first tests, pure hydrogen was fed into the reactor in order to calculate \(E_a\) and \(P_0\); other tests were carried out feeding the reactor with \(H_2/N_2\) or \(H_2/H_2O\) mixture to estimate possible absorption of other species on the membrane surface or the effect of polarization concentration on mass transfer. As shown in Fig. 2(a), hydrogen flux is proportional to the hydrogen partial pressure, so the exponent value of the hydrogen partial pressure is about 1. This factor is in agreement with experimental results on membranes having thickness below 6 μm [2][3]. This means that the hydrogen permeation process is likely to be controlled by the surface reaction rather than by bulk diffusion, due to the much thinner Pd layer of this composite membrane.

Therefore, the activation energy and the pre-exponential factor could be determined and are respectively 7.72 kJ/mol and 3.05·10^{-12} mol/(m·s·Pa). Fig. 2(b) shows the hydrogen flux resulting from Eq. 1 for all tests versus the measured flux: this reveals that the membrane behavior is not affected by the feed composition.

**IV. CONCLUSION**

The measured membrane permeance is quite close to the values present in the literature. Permeation tests revealed that the parameters (\(E_a\), \(P_0\) and \(n\)) of the general expressions for the hydrogen flux are not affected by the operating conditions or the mixture feeding. The tests have demonstrated that this membrane has the capability to separate hydrogen from gas mixtures with a complete hydrogen selectivity.

Future works will be dedicated on an experimental campaign to value the performance of the membrane reactor feeding natural gas and bio-ethanol: hydrogen recovery factor and fuel conversion will be evaluated at different operating conditions.

**ACKNOWLEDGMENT**

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**REFERENCES**

PROGRESS IN ALKALINE MEMBRANE FUEL CELLS AND ELECTROLYSERS

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Abstract - The effect of amine and sulfide anion functional group on the conductivity and performance of alkaline anion exchange membrane fuel cells (AAEMFCs) are reported. TMA functionalized LDPE-co-VBC offered the highest conductivity with values of up to 0.043 S cm\(^{-1}\). TMA functionalized electrodes showed superior cell performance in comparison to the other functional groups with a current density of 0.72 A cm\(^{-2}\) at 0.6 V and a peak power density of 478 mW cm\(^{-2}\) under air 1bar (gauge). The membrane exhibited good long term stability at temperatures up to 80°C. A study of a water electrolyser with alkaline anion exchange membranes with Cu\(_{x}\)Mn\(_{1-x}\)O\(_2\) (CuMnO) catalysts gave promising performance using a quaternary OH\(^{-}\) ionionomer binder based on polymethacrylate.

I. INTRODUCTION

Alkaline fuel cells utilize hydrogen and oxygen to produce electricity and water. Reversing the process, a regenerative fuel cell is integrated with an electrolyser to produce hydrogen and oxygen using water and electricity. The work presented herein highlights the current research progress in both alkaline membrane fuel cells and regenerative fuel cells.

II. METHODOLOGY

A. Membrane Performance

The effect of functional groups has been studied in terms of OH\(^{-}\) conductivity and ionomer suitability for fuel cell electrodes. Amine and sulfide functional groups studied were Trimethyl amine (TMA), 1,4-diazabicyclo[2.2.2]octane (DABCO), Dimethyl sulfide (DMS), Diethyl sulfide (DES), Triethyl amine (TEA), N,N,N',N'-Tetramethyl-1,6-hexanediamine (TMHDA). The aminated poly (LDPE-co-VBC) membrane (DOG 26%) were produced by the mutual radiation grafting technique wherein low density polyethylene was used as the base polymer. The membrane conductivities were measured using the four point probe technique (in plane) and two point technique (through plane).

The stability of the LDPE membrane with TMA functionalization was evaluated by first soaking the membrane in 0.1 M KOH for 10 days and rinsing it several times with deionized water prior to evaluating its conductivity under vapor phase operating conditions.

B. Fuel Cell and Electrolyser Test

Fuel cell electrodes were made from catalyst inks to which poly(vinyl benzyl chloride) (PVBC) was added to facilitate ionic conductivity. The ink was then air-brushed onto a gas diffusion electrode (non-woven carbon cloth) incorporated with wet-proofed micro porous layer (Freudenberg (FFCCT), Germany). The experimental single cell used coated titanium with a 1 cm\(^2\) serpentine flow fields. Trimethylamine functionalized radiation grafting poly (LDPE-co-VBC) CEAM-2 was used as membrane with catalyst loadings of 0.4 mgPt cm\(^{-2}\) for both anode and cathode.

In order to develop the alkaline anion exchange membrane water electrolyisers (AAEMWE), a quaternary OH\(^{-}\) conductive ionomer binder based on polymethacrylate was synthesized by copolymerization of three kinds of methacrylate monomers, which was followed by quaternization. The cathode was a copper cobalt oxide deposited onto a stainless steel mesh coated with the ionomer.

III. RESULTS AND DISCUSSION

Figure 1 shows the through plane conductivities of poly (LDPE-co-VBC) membrane with various functional groups in OH\(^{-}\) form at 100% RH. Membranes functionalized with TMA, DES, DABCO and TMHDA exhibited increase in conductivity with temperature up to 70°C; beyond which conductivity decreased. At 80°C when the conductivity measurement was repeated after 40 mins, a large fall in conductivity occurred for all studied membranes. Sulfide based groups showed lower
stability with temperature in comparison to amine based groups. The increase in length of the chain in the aryl group (for example from methyl to ethyl) attached to the nitrogen (amine) or sulphur (sulfide) led to lower conductivity and poorer thermal stability. Membranes functionalised with TMA showed the highest through conductivity up to 0.043 S cm$^{-1}$.

![Figure 1. Through-plane conductivity of poly(LDPE-co-VBC) membrane with various functional groups in OH$^-$ form](image1)

Fig. 2 shows the fuel cell performance at 50°C and 100% RH, O$_2$ (atm). TMA functionalized electrodes showed superior performance in comparison to the other studied functional groups with a current density up to 1 A cm$^{-2}$ at 0.6V.

Figure 2. Polarisation curves of poly(LDPE-co-VBC) membrane, 50°C, 100% RH O$_2$ (atm).

![Figure 3. Membrane stability tests as a function of temperature.](image2)

Figure 3 shows stability tests of the membrane. There was a steady fall in conductivity for approximately 9 days with then a constant conductivity at 40 °C. This can be explained by wash off of residual alkaline solution in the membrane with the constant humidity feed. Stepwise increase in temperature resulted in increase in conductivity which were stable for the period of the tests for up to 10 weeks.

![Figure 4. Polarization curves of AAEMWE. Dash line is IR corrected data. Insert is EIS response at 2.1 V.](image3)

The conductivity of this ionomer reached 0.059 S cm$^{-1}$ at 50 °C (100% RH). With this electrode in the AAEMWE, a current density of 100 mA cm$^{-2}$ was obtained at a voltage of 1.9 V as shown in Figure 4. Satisfactory stability of the membrane electrode assembly was observed from chronocoulometry.

![Figure 4. Polarization curves of AAEMWE. Dash line is IR corrected data. Insert is EIS response at 2.1 V.](image4)

IV. CONCLUSIONS

Poly(LDPE-co-VBC) membranes functionalized with TMA showed the highest through-plane conductivity with superior fuel cell performance compared to other functional groups

ACKNOWLEDGMENT

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FCpoweredRBS: A DEMONSTRATION PROJECT TO SUPPLY TELECOM STATIONS THROUGH FC TECHNOLOGY


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Abstract – H₂-PV hybrid systems may represent a valid solution to foster the use of renewable sources and power off-grid Radio Base Stations (RBS) for telecom applications. A demonstration project has been funded in the FCH-JU named FCpoweredRBS. The activities of the project are described in this paper.

Index Terms – PEM Fuel Cells, alkaline electrolyzers, Radio Base Stations, Renewable sources.

I. INTRODUCTION

The use of FC and H₂ electrolyzers joint to PV modules is an enabling technology for the diffusion of Radio Base Stations (RBS) fueled by renewable sources [1]. The FCpoweredRBS EU project has been funded to demonstrate this potential, and consists of the experimental implementation of 18 operating sites in Italy, which will be tested on the field for at least 6 months.

II. SYSTEM LAYOUT AND CONTROL

The system layout is provided in Fig. 1. It includes a PV module (5 or 10 kWp), feeding a battery charger that is connected to a 48V DC bus supplying power to the RBS load. In case of excess PV power, the energy can be stored in a battery pack or to power an electrolyzer (that in turn fills up 30 bar H₂ bottles). Both batteries and electrolyzer are hooked-up in parallel to the DC bus. In case, instead, of PV power lack, batteries or Fuel Cells (fuelled by 30 bar or 200 bar H₂ bottles) can supply power to the RBS load, thus ensuring its continuous operation. A rule-based control strategy has been optimized to maximize the exploitation of renewable sources and maximize FC lifetime.

Fig. 1. System schematic.

The project includes all the aspects of the realization of FC-powered RBS systems, from system design, testing, site engineering and on-site demonstration.

III. NUMERICAL MODELS AND EXPERIMENTAL SETUP

In addition to the use of validated Matlab-Simulink models mainly used for system design and optimization, the University of Rome Tor Vergata has setup a lab for FC-powered-RBS testing, capable of data acquisition with regard to all charge and H₂ fluxes, including 2 electronic loads (EL) (11 kW total), 4 DC Power Supply Units (PSU, 16 kW total). The system is

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A benchmark has been defined according to a 72h radiation profile, reported in Fig. 6, that is representative of the FC-RBS system behavior over different seasons (winter first day, summer second day, intermediate seasons third day). Results gathered so far, for the Dantherm system w/o electrolyzer, tell that performances of the sub-systems are in line with the expected nominal performance parameters (efficiency, H\textsubscript{2} consumption, etc), and no power interruptions have been observed at the load. Current evolution, measured on the different components, is provided in Fig. 7. The system operation allows for having a FC efficiency defined as \( \eta_{FC} = \int_0^T \frac{P_{FC-out}}{P_{FC-in} + P_{bat-in}} dt \) and higher than 50%. System efficiency defined as \( \eta_{RBS} = \frac{\int_0^T P_{load}(t) dt + \int_0^T P_{bat-in}(t) dt}{\int_0^T P_{FC-out}(t) dt + \int_0^T P_{FC-out}(t) dt + \int_0^T P_{bat-out}(t) dt} \) has been measured in the range of 95%. Tests will be done on the field for at least 6 months to correlate benchmark results with real ones.

IV. RESULTS

A graphic showing the current measured over time during the benchmark testing of Dantherm system.

V. CONCLUSION

FCpoweredRBS is a project funded by the FCH JU aiming at demonstrating the performance of FC based system to ensure continuous operation of radio-base-stations powered by PV modules. At the current stage two solutions for the energy generation of Radio Base Stations have been designed and realized, and are being tested in the lab by means of a testing procedure specifically developed in the project. Results obtained so far tell that the system ensures continuous operation, and that single components efficiencies are in-line with the declared rated performance, thus proving the good performances of the overall system. Tests on the field will be done in the next months to have data about real performance parameters during operation.

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INNOVATIVE SORBENTS FOR SE-SR: TEST BENCH AND PROCEDURE SETUP

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Abstract - The implementation of a hydrogen energy policy will be an interesting way to reduce the greenhouse effect. In this perspective, sorption-enhanced steam reforming (SE-SR) is a promising process for the hydrogen generation. In fact, it allows, in a single reactor, the production of a hydrogen-rich syngas, from natural gas or not fossil gas (syngas from biomass or landfill gas), while capturing CO₂ by reaction with a solid sorbent mixed with the catalyst. In order to overcome main limitations of standard CaO, innovative sorbents must be developed and tested. The worldwide research activity moves mainly in two directions: the use of synthetic sorbents and performance improvement of CaO-based sorbents. The authors are approaching the second one and the first step, described in the following, was the development and setup of all instruments and procedure for the synthesis, characterization and experimental testing of innovative sorbents.

Index Terms - CaO-based sorbent, CO₂ capture, SE-SR

I. INTRODUCTION

The conventional catalyst/sorbent materials used in SE-SR are respectively nickel and CaO. Latter one is characterized by low cost, good sorption capacity and acceptable sorption rates achieved at temperatures higher than 500°C. Anyway, critical issues are highlighted for SE-SR process involving CaO-based sorbents: 1) rapid decay in the CO₂ sorption capacity [1][2] in multi-cycles process, 2) energy penalties due to the high temperature required for sorbent regeneration (900°C) with risks of catalyst sintering.

Relative to point 1), this research activity addresses the development of sorbents with improved long-term stability. In particular, the attention is focused on sorbents based on incorporation of CaO particles into inert materials which, by acting as structural supports, significantly reduce the performance degradation due to surface area and pore volume loss. Different techniques of synthesis will be investigated and sorbent performance will be validated on bench scale (about 50-100g) through a wide experimental campaign. To this aim, suitable reactor and test bench were designed and realized; moreover test procedures were defined. In the following the test bench description, beyond that details relating instruments required for sorbents synthesis and characterization.

II. INSTRUMENTS FOR SYNTHESIS AND CHARACTERIZATION

Pointing to strategies of synthesis based on sonochemical methods that improve the mixing of compounds through acoustic cavitation [3], an Ultrasound generator titanium horn type 750 W (20 kHz) with a tip diameter of 13 mm and with Amplitude of 40% will be used. The structure of sorbents will be characterized by X-Ray diffraction (XRD) with Cu Kα radiation and a 2θ range of 30-90°. The morphology of the sorbents will be observed, after metallization with Cr, using a Field Emission Gun Electron Scanning Microscopy LEO 1525. Elemental composition will be determined using Bruker Quantax EDS. TEM images will be obtained using a Philips 208 Transmission Electron Microscope preparing samples by putting one drop of an ethanol dispersion of the catalysts on a copper grid pre-coated with a Formvar film and dried in air.

III. SE-SR REACTOR AND TEST BENCH

As shown in Figure 1, the test rig was equipped with a fixed-bed tubular reactor in Hastelloy X in order to allow possible simultaneous high operating pressure and temperature (10 bar, 900°C). The sorbent/catalyst bed was placed in the isothermal zone between two pieces of glass wool. Following past modeling activities [4], relating reactor geometry optimization to maximize process performance, a ratio length/inner diameter equal to 20 was used for the reactor design. Three thermocouples were placed inside the reactor, through the outlet, in contact with the catalyst bed. The reactor was housed inside a 3-zones furnace that ensures an isothermal profile in throughout the reactor length. As evident from Figure 1, gas lines are fed from cylinders provided with pressure reducing valves that guarantee a 3-10 bar line pressure. After passing through a line shut-off valve, the reactant gases are fed into the reactor by means of dedicated mass flow controllers; check-valves are installed to prevent products flowing back. Water is dosed by means of an alternative positive displacement pump supplying 0.01 and 5 ml/min and pressures up to 600 bar. A
temperature controlled gas preheater and a liquid evaporator prevent condensation inside the reactor.

![Figure 1 Test bench scheme](image1)

![Figure 2 test bench](image2)

At both reactor inlet and outlet, the flow passes through 15 μm sintered filters made of 316 stainless steel for particle capture. At the reactor outlet, reaction products pass through a liquid/gas separator fitted with a high-resolution capacitive level sensor. This system allows the condensation of liquids at low temperature; liquid draining is performed automatically. Gases leave the separator through the upper part towards the pressure control system. It consists of a servo positioned micrometric regulating valve providing a continuous and constant flow of gases at the outlet.

After the pressure control system, exhaust gas passes through a flow meter for flow rate determination and then it is analyzed by two micro-GC columns for detection of H₂, N₂, CH₄, CO₂ and H₂, O₂, N₂, CO, CH₄ respectively. A sample every 1.5 min is analyzed and recorded.

The whole bench, shown in Figure 2, is controllable remotely by a dedicated software that allows the programming of each test phase by varying one or more operating parameters.

IV. TESTING PROCEDURE

Firstly, sorption capacity and its stability in multi-cycles processes will be experimentally determined for each developed sorbent. Cyclic carbonation and calcination will be performed at suitable temperatures, T_{CARB} and T_{CALC} respectively. Carbonation phase: a fixed flow rate of CO₂ feeds the reactor until the sorbent is saturated and CO₂ appears in the outlet gas; then, the gas mixture is switched to pure N₂ and reactor heated to T_{CALC}. Regeneration phase: it is conducted in pure N₂ until the CO₂ content in the outlet gas, determined by the GC, is negligible; after complete calcination, the temperature is decreased to T_{CARB} for next cycle.

Then, during the second section of experiments, sorbents with best performance will be tested in SE-SR process. The procedure for the execution of SE-SR tests includes 4 main steps: pre-calcination of the sorbent material, catalyst activation, hydrogen production process, sorbent regeneration. Sorbent pre-calcination: the sorbent, mixed with the catalyst in particular weight ratio, is pre-treated in N₂ atmosphere at T_{CALC} and ambient pressure; this phase runs out when no CO₂ is observed in the effluent gas. Catalyst activation: to reduce the catalyst, the reactor is cooled down to T_{CARB} in H₂/N₂ atmosphere, increasing the pressure to operational value. Reforming: reactor feeding is switched to the fuel composition gas and, by means of the GC section, the system performances, in terms of H₂ purity and CH₄ conversion, are determined; at the end of the reforming step, the sorbent is completely carbonated. Sorbent regeneration: in presence of the catalyst and at T_{CALC} and ambient pressure, the sorbent is regenerated in N₂ atmosphere in order to avoid oxidation and, therefore, the re-reduction of the catalyst at the beginning of each cycle. The regeneration progress is monitored by the CO₂ content in the product gas.

Both experiments sections will be carried out with different T_{CARB} and T_{CALC}, in order to determine the values which maximize the efficiency of the overall SE-SR process.

V. CONCLUSION

Main results obtained in this research activity are:

- Design and realization of a SE-SR reactor and relative test rig for the testing of innovative CO₂ sorbent materials.

Operating conditions: material weight loaded in the reactor of 50-100g; variable feeding fuel mixture; variable process temperature and pressure up to simultaneous values of 900°C and 10 bar respectively.

- Definition of test procedures.

ACKNOWLEDGMENT

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REFERENCES


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THERMAL TRANSIENTS MODELLING OF A REFORMER UNIT FOR DIAGNOSTIC ANALYSIS OF SOFC-BASED SYSTEMS

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Abstract - Solid oxide fuel cell-based systems constitute one of the most promising technologies for future power generation. In order to make them marketable, many issues as durability and operational management have to be overcome. Therefore the understanding of thermodynamic and chemical mechanisms, that govern SOFC BoP components (beyond that the stack one) behaviour in both steady-state and transient operation, becomes fundamental. In this context, after stack dynamic analysis [1] and investigations relative to SOFC-based systems [2,3], the study was extended to the methane steam reformer unit, with particular attention to its dynamic thermal behaviour. In particular the overall analysis methodology and the required experimental campaign were defined as described in the following. Future work will deal with the execution of all the scheduled tests and the model setup according to the developed methodology.

Index Terms – Reformer thermal transient, dynamic modeling, SOFC-based systems

I. INTRODUCTION

Object of the present study is the thermal transients modelling, starting from experimental data, of a reformer unit for SOFC-based applications. In particular the steam methane reforming is considered. The reformer thermal modelling is of great interest for diagnostic scopes, beyond that for the unit management optimization. In fact, it can predict, varying the main operating parameters, the temperature time variation, providing information useful to avoid unwanted operational states and to prevent system malfunctions. Aiming to the modelling of the reformer thermal transients, this paper describes both followed methodology analysis (Section II) and procedures (Sections III and IV). In particular, considering the complexity of thermal phenomenon that occur in the reforming unit, the application of experimental system identification techniques is proposed. Consequently, also the test bench setup and the definition of the experimental campaign needed for model development are described.

II. THERMAL ANALYSIS METHODOLOGY

In order to identify the input and output parameters that influence the reformer thermal dynamic behaviour and the related transfer functions, the reformer thermal balance was characterized as a first order phenomenon, as shown in (Eq.1).

\[ C \frac{dT_R}{dt} = Q_b - \dot{m}_{\text{CH}_4} \Delta h_{\text{reac}} - b \dot{Q}_c - T_{\text{amb}} \dot{Q}_{\text{stream, in}} - \dot{Q}_{\text{stream, out}} \]  

(1)

Where:
- \( C = \dot{Q}_b + \dot{m}_{\text{CH}_4} (1 + SC \cdot \frac{r_{\text{mv}}}{r_{\text{mw}}}) \) is the reaction specific enthalpy (kJ/kg),
- \( b \) is the product of heat transfer coefficient and surface area,
- \( Q_b \) is the thermal power externally supplied,
- \( \Delta h_{\text{reac}} \) is the reaction specific enthalpy (kJ/kg),
- \( \dot{m}_{\text{CH}_4} \) is the methane flow rate (kg/s),
- \( T_R \) and \( T_{\text{amb}} \) are respectively the reformer and the ambient temperature,
- \( \dot{Q}_{\text{stream, in}} \) and \( \dot{Q}_{\text{stream, out}} \) refer to the enthalpy flux of the reformer input and output streams.

Passing, through suitable steps, to the Laplace domain (Eq.2) it can be possible to identify input and output of each transfer function (TF). Thanks to the superposition principle, the three TFs of Eq. 2 allow to determine the reformer temperature behaviour.

\[ T_R(s) = \frac{\dot{Q}_b}{C} + \frac{b}{C} T_{\text{amb}} + \frac{k}{C} \dot{m}_{\text{CH}_4} \]  

(2)

With: 
- \( \dot{Q}_b \)
- \( T_{\text{amb}} \)
- \( \dot{m}_{\text{CH}_4} \)
- \( k \) the reactor operating temperature \( T_R \)

Therefore model input parameters are identified in \( \dot{Q}_b \), \( T_{\text{amb}} \) and \( \dot{m}_{\text{CH}_4} \); the reactor operating temperature \( T_R \) is obviously the model output. It was stated to calculate the gains and time
constants of each transfer function on the basis of experimental data, by applying experimental system identification techniques and, in particular, the area method. Consequently, the test bench was setup and a suitable testing campaign was defined as detailed in Section III.

III. TEST BENCH AND TEST PROCEDURE OVERVIEW

A suitable test bench is necessary for the execution of experimental activities: so, the reactor was hosted and particular operative conditions, in terms of \( \dot{n}_{\text{CH}_4} \) and \( \dot{Q}_b \), were established. According to Eq. 2, in fact, it is not necessary to experimentally investigate the \( T_{\text{amb}} \) variation (therefore kept at about 20°C). This because both gain and time constant of the related TF are equal to the \( b/C \) term, i.e. the time constant value of the other two TFs. In details, the bench (Figure 1) is composed of three main units: evaporator, gas mixer and reformer. The gas feed line containing desulphurized natural gas is mixed with the steam from the evaporator and then sent to the reactor. Both evaporator and reformer temperatures are controlled by thermoregulator and can be set at desired values. In addition thermoregulator can be set at constant power. Reformer temperature is measured in three different points: input, middle and output; the latter is the one used for reactor control and, therefore, considered as \( T_R \) parameter of Eq.2. Flow meter controllers permit to set water flow rate to the evaporator and natural gas to the gas mixer.

![Figure 1 Test bench](image)

Test campaign was designed to study the thermal transients of the system, when specific step-variation of only an input parameter at a time was given. The reference conditions to execute \( \dot{n}_{\text{CH}_4} \) step-variations are shown in Table 1 in terms of fuel and steam flow rates (a \( S/C \) ratio of 2.5 is kept for all conditions). Step-variations were defined following the order A→B→C→D and reverse.

<table>
<thead>
<tr>
<th>Natural Gas [l/min]</th>
<th>Steam [g/h]</th>
<th>( S/C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.5</td>
<td>421.8</td>
</tr>
<tr>
<td>B</td>
<td>3.2</td>
<td>379.6</td>
</tr>
<tr>
<td>C</td>
<td>2.8</td>
<td>337.4</td>
</tr>
<tr>
<td>D</td>
<td>2.5</td>
<td>283.4</td>
</tr>
</tbody>
</table>

Table 1 Reference conditions for \( \dot{n}_{\text{CH}_4} \) step-variation tests

The first condition A was established to guarantee a SOFC operative delivered power of 1250 W at 60% of efficiency. It corresponds to a system nominal power of 1 kW, considered as potential size for European single house market [4]. Further gas conditions were selected for power rate modulation of 90, 80 and 70% of SOFC nominal value respectively for case B, C, D. Moreover, \( \dot{Q}_b \) step-variations were scheduled. In particular, step modulation from 1.3 kW, nominal value up to 90, 80 and 70% were considered, at fixed \( \dot{n}_{\text{CH}_4} \). At each input step-variation, it was stated to measure \( T_R \) for one hour, because sufficient for temperature stabilization.

IV. PROCEDURE FOR THERMAL TRANSIENTS MODELLING AND CONCLUSIONS

In particular for each TF of Eq.2 and for each relative input step-variation, time constant and gain (1/C, b/C and k/C, b/C respectively for \( \dot{Q}_b \) and \( \dot{n}_{\text{CH}_4} \) steps) will be determined by applying the area method to the system experimental response. The mean gain and time constant values, obtained for each input parameter, will be used for the development of the reformer transients model. To provide an example, the area method was applied to a \( \dot{n}_{\text{CH}_4} \) single step response, from A to B (Table 1) at \( \dot{Q}_b \) fixed value of 1.3 kW. Values of 73 and 1340 were calculated respectively for gain and time constant. In Figure 2, simulated and experimental \( T_R \) trends are shown together with the considered \( \dot{n}_{\text{CH}_4} \) step.

![Figure 2 Trends of \( \dot{n}_{\text{CH}_4} \), simulated \( T_R \) and experimental \( T_R \) Vs time](image)

In conclusion, all procedures and tests required for transients modelling were defined; moreover the bench was realized. Future work will deal with the execution of all the tests and the model setup according to the proposed methodology. The European project H2FC (FP7-Infra-2011-1.1.16 GA n. 284522) is acknowledged for funding.

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THE SO₂ POISONING INFLUENCE ON THE KINETICS OF MCFC

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Abstract - The aim of this work is to test the effect of SO₂ poisoning on the performance of MCFC and their operating variables, investigate the relationships, propose phenomena reading and obtain new information to define tolerance limits. In particular, chemical, electrochemical and physical poisoning mechanisms were taken into account.

To support the investigation, experimental tests were performed at the Fuel Cell Research Center laboratories of KIST (South Korea) and a theoretical analysis was also proposed to suggest operating strategies.

Index Terms - Fuel contaminants, Molten Carbonate Fuel Cells, poisoning mechanism, sulphur dioxide.

I. INTRODUCTION
The research activity on MCFCs paid special attention to the possibility to use different fuel gases (natural gas, coal gas, biofuels, landfill gas, etc.). As the fuels can contain components harmful to MCFC operation, many works about anode poisoning mechanisms and effects can be found in literature.

Now the new application of MCFCs in the framework of the CCS (Carbon Capture and Storage) leads to focus attention on the risk of poisoning at the cathode side. In fact, MCFCs can be proposed as an interesting CCS solution taking account that MCFC cathode fed with air containing CO₂ can return fresh air. This peculiar property is related to the electrochemical reactions that take place inside MCFCs and allow CO₂ and O₂ to move from the cathode to the anode selectively. So MCFCs can be used, for example, to reduce the CO₂ emissions per kWh of a conventional power plant by feeding its exhaust to MCFC cathode: the CO₂ is concentrated at the anodic side and then more easily separated from this stream characterised by lower flow-rate and higher CO₂ concentration. Moreover, additional power is produced during the separation process. As a number of contaminants can be present in the flue gas to be fed to the cathode, specific tests need to clearly define MCFC tolerance limits.

II. RESULTS AND DISCUSSION
Only few works on this topic can be found in literature, and it is not completely clear what the MCFC tolerance limit for sulphur compounds is, as the limit depends on many factors such as temperature, pressure, gas composition, current density, cell components and system configuration (e.g. recycle and clean-up). Also, the mechanisms proposed in the literature have to be verified with experimental data.

The SO₂ in the cathodic gas seems to react with the cathodic compounds and form sulphur ions which migrate through the electrolyte and reach the anodic side. Here, they can chemically and electrochemically react with the anodic gas and form other sulphur compounds. In particular, hydrogen can react with sulphur ions and form hydrogen sulphide, whose harmful effect has already been discussed in several works [1,2].

\[
\begin{align*}
\text{CO}_3^{\text{2-}} + \text{SO}_2 + \frac{1}{2} \text{O}_2 & \rightarrow \text{SO}_4^{\text{2-}} + \text{CO}_2 \quad \text{(Cathode)} \quad (1) \\
\text{SO}_4^{\text{2-}} + 4\text{H}_2 & \Leftrightarrow \text{S}^\text{2-} + 4\text{H}_2\text{O} \quad \text{(Anode)} \quad (2) \\
\text{S}^\text{2-} + \text{H}_2\text{O} + \text{CO}_2 & \Leftrightarrow \text{CO}_3^{\text{2-}} + \text{H}_2\text{S} \quad \text{(Anode)} \quad (3)
\end{align*}
\]

These mechanisms and in particular the main role of the transfer of SO₄²⁻ ions to the anode side has already been verified by the authors in a previous work which is now under revision for the publication on the International Journal of Hydrogen Energy. The presence of H₂S at anode side outlet was detected and post-tests on anodic samples showed a sintering effect typical of H₂S poisoning. Also, an increment of the charge transfer and the internal resistance was detected from the EIS analysis. In the present work, experiments about the exposure time effects have been performed in the laboratories of the Center for Fuel Cell Research at KIST, in particular focusing...
on the effect of different operating parameters (temperature, current density, gas partial pressures) and poisoning the cell with a fixed amount of SO\textsubscript{2}. Electrochemical Impedance Spectroscopy at open circuit voltage and gas analysis have been used to support the investigation.

\textit{A. Effect of different temperatures}

Polarization curves obtained at different operating temperatures highlighted the well-known effect on the OCV, which increases when the temperature decreases, in accordance with the Nernst equation. When the MCFC is running under load, the higher temperature favors behavior involving lower resistances. At a high current density, where diffusive phenomena are limiting, the lower temperature penalizes the mass transport coefficients and so the performance. When SO\textsubscript{2} was fed, no significant effects on the voltage were observed at a low current density, but at a higher current density the temperature influence was emphasized (Fig. 1).

The deterioration in performance seemed to be higher at a lower temperature, suggesting that the phenomenon is not driven by kinetics but thermodynamics.

\textbf{Fig. 1: I-V curves at 580 and 680°C in clean condition and under 2ppm SO\textsubscript{2} poisoning (*)}

\textit{B. Effect of different H\textsubscript{2} concentrations}

Polarization curves obtained under different H\textsubscript{2} concentrations show that SO\textsubscript{2} poisoning effect slightly increases at lower H\textsubscript{2} concentration.

\textbf{Fig. 2: I-V curve at 70% H\textsubscript{2} concentration in clean condition and after 3 days of SO\textsubscript{2} poisoning (2 ppm)}

\textbf{III. CONCLUSION}

From these first results again sulphur compounds seems to have a main role in MCFCs poisoning, since the cell is affected by the presence of even less than 1 ppm of SO\textsubscript{2} and the cell life is drastically reduced by this effect.

From this experimental campaign it has been noticed that the effects on the cell do not depend only on the composition of SO\textsubscript{2} fed, but also by the overall gas concentration, the total flow ratio, the exposure time, the cell temperature and the current density.

The proposed mechanism involving the formation of SO\textsubscript{4}\textsuperscript{2-} ions which accumulate and migrate to the anode side where they react with H\textsubscript{2} to form H\textsubscript{2}S have been confirmed and the role of anode poisoning seems to be significant.

Currently the single effects of other operating parameters are under study in order to have a deeper evaluation of the effects that SO\textsubscript{2} has on the kinetics.

\textbf{ACKNOWLEDGMENT}

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\textbf{REFERENCES}


ABSTRACT

Direct-fired fuel cell turbine hybrid power system response to open-loop transients were evaluated using a hardware-based simulation of an integrated gasifier/fuel cell/turbine hybrid cycle (IGFC), implemented through the Hybrid Performance (Hyper) project at the National Energy Technology Laboratory, U.S. Department of Energy (NETL). System response to disturbances in cathode airflow and fuel cell load were studied, and transfer functions were developed to be used in future controls development. The evaluation includes distributed temperatures and current densities along the fuel cell over the course of the transient along with localized temperature gradients. The importance of cathode airflow regulation is quantified through transfer functions.

INTRODUCTION

A hybrid system composed of a gas turbine and a solid oxide fuel cell is a key technology in reaching power efficiency targets that will help to eliminate emission at competitive costs [1]. These systems are highly coupled, and the fuel cell transient performance affects the gas turbine response, resulting in complicated control issues.

The Hybrid Performance (Hyper) project at NETL makes use of hardware in the loop simulation (HILS) of a 200kW to 700kW solid oxide fuel cell (SOFC) system numerical model coupled through hardware to a 120kW gas turbine with exhaust gas recuperation [2]. The major hardware components of the Hyper facility are shown with the integrated fuel cell and gasifier models in Figure 1.

This configuration is unique because it allows examination of coupled electrochemical transient impact on compressor dynamics without the risk of destroying an expensive real fuel cell. The big advantage of this configuration is that a more detailed model is used to predict the electrochemical transient dynamics, reducing the computational effort compared to a dynamic model of the entire system [3].

DESCRIPTION OF TESTS

The experiment was focused on the impact of a 10.5% reduction in cathode inlet air flow on the dynamic performance of the hybrid system. To target the step change of a 10.5% cathode airflow reduction, the hot-air bypass valve (FV-380) was opened by 8%.

Two different tests were performed in this experiment:

- A hardware-in-the-loop simulation was conducted. The fuel valve (FV-432) was dynamically controlled by fuel cell model to evaluate the impact of electrochemical transient on the hybrid system.

- The fuel flow to the combustor was set constant to determine the effect of FV-380 on the turbine speed without fuel cell simulation under the test conditions.

Figure 1: Hybrid Performance Facility at NETL
Since the hot air bypass valve does not affect overall system efficiency, it was expected that only the fuel cell $\Delta T$ would be increased without any other system impact.

**RESULTS**

Figure 2 shows the impact of cathode inlet air flow reduction on solid temperature of 20 nodes in the fuel cell. Due to large heat capacity of fuel cell, the solid temperature increased only slightly and gradually in the first 10 minutes.

The fuel cell model was coupled to the fuel valve in the system during the open loop simulation, and the impact on turbine speed is shown in Figure 3 by the blue line. It is shown that the reduction of air mass flow resulted in a significant reduction of the thermal effluent from fuel cell. Less heat went to the turbine in response and the speed was consequently lowered dramatically over a 5 second period. The heat flux from solid to gas in the fuel cell remained constant, due to the negligible temperature change between the solid and the air; the reduction in cooling mass flow results in a corresponding reduction in total thermal effluent. In the following test, the fuel cell model was not coupled and the change in hot air bypass had no effect on the heat balance of the system, thus the turbine speed did not change significantly, as shown in Figure 3 by the red line.

**TRANSFER FUNCTIONS DEVELOPMENT**

The coupling between the fuel cell and the turbine can be studied by developing empirical transfer functions, to capture the dynamic from hot-air valve change to turbine speed. For simplicity, all empirical transfer functions of higher order are generally approximated as First Order Plus Delay Time (FOPDT):

$$G_1(s) = \frac{0.013 \cdot e^{-20s}}{(25 \cdot s + 1)}; \quad G_2(s) = \frac{-0.1 \cdot e^{-1.9s}}{(5 \cdot s + 1)}$$

The gain is the ratio between the change in actuator output and the change in the process variable. Regarding the uncoupled test, just a very small variation in turbine inlet temperature causes a very little change in turbine speed, as shown by the red line in Figure 3. The dynamic is very slow, and thus the dead-time of this actuator has been considered to be 20 seconds, and the time constant to achieve 63% of the new steady state speed is 25 seconds.

The fuel cell simulation test shows a higher coupling between cathode air flow change to the fuel cell and turbine speed. The gain is ten times bigger than $G_1$, the dead-time and the time constant show a stronger interaction with the turbine speed. A change of just 10.5% in cathode air flow reduction shows a change of 400 rpm in turbine speed, in just 5 seconds.

Future works are going to examine larger step changes in cathode air flow to study stronger interactions between the turbine and the fuel cell performance in more detail.

**REFERENCES**


DETECTION AND IDENTIFICATION OF FUEL PROCESSOR DEGRADATION OR FAILURE IN SOFC SYSTEMS

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Abstract – We focus on a laboratory-size SOFC system and we investigate reformer degradation and failure both experimentally and through a model; comparison between experimental and modeling results is presented and discussed. The results show that reforming faults are highly dangerous because they can generate large thermal gradients in the SOFC stack. Fault maps are presented and discussed, which are the basis of a fault detection and identification tool.

Index Terms - Fault Detection and Identification, Degradation, Solid Oxide Fuel Cell.

I. INTRODUCTION

Degradation is now considered the main barrier to be overcome for Solid Oxide Fuel Cell (SOFC) systems to step into the commercialization phase. In this work, we focus our attention on the degradation/failure of the reformer, which, when coupled to an SOFC stack in a system, is expected to impact the stack performance and even to trigger serious SOFC stack degradation. Indeed, when the reformer deteriorates, methane conversion is low and unreacted methane exits the reformer and undergoes endothermic steam reforming reaction directly inside the SOFC stack. This reaction is expected to be concentrated at the stack entrance, causing steep temperature gradients and thus mechanical stresses and eventually cracks. In this work, we analyze reformer degradation from two points of view: i) impact on SOFC system performance; ii) Fault Detection and Identification (FDI).

II. SYSTEM: EXPERIMENTAL AND MODEL

The experimental equipment is a laboratory-size SOFC system manufactured by Staxera (D) and experimented at EBZ (D). In this system, a reformer is fed with a mixture of methane and steam and a suitable catalyst activates the conversion into hydrogen and carbon monoxide. These are partially electrochemically consumed in the SOFC stack, generating reaction products (steam and carbon dioxide) together with electrical power and heat. The anode and cathode exhausts are then mixed and burned in the off-gas burner. The system is controlled and in particular the average temperature of the stack is maintained at 1123 K by varying the cathode air flow rate. A model of the entire system was developed at TPG (University of Genoa, I) in MATLAB®/Simulink, by coupling among them first-principle models of the three system components. The model was validated against experimental data obtained under both steady state and transient operating conditions (in case of non-faulty system operation). A description of the experimental system, of the model and its validation was presented in a previous paper [1].

III. FAULT IMPLANTATION: EXPERIMENTAL AND SIMULATION

In this work, we focus on reformer degradation and failure, which are investigated both experimentally and through a modeling approach. Thus, the first step has been the implantation of reformer faults in the experimental system. Reformer faults can be of different types: (i) fuel leakage, due to leaks in the fuel feeding circuit; (ii) water leakage, due to leaks in the water feeding circuit; (iii) reduced conversion of the steam reforming reaction, usually due to catalyst degradation and/or carbon deposition on the catalyst surface; this latter type of fault can be due either to a gradual catalyst degradation or to an abrupt reactor failure. These three types of faults have been mimicked experimentally by varying fuel flow rate, water flow rate and reformer temperature during time. Then, the faults have been simulated through the system model, to investigate the model reliability also in defective working conditions. Fig. 1 compares experimental and modeling results of SOFC stack temperature during an implanted reformer fault:

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during the fault, unreacted methane exits the reformer and undergoes endothermic steam reforming reaction inside the SOFC stack, causing a decrease of the average stack temperature. The agreement between modeling and experimental results is very satisfactory. Additional results (not reported here) demonstrate that the model shows a maximum error of $\approx 2\%$ when simulating experimental data of (i) temperatures measured from three different thermocouples located within the stack, and (ii) stack voltage (the stack is operated in galvanostatic mode).

**IV. SIMULATION OF REFORMER FAULTS**

The validated system model has been used to simulate reformer faults, and to draw fault maps. In Fig. 2, each point represents one faulty condition; the three types of reformer faults are all represented, and the fault magnitude is different from point to point. The residuals of measurable parameters, i.e. the power released by the system and the post-burner temperature, are employed as co-ordinates. Residuals are defined as the difference between the values of co-ordinate parameters in presence and in absence of faults.

Fig. 2 shows that when (i) fuel leakage occurs, both the system power and the post-burner temperature decrease; when (ii) water leakage occurs (the steam to carbon ratio $S/C$ has been reduced from the nominal value of 3 to 1.8, to remain in the safe area from the point of view of carbon deposition) both the system power and the post-burner temperature increase; and finally when (iii) reduced conversion occurs, the power supplied by the system remains almost constant while the post-burner temperature increases. These results can be explained taking into account that the controller varies the air flow rate fed into the system to keep the average temperature of the SOFC stack constant at 1123 K. Still concerning the SOFC stack temperature, further modeling results (not reported here) show that temperature gradients within the stack are below 10 K/cm with fault (i), but they easily increase above 10 K/cm with both faults (ii) and (iii), which confirms that these two latter faults are particularly dangerous because temperature gradients above 10 K/cm can cause the formation of cracks in SOFCs.

**Fig. 2. Modeled system performance in presence of reformer faults: o fuel leakage, * water leakage, □ reduced conversion.**

Maps such as that reported in Fig. 2, when completed with additional data representing the other possible faults occurring in the system, can be employed for FDI in SOFC systems during their operation, because they allow to identify the type of failures occurring in the system. Difficulties may arise from (i) superimposition of points representing different types of faults; (ii) reliable knowledge of the system performance in absence of faults (data necessary to calculate the residuals). This is available if a validated simulation model has been developed (as in the present case) or if a wide database of experimental data exists for the system under consideration.

**V. CONCLUSION**

We have analyzed reformer faults in SOFC systems by applying both an experimental and a modeling approach. Our results show that reformer deterioration or failure can trigger degradation of the SOFC electrochemical stack. Thus, early detection, diagnosis and correction of reformer faults is an issue of primary importance in SOFC systems. Simulated reformer fault maps have been presented and discussed, and can be employed for FDI in SOFC systems during their experimentation and operation.

**ACKNOWLEDGMENT**

We thank Staxera GmbH (Dresden, D) for providing the experimental SOFC system. This work was developed within the GENIUS Project FP7-JTI-245128. Financial support is gratefully acknowledged.

**REFERENCES**

BIOMASS-TO-FUEL CELL SYSTEMS: AN ALTERNATIVE FOR RENEWABLE DISTRIBUTED POWER GENERATION

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Abstract - The combination of biomass and fuel cell enables high efficiency utilisation of a renewable energy source, maximizing the energetic yield and minimizing the environmental impact in terms of polluting emissions. Fuel cells are expected to become an attractive option for being used with fuel gas produced either from anaerobic digestion or thermal gasification of biomass. The objective of this work is to assess the technical and economic feasibility of distributed generation via biomass powered fuel cells, using two different types of feedstock: lignocellulosic biomass and residues with high organic content. For this purpose, possible combinations of biomass gasification and anaerobic digestion with molten carbonate fuel cell are analysed and compared to conventional solutions.

This study has been carried out through the A.I.D.A. web software tool, developed by ENEA in collaboration with the University of Naples Federico II, which allows to analyse various business scenarios.

Index Terms - Anaerobic digestion, biomass availability, decentralised power generation, thermal gasification.

I. INTRODUCTION

Fuel cell technology is generally considered as a promising solution for decentralized electricity generation with high efficiency and very low environmental impact, especially if feed fuel gas is produced via renewable energy sources, such like biomass [1].

In order to assess the actual potential of biomass fuelled molten carbonate fuel cell (MCFC), a feasibility analysis has been carried out by using a standard methodology [2]. Both lignocellulosic biomass and organic residues have been included as possible feedstocks, therefore different conversion technologies, such as thermal gasification and anaerobic digestion, have been assessed. Finally the case study of a decentralised power generation system to be installed in the territory of Caserta, in the South of Italy, has been analysed.

A comparison with more traditional technologies for biomass to electricity conversion, such like anaerobic digestion or thermal gasification combined to ICE (internal combustion engine) and combustion coupled with ORC (organic Rankine cycle) has been also performed. Results have been finally compared to those provided by the web software tool A.I.D.A (Advanced and Innovative tool for Developing feasibility Analysis of biomass plants), developed by ENEA in collaboration with the University of Naples Federico II [3, 4].

II. METHODOLOGY

A. Biomass availability

The first step of the study is a reliable estimation of the available quantity of lignocellulosic biomass and organic residues (primarily manure) actually distributed on the area under investigation (the Province of Caserta).

Regarding the availability and distribution of forestry and agricultural biomass a methodology developed by ENEA in partnership with University of Naples “Federico II”, University of Tuscia, University of Perugia, University of Florence, University of Bologna, ITABIA and CRPA has been used [5]. Residual biomass from agricultural pruning has been evaluated as the most suitable, both for abundance and concentration, for a potential energetic valorisation.

As far as the organic residues are concerned, the focus has been pointed on the manure from buffalo’s cattle in the area, which proves to be the most important activity in the Province...
of Caserta. Cattle’s data, such as numbers, age and species, have been provided by the National Database for livestock, by the IZS of Teramo. The evaluation of manure and consequent deliverable biogas has been made using previous ENEA studies [3].

A GIS elaboration, which is showed in Figure 1, resumes the results of the biomass availability.

![GIS elaboration for agricultural pruning residual biomass and buffalo distribution on the territory of Caserta](image)

**Fig. 1. GIS elaboration for agricultural pruning residual biomass and buffalo distribution on the territory of Caserta**

**B. Techno-economic analysis**

The second part of the work focused the attention on the evaluation of the economical and energetic potential of the different options for the production of CHP (combined heat and power) by using the selected biomass. Fixed costs (CHP system, construction), as well as variable costs (maintenance, staff, biomass, assurance) and revenues resulting from the government incentives and from the selling of the thermal energy, where possible, have all been included in this economical comparison.

Figure 2 shows the NPV (net present value) of three different plants for CHP production via lignocellulosic biomass with an electrical output of 1 MW. A similar result has been obtained for organic residues.

![Net Present Value of different solutions](image)

**Fig. 2. Net Present Value of different solutions**

**C. A.I.D.A.**

The web tool called A.I.D.A. can supply data related to the availability of different types of biomass (wood, shells, sludge, manure, organic fraction of municipal solid waste, etc.) and the corresponding location; biomass qualitative and quantitative characteristics; detailed information on the different typologies of both anaerobic digestion and gasification plants currently available on the market, as well as on the different cogeneration technologies such like internal combustion engine, gas turbine, fuel cell. The modularity and versatility of the A.I.D.A. programming language offer the opportunity to expand and refine this instrument and allow the system to develop additional scenarios and solutions such as combustion, pyrolysis, etc..

**III. Conclusion**

The performed analysis has pointed out that:

- lignocellulosic biomass availability is delimited in a restricted area of the territory of Caserta, whereas the fermentable biomass has a quite homogeneous distribution;
- estimated availability of organic residues allows to produce much more energy than the lignocellulosic one;
- nowadays the best economical solutions for energy conversion of lignocellulosic and fermentable biomass are traditional technologies such as ICE and ORC;
- fuel cells seem to have good energetic and environmental performances but they still suffer the high investment and operational costs, especially those related to maintenance;
- whereas actually is possible to find “turnkey” solutions for MCFC feed by biogas from anaerobic digestion, coupling of gasification and fuel cells is still object of study; better results are expected from SOFC (solid oxide fuel cell) which seems to be more suitable than MCFC;
- first results obtained by A.I.D.A. are interesting and the implemented system seems to be suitable for several users, above all considering that one of the main challenge for the future is to promote the concept “from waste to resource”, producing innovation and creating new jobs in each area according to local natural resources.

**References**


DIESEL STEAM REFORMING CAPABLE OF POWERING 1KW PEM TYPE FUEL CELL


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Abstract – The project has focused on the development of a fuel processor based on steam reforming of hydrocarbons. The aim of this system is to reach a hydrogen flow of 1 Nm³/h, capable of powering 1kW PEM (proton exchange membrane) type fuel cell, and with a CO concentration lower than 10ppm.

In the first part of the project, different hydrocarbons were evaluated as feedstock to the reaction unit of steam reforming, and also different reforming catalysts. In addition, different catalysts for water gas shift reaction and for selective oxidation of CO were evaluated. The most appropriate operation conditions for each reforming unit aiming for a maximum hydrogen production and complete diesel conversion have been studied and the effect of increasing the quantity of diesel and water simultaneously on the performance has been too.

Index Terms – Hydrogen, steam reforming, diesel, fuel cell.

I. NOMENCLATURE

CO: Carbon monoxide.
CO₂: Carbon dioxide.

II. INTRODUCTION

To make progress in an economy based on hydrogen, one of the best options is the production of hydrogen from hydrocarbons. Liquid hydrocarbons are suitable to use as feedstock in order to produce hydrogen by means of steam reforming reaction if their high availability, their low toxicity and high energy density are taken into account [1-3].

Steam reforming process is one of the hydrogen production processes most used due to the following considerations [2, 4]:

• Higher hydrogen concentration in the syngas mixture (up to 70%).
• Higher efficiency of hydrocarbons conversion.
• The lowest CO₂ concentration per mole of hydrogen produced.

For a fuel processor of hydrocarbons to produce hydrogen capable of powering a PEM (proton exchange membrane) type fuel cell by means of steam reforming process, other additional stages like: water gas shift reaction (WGS) and selective oxidation of CO (COPROX) could be needed [5].

III. REACTION STAGES, HYDROCARBONS AND CATALYSTS EVALUATED AND OPERATIONAL CHARACTERISTICS

The reaction stages considered in this fuel processor are the following: steam reforming, water gas shift reaction and selective oxidation of CO. The system units are able to work either independently or jointly [6].

The basic operation of this reformer is: first, water and diesel are vaporized and mixed. The mixed stream enters the reformer which has a temperature of 700 °C. The outlet gas is a hydrogen-rich stream. This stream enters the WGS reactor which has a temperature of 325°C, with the aim of reducing CO and increasing hydrogen concentration further. Finally, the outlet gases of the WGS enter the COPROX reactor to achieve a CO concentration lower than 10 ppm. The reactors are electrically heated which are controlled with a PWM (pulse width modulation) control.

Figure 1 shows the system block diagram with all elements that integrate the diesel steam reforming.
Experiments in the fuel processor were done with the optimum catalyst which had been previously created [6]. The base material of the catalyst is a mixed oxide created by means of decomposition of a laminar double hydroxide (HDL), aluminum, magnesium and a percentage of nickel (NiMgAl). Figure 2 shows the comparison between the best catalyst and a commercial one. It should be pointed that it exist a big activity difference between them.

In order to study the effect of increasing the quantity of diesel and water simultaneously, different experiments were done at different scales. The main problem when the fuel processor is working at scale 1/1 is the vaporization and mixture of the water and diesel. In fact, in order to improve heat and mass transfer it is recommended to use a vaporizer-mixer filled with iron balls. Figure 3 shows flows of diesel, water and air to different scales.

<table>
<thead>
<tr>
<th>Scale</th>
<th>Qv diesel (ml/min)</th>
<th>Qv water (ml/min)</th>
<th>Qv air (ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/11</td>
<td>0.49</td>
<td>1.48</td>
<td>204</td>
</tr>
<tr>
<td>1/10</td>
<td>0.54</td>
<td>1.63</td>
<td>224</td>
</tr>
<tr>
<td>1/9</td>
<td>0.60</td>
<td>1.81</td>
<td>249</td>
</tr>
<tr>
<td>1/8</td>
<td>0.68</td>
<td>2.03</td>
<td>280</td>
</tr>
<tr>
<td>1/7</td>
<td>0.77</td>
<td>2.32</td>
<td>321</td>
</tr>
<tr>
<td>1/6</td>
<td>0.90</td>
<td>2.71</td>
<td>374</td>
</tr>
<tr>
<td>1/5</td>
<td>1.08</td>
<td>3.25</td>
<td>449</td>
</tr>
<tr>
<td>1/4</td>
<td>1.35</td>
<td>4.06</td>
<td>561</td>
</tr>
<tr>
<td>1/3</td>
<td>1.80</td>
<td>5.42</td>
<td>748</td>
</tr>
<tr>
<td>1/2</td>
<td>2.70</td>
<td>8.13</td>
<td>1122</td>
</tr>
<tr>
<td>1/1</td>
<td>5.40</td>
<td>16.25</td>
<td>2244</td>
</tr>
</tbody>
</table>

Figure 3 shows diesel conversion at different scales (1/10, 1/5, 1/3). It should be pointed out that activity decrease when the scale is increased. Therefore, to solve this problem, it is necessary to increase the contact time (F/W).

In summary, it is necessary to continue studying the influence of scale in the process and stability tests of longer duration that allow us to successfully work with linked units.

REFERENCES

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MPL BASED ANODE FOR IMPROVED PERFORMANCE IN MICROBIAL FUEL CELLS

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Abstract – Two different anode materials, carbon veil and carbon cloth, were modified with a micro-porous layer for microbial fuel cells. 2.2 and 1.8 times higher power was achieved as a result of this modification. Increase of anode surface area and conductivity through the modification are thought to contribute to this improvement.

Index Terms – anode modification, microbial fuel cells, micro-porous layer

I. INTRODUCTION

Anode materials play an important role in the performance of microbial fuel cells (MFCs) for practical applications. Amongst the various possibilities, carbon based materials are the most commonly used as anode substrata due to their chemical inertness and biocompatible properties. A number of modifications of the carbon-based materials have been made in order to increase their surface area and adhesion of microorganisms onto the anode interface [1-3]. A suitable MFC anode material requires high electrical conductivity, chemical resistance, large surface area, mechanical strength and biological compatibility. In this study, carbon fibre veil and carbon cloth electrodes were modified with carbon powder, in order to introduce a micro-porous layer (MPL) of improved surface area and conductivity. This approach has been widely used for developing cathode electrodes; this is the first attempt at employing these electrodes as anode materials.

II. MATERIALS AND METHODS

A. Anode Preparation

Three different carbon fibre veil (CV) electrodes and two carbon cloth (CC) electrodes were tested in triplicates, for this line of work. The MPL was a mixture of carbon black (Vulcan XG-72, main component) and PTFE (binder). The preparation of MPL material was according to Santoro et al. [4]. The resulting additional carbon loading from the MPL modification was approximately 18 g/m\textsuperscript{2}. The five types of anode electrodes were made of 16 layers of 4.2 cm\textsuperscript{2} (width: 2.2 cm, length: 1.9 cm) of electrode material, resulting in a total macro-surface area of 67 cm\textsuperscript{2}. Details of each electrode are presented in table I.

| TABLE I |
| DETAILS OF ANODE MATERIAL USED IN THE STUDY |
| Abbreviation | Composition | Original carbon content (g/m\textsuperscript{2}) | Total carbon content (g/m\textsuperscript{2}) |
| CV20 | Unmodified carbon veil | 20 | 20 |
| CV30 | Unmodified carbon veil | 30 | 30 |
| CV20-MPL | Modified carbon veil with MPL | 20 | 38 |
| CC | Unmodified carbon cloth | 115 | 115 |
| CC-MPL | Modified carbon cloth with MPL | 115 | 133 |

B. MFC Design and Operation

The MFCs consisted of 6.25 mL of anodic volume and open-to-air cathodes. The anode chambers had inlets and outlets (d=4 mm) on the bottom and the top respectively for continuous feeding. A cation exchange membrane (CMI-7000, Membrane International), 25 mm diameter, was placed between two electrodes. The cathode electrodes were made of hot-pressed activated carbon onto untreated carbon cloth and had a total macro surface area of 4.9 cm\textsuperscript{2}. Activated sewage sludge with 0.1M acetate was used as the inoculum and initial feedstock. Then the MFCs were fed continuously with human urine.
Power output was monitored in real time and polarisation experiments were performed periodically.

III. RESULTS AND DISCUSSION

As shown in Fig. 1, the MPL modification improved significantly the MFC performance when compared with the unmodified anode materials. The best performing anode material, CV20-MPL, produced a maximum power of 304.3 µW (45.4 mW/m² normalised according to the anode total macro surface area). This is 1.2 fold higher than the second best performing anode material, CC-MPL, which produced a maximum power of 253.9 µW (37.9 mW/m²). When this power is compared with that produced from unmodified material, the difference is much bigger. The maximum power produced by unmodified electrodes, CV20, CV30 and CC, was 140.0 µW (20.9 mW/m²), 180.7 µW (27.0 mW/m²) and 143.4 µW (21.4 mW/m²) respectively. Considering that the MPL modification was done on the carbon veil with a carbon content of 20 g/m² and plain carbon cloth, 2.2 and 1.8 fold higher power generating performance was achieved by modifying the carbon materials. Since a higher carbon loading (i.e. 30 g/m² as opposed to 20 g/m²) increased the performance of the unmodified carbon veil substrata, it is valid to assume that a higher carbon content (through MPL modification) contributed to the higher MFC power generation.

Another possible explanation for the performance enhancement with MPL modification, may be its surface characteristics. The investigated anode materials were characterised by scanning electron microscopy (Fig. 2). As can be seen, the MPL modification resulted in an uneven and rough finish on the plain carbon veil and carbon cloth electrodes, which results in higher surface area for bacterial attachment.

![Fig. 1. Polarisation curves of different anode materials](image)

![Fig. 2. SEM images of anode electrodes; (a) CV20; (b) CV30; (c) CC; (d) CV20-MPL; (e) CC-MPL; (f) MPL structure](image)

Conductivity improvement is also expected by increasing the amount of carbon. From the polarisation curves, the internal resistance of each MFC system was calculated and the MPL modified anodes showed much smaller internal resistance values of approximately 0.2 kΩ, whereas the unmodified anode MFCs had 0.7 kΩ (CV30), 1 kΩ (CV20) and 1 kΩ (CC).

IV. CONCLUSION

The new anode material modified with MPL outperformed the control carbon fibre veil and carbon cloth electrodes in terms of power generation. Considering that the plain carbon cloth material was 45 times more expensive than the carbon veil material used in this study, improvement of anode performance can be achieved at low cost through the MPL modification. This is the first time that the MPL has been reported as a good anode electrode for MFCs.

ACKNOWLEDGMENT

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REFERENCES


RESULTS ANALYSIS OF A MICROGRID COMPOSED BY PHOTOVOLTAIC GENERATORS AND FUEL CELL

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Abstract - Nowadays it has become almost mandatory to make use of the renewable energy sources which are a sustainable, cost-effective and environment friendly alternative for conventional energy sources. There are many studies that demonstrate the advantages of using micro grids (an aggregation of loads and micro sources operating as a single system providing power) but despite of that, micro grid concept is not usual in our ordinary world.

In this study, a prototype of micro grid is showed and an analysis of its performance is carried out. The micro grid under consideration involves four subsystems; generation, storage, demand and control subsystem. Generation is provided by photovoltaic panels (PV), and a fuel cell. The fuel cell is used as an alternative generator when the batteries reach the minimum allowable charging level and the load exceeds the power produced by the PV generator. The storage subsystem consists of the bank of batteries mentioned before and also several tanks of metallic hydrides which provide the fuel cell with hydrogen. Demand is simulated with an electronic load, letting apply different consumption profiles. The current control strategy is mainly based on the state of charge of the batteries but a high amount of variables is recorded to collect as much information as possible. Specifically, the data used in this study corresponds to a period of four years during which, the micro grid has been operating and undergoing several updates.

Index Terms -

I. INTRODUCTION

Despite the amount of variables measured in the micro-grid showed [1,2] the state of charge of the battery (SoC) is the main variable used by the control system. Thus this study focuses on the storage subsystem, especially in the electric storage.

The Coulomb Counting has been the method used to estimate the state-of-charge of the batteries in the micro-grid showed. This method calculates the SoC by measuring the battery current and integrating it in time according the equation

\[
SoC = Q_0 + \int_{Q_n}^{i_{battery}} dt \quad \text{(1)}
\]

where \(i_{battery}\) is the current extracted from the battery (which is assumed positive while discharging the battery), \(Q_0\) is initial charge, \(Q_n\) is nominal battery capacity and thus \(Q_n/Q_0\) is the starting value of SoC. The initial charge \(Q_0\) is set to be \(Q_n\) when the system starts from full battery charge. This method suffers from long-term drift and lack of a reference point, therefore, for long time periods of inactivity and certain punctual moments another method is used to calculate the state-of-charge that it is called the open-circuit voltage method. This method converts a reading of the battery voltage to SoC, using the known discharge curve (voltage vs. SoC) of the battery. The advantage of this method is its simplicity; however, it presents a serious drawback, related to the time the battery should rest before the open circuit voltage (OCV) can be measured.

Analyzing the overall system behavior, effects on photovoltaic generation system have been found as shown in Fig 1. Those effects may appear when the batteries are completely full because the batteries are unable to absorb more energy and the solar generation is limited.

When such effects have appeared, the SoC was estimated by the system with a value lower than 100% when in fact it has already reached that value. These phenomena mean energy losses in the system and therefore efficiency losses (Fig. 1).
II. METHODOLOGY

To solve this problem, we propose the use of a correction factor $\eta$ (equation 2). Where the values of $A_1$, $B_1$, $A_2$, $B_2$ and $D$ are empirically obtained based on historical data.

$$SoC = SoC_0 + \frac{\eta}{C} \int_{battery} dt$$  \hspace{1cm} (2)

Case 1 ($SoC_0 < D$): $\eta_1 = A_1 + B_1 \cdot SoC_0$
Case 2 ($SoC_0 > D$): $\eta_2 = A_2 + B_2 \cdot SoC_0$

By using this correction factor we achieve less difference between the estimated SoC with the correction method and the real current SoC, avoiding the effects mentioned before. Greater accuracy in the state of charge allows the control system manage more efficiently the different subsystems.

In the Fig. 2 it can be seen the comparison between the conventional method (green) and the simulation results of the proposed method with correction (red). With the proposed method the points when the SoC reaches the value of 100% matches with the points of drop in the solar generation, which indicates a good estimation, better than with the conventional method.

III. CONCLUSION

With the correction factor proposed, the SoC can be remained between 60% and 90% in order to get a better performance (Fig.3). Applying this method, energetic losses are avoided.

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SYSTEM LEVEL STRATEGIES TO COUNTER DEGRADATION IN SOEC PLANTS

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Abstract - Numerous studies have dealt with the degradation of SOEC cells and stacks, but very little information has been published concerning the system level impact.

The paper will compare different operating strategies to counteract ageing/degradation in SOEC plants:

• Increasing operating voltage
• Varying current densities
• Decreasing per stack conversion
• Increasing air flow
• Increasing operating temperature

The consequences and limitations of each strategy will be discussed.

Index Terms - Degradation, Mitigation, Operating strategies, SOEC.

I. NOMENCLATURE

SOEC: Solid Oxide Electrolyser
ASR: Area specific resistance.

II. INTRODUCTION

A number of degradation mechanisms have been identified for SOEC cells and stacks. They are all giving rise to an increase in the ASR, Traditionally the degradation has been measured at galvanostatic (constant current) conditions at fixed operating temperature letting the operating voltage increase. Although the degradation rates reported in the literature has decreased considerably it is still a major issue to be dealt in real systems. This paper discusses varies strategies on a system level to counteract degradation/ageing.

III. SYSTEM CONSIDERED AND COMPUTATIONAL METHODOLOGY

The system considered is a generic hydrogen plant based on SOEC as shown on Fig.1.

Steam is generated by means of heat exchange with the effluent from the SOEC stack(s) and an electrical heated boiler. A final electrical trim heater is also used for the final preheat before the stacks. The produced hydrogen with unconverted steam is cooled down. The condensed water and a part of the hydrogen is recycled back to the process.

The system calculations have been performed with proprietary Topsøe mass- and heat balance software using a 2D stack model. A generic adiabatic stack with a start ASR_{SOE} of 0.42 Ω*cm² at 725 °C has been used in the calculations.

IV. RESULTS

The consequences of a doubling of the ASR have been investigated using 5 different operating strategies:

A: Operate at unchanged operating temperature and let the current density decrease as the ASR increases. Operating at the thermoneutral voltage mean isothermal conditions for the cells which is minimizing any mechanical strains on the stacks. This
strategy naturally leads to a drop in productivity. If the ASR doubles the hydrogen production drops by 54 %, which, of course, is not very attractive for the plant owners point of view.

B: If the inlet temperature instead is fixed at 750 ºC and the current density at 0.6 A/cm the voltage will gradually increase as the stacks ages. Initially the operation will be endothermal resulting in a temperature drop across the stacks. Later the operation becomes exothermal and when the exit temperature reaches approximately 800 ºC end of run conditions have been reached due to rapidly increasing degradation of the interconnects and strain on balance of plant components. Productivity is, however, unchanged as well as energy efficiency at 3.07 kWh per Nm³ H² for the stack and 3.6 for the system.

C: In the base case at start of run the steam conversion chosen is 80 %. A lower steam conversion can compensate for some increase in ASR. Lowering the conversion of steam to 29 % per pass can compensate for only 21 % increase in ASR. The specific power consumption increases 3.5 % and what is more unacceptable is a necessary increase in heat exchanger duties by a factor of 2.7.

D: Another strategy also plays on using an improved Nernst potential like the decreased steam conversion in strategy C. This is instead achieved by using an air sweep on the oxygen electrode. An ASR increase of 25 % can be partly counteracted by increasing the air flow from zero to 5 times the steam flow. The average Nernst potential drops by 34 mV. The specific power consumption increases, however, by 5.6 %.

E: The preferred strategy is to maintain thermoneutral operation but raising the overall temperature level of the stacks as degradation progresses. A doubling of the ASR can be counteracted without any loss of efficiency by increasing operating temperature by 98 ºC. The required temperature to maintain productivity versus ASR is shown on Fig. 2.

Neither alkaline or PEM cells or stacks are capable of using this strategy because they need to operate in a narrow temperature window.

V. CONCLUSIONS

- At constant operating conditions the H₂ production will drop by 54 % as the ASR doubles
- Varying steam conversion can only compensate for a 21 % increase in ASR. The specific power conversion increases by 3.5 % and the heat exchanger duties by 273 %
- Air flow increase to the anode can accommodate a 25 % increase in ASR by going from no flow to 5 times the cathode flow. Power consumption increases by 5.6 %
- Fixing the inlet temperature and increasing voltage will transition the operation from endo- to exothermal. A doubling of ASR can be counteracted with almost unchanged specific power consumption
- Operating at thermoneutral conditions and increasing operating temperature by 98 ºC can compensate an ASR doubling without efficiency or productivity loss
- This is a unique feature of SOEC technology

Fig. 2
STRATEGIES FOR TAR REDUCTION IN WOOD-GAS FOR HIGH TEMPERATURE FUEL CELLS WITH DIFFERENT INNOVATIVE TECHNOLOGIES

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Abstract - The purpose of this paper is to assess techniques capable to ensure satisfactory removal efficiencies of tar from wood-gas produced by biomass gasification to be used in high temperature fuel cells.

The proposed approaches are compared with water absorption that is the most common technique used to remove contaminants and tar in many gasification plants even if most of the pollutants contained in the tar have low or no solubility in water, due to their hydrophobic characteristics.

The results are discussed by analyzing the Classes of Tar 2, 3, 4 and 5 and by comparing the removal efficiency of water absorption with waste-cooking oil absorption and the tar conversion evaluated by means of catalyst Nickel-Mayenite (5%) at two different temperatures (700-800 °C).

Index Terms - Absorption, Biomass, Gasification, Tar.

I. NOMENCLATURE

Tar Topping Atmospheric Residue

\[ C_{\text{tar}} \] TAR concentration in the gas (g/Nm³) before (in) and after (out) tar cleaning systems

\[ \eta \] Tar removal efficiency of the cleaning systems

II. INTRODUCTION

Gasification is a thermo-chemical conversion process by which the biomass is converted into a mixture of combustible gas (syngas or synthesis gas), Char and Tar () by the use of a gasifying agent such as air, steam and/or other. If just steam is used as gasifying agent, the syngas obtained is rich of H₂ and CO and it could be suitable to produce electric power by High Temperature Fuel Cells (SOFC, MCFC). Tar is a complex mixture of cyclic and polycyclic aromatic hydrocarbons [1] which is highly detrimental to human’s health. Moreover, the presence of these pollutants in the gaseous effluent makes unusable the syngas produced within turbines, engines and fuel cells devoid of an appropriate mechanical/physical gas cleanup systems.

III. RESULT AND DISCUSSION

A. Methods

The system used to perform the tests is a fluidized bed gasifier fed with steam as gasifying agent. The biomass used in the experiments was hazelnut shells. A cyclone and a high temperature ceramic filter were used to completely remove particulate from the syngas. Two different Tar cleaning systems were afterward investigated to verify their efficiency to remove tar from syngas:

1. Scrubbing by absorption in water or waste cooking oil
2. Catalytic steam reforming in a secondary fixed bed reactor using the new catalyst Ni/Al₁₄Ca₁₂O₃₃ (Ni 5% weight)

Downstream from the tar cleaning systems, residual tar in the gas was sampled by means of absorption and condensation in isopropyl alcohol at -10 °C. The gas yield is measured by a volumetric gas-meter. The tar are then measured by means of GC-MS, while gas products are analyzed by GC-TCD.

Once the concentration of tar is known before and after the cleaning system, the removal efficiency was calculated as follow:

\[ \eta = \frac{C_{\text{tar}}^{\text{out}} - C_{\text{tar}}^{\text{in}}}{C_{\text{tar}}^{\text{in}}} \times 100 \]

The exp setup conditions are summarized in Table I.

<table>
<thead>
<tr>
<th>Temperature of gasifier (°C)</th>
<th>Carrier gas rate (l/min) at 25°C</th>
<th>Biomass rate (g/h) at 25°C</th>
<th>Steam Rate (l/min) at 25°C</th>
<th>Temperature of ceramic filter (°C)</th>
<th>Temperature of impinger (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>850</td>
<td>1.5</td>
<td>345.6</td>
<td>20.6</td>
<td>200</td>
<td>-10</td>
</tr>
</tbody>
</table>

TABLE I

INITIAL EXPERIMENTAL SETUP CONDITIONS.
B. Technologies of Tar Reduction

The results of the tests are shown in Table II and Fig. 1. Test 1 was performed without the use of any technology of Tar reduction as reference input to verify the actual decrease of Tar for the different technologies tested.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Test 1</th>
<th>Test 2</th>
<th>Test 3</th>
<th>Test 4</th>
<th>Test 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technologies of Tar Reduction</td>
<td>-</td>
<td>Water absorption</td>
<td>Waste-cooking oil absorption</td>
<td>Catalyst Nickel-Mayenite at 700°C</td>
<td>Catalyst Nickel-Mayenite at 800°C</td>
</tr>
<tr>
<td>Volume (ml)</td>
<td>-</td>
<td>200</td>
<td>200</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Sampling (min)</td>
<td>1 test of 20 min each</td>
<td>5 tests of 20 minutes each</td>
<td>5 tests of 20 minutes each</td>
<td>4 tests of 35 min each</td>
<td>4 tests of 35 min each</td>
</tr>
<tr>
<td>Measured Concentration of Tar (g/Nm³)</td>
<td>27.85</td>
<td>18.47</td>
<td>9.19</td>
<td>8.21</td>
<td>4.11</td>
</tr>
<tr>
<td>Average reduction of Tar (g/Nm³)</td>
<td>-</td>
<td>9.37</td>
<td>18.65</td>
<td>19.64</td>
<td>23.73</td>
</tr>
<tr>
<td>Average Reduction Efficiency of Tar (%)</td>
<td>33.64</td>
<td>66.97</td>
<td>70.52</td>
<td>85.21</td>
<td></td>
</tr>
</tbody>
</table>

As shown in Fig 1 water has an absorption efficiency of 37.50% for the Tar Class 3 (Styrene, Xylene, Toluene, Benzene) compared to 68.37% shown by the oil. Regarding Class 4 (Acenapthylene, Fluorene, Phenanthrene, Anthracene and Naphtalene) and Class 5 (Pyrene) water showed absorption efficiencies similar or slightly greater than those of the oil. These results are in line with those obtained by Phuphuakrat et al [3]. The low absorption efficiency of water for Class 3 is explained by the low solubility of PAHs in water and the partial absorption of these compounds in water is essentially due to condensation at the ambient temperature. Water instead of oil shows good absorption due to its non-polar characteristic. On the contrary Tar compounds are able to dissolve in the oil. This makes the oil scrubber capable of tar removal [3]. As reported in Table II the catalyst at 700 °C showed a Tar reduction of 19.64 g/Nm³ and the total tar concentration (average value of 4 tests each with a duration of 35 minutes) was 8.21 g/Nm³. After the thermal cracking at 700 °C the Tar is mainly composed (by weight) of 75% phenol, 18% toluene, 6% styrene and 1% others. The total Tar removal efficiency was 70.52%, while for benzene and toluene, which are the most abundant pollutants, were respectively 70 and 82%. The same catalyst was tested at 800 °C. The total conversion efficiency was equal to 85.21% while that of the benzene and toluene were respectively 82 and 86%. The total tar concentration after the catalyst at 800 °C is equal to 4.11 g/Nm³. After the thermal cracking at 800°C Tar is constituted for 75% of phenol, 14% toluene and 10% of styrene. Furthermore in the tests with the catalyst no degradation was observed, the removal efficiency was stable during time.

IV. CONCLUSION

This work demonstrated that the catalytic steam reforming at 800 °C with the new catalyst Ni/Al₂₃Ca₁₂O₃₃ is the best and most reliable solution in term of tar removal performance with an efficiency of 83%. The produced wood gas requires minor purification efforts before being used in high temperature fuel cells. The results of this work showed no performance degradation for the new catalyst during all the tests. New and longer tests will be necessary in future works to verify this result. On the opposite, the use of a waste-cooking oil absorber produces greater removal efficiencies for non-polar compounds and in general it has a removal efficiencies comparable to those resulting from the use of catalytic cracking at 700 °C (with a total removal efficiency of 67% compared to 33% water).

Furthermore, water requires purification after absorption, while the waste-cooking oil can be reused as fuel within the gasifier in addition to the same biomass or transferred to an another plant, with a significant reduction of the costs for disposal and treatment [4].

REFERENCES

AN EXPERIMENTAL STUDY ON THE EFFECT OF THE LAND/CHANNEL WIDTH RATIO OF BIPOLAR PLATES ON CROSSOVER

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Abstract - In this study, the effect of the land/channel width ratio on crossover was investigated experimentally. Experiment was performed with three metallic bipolar plates which have different land/channel width ratio. To understand the effect of the land/channel width ratio only, the pitch, which is the sum of land and channel width, was fixed for all bipolar plates. After conducting the calibration process, the crossover rates were measured at the outlet. By the crossover rates which were obtained from this experiment, it is clearly explained that the crossover rate is increased as the channel width is decreased in a fixed sum of land and channel width condition. From this result, it is discovered that flow channel designs affect not only the performance but also the durability of the material of fuel cells such as membranes.

Index Terms - Crossover, Land/channel width ratio, Metallic bipolar plate (MBP), Polymer electrolyte membrane fuel cell (PEMFC)

I. INTRODUCTION

Recently, environmental problems have become an significant issue in the world. Therefore, the ways of removing the sources, which cause pollutions, have lastly attracted considerable attention. One of the priority targets is to change vehicles from oil-based ones to eco-friendly ones. Even though new vehicles which are powered by PEMFC systems, have emerged as a promising candidates, a few problems should be solved to commercialize them. To solve some of those problems, many ideas, such as designing optimized flow channels, are suggested.

By only considering the performance and easiness of the manufacturing process, wrongly adopted flow channel designs could cause the durability problem. Because the design can change some conditions such as pressure, it can have the effect on crossover phenomenon which is strongly related with the durability of the membrane[1].

Because not only the hydrogen ions but also other gas molecules can move through the membrane, crossover is occurred in a fuel cell[2]. So by many researchers, the researches about the crossover have been studied actively. Cheng et al.[3] and Broka et al.[4] measured the amount of hydrogen crossover according to the temperature and relative humidity conditions. Furthermore, Baik et al.[5] determined how much each operating parameters, such as membrane thickness, pressure, relative humidity, and temperature, affect crossover. However, the effect of the mechanical property likes flow channel type on crossover has not been studied yet.

Therefore, in order to clarify the effect of the land/channel width ratio on crossover, experiment was conducted with three different metallic bipolar plates for various temperatures in this study.

II. EXPERIMENTAL SETUP

A. Membrane and single fuel cell

In this study, Gore PRIMEA 57 series MEAs, GDLs, gaskets were used with a 25 cm² single fuel cell for each metallic bipolar plate. Three different bipolar plates whose pitch is same were prepared and the geometrical characteristics of the bipolar plates are arranged in Table 1.
TABLE I  GEOMETRICAL CHARACTERISTICS OF THE MBPs

<table>
<thead>
<tr>
<th>MBP types</th>
<th>Land width</th>
<th>MBP types</th>
<th>Land width</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBP 1</td>
<td>0.38</td>
<td>MBP 1</td>
<td>0.27</td>
</tr>
<tr>
<td>MBP 2</td>
<td>0.75</td>
<td>MBP 2</td>
<td>0.71</td>
</tr>
<tr>
<td>MBP 3</td>
<td>1.12</td>
<td>MBP 3</td>
<td>1.65</td>
</tr>
</tbody>
</table>

B. Experimental apparatus and mass spectrometer

Simply, two measurements were used in this research. One is the commercial tester (1kW test station, Chino Co., Korea) for obtaining electrical performance and another is the mass spectrometer (HPR-20 QIC, Hiden analytical, UK) for measuring hydrogen crossover rate for each PEMFC. To perform experiment accurately, calibration process was specially preceded with nitrogen-based standard gas mixture containing 300 ppm of hydrogen for mass spectrometer5).

III. RESULTS AND DISCUSSION

A. I-V performances of PEMFCs

In Fig. 1, the electrochemical I-V performance of PEMFC for three MBP types are represented. I-V performances were measured at RH 100% conditions. With same flow rate, the most narrow channel width design, MBP 3, had the highest performance until 1.0 current density point. However, standard type, MBP 2, was the only case where it is possible to measure the performance at higher current density than 1.0. It means that MBP 3 has the best performance in some selected regions. However, MBP 2 has the uniform performance in the whole region. It is because channel is too narrow to remove lots of water at high current density in MBP 3.

B. Hydrogen crossover rates of PEMFCs

Fig. 2 shows the hydrogen crossover rates according to the various temperatures for each bipolar plate. All PEMFCs were composed with Gore PRIMEA 57 series, so the hydrogen crossover rate in this study is smaller than that in other research paper reported. Furthermore, even though, originally contained hydrogen in nitrogen at a non-humidification condition is included, the differences between each case are clear. The most narrow channel type MBP 3 has the highest hydrogen crossover rate. That would be caused by high pressure due to the same flow rate in narrow channel.

IV. CONCLUSION

From this study, the relation between the flow channel design and the crossover rate was determined. With this result, we can predict that the flow channel design could affect the durability of the material in PEMFCs. Therefore, we should make sure to test both performance and durability for newly developed flow channel designs.

ACKNOWLEDGMENT

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REFERENCES

REFORMING BY EXCESS ENTHALPY FLAME FOR HIGH TEMPERATURE FUEL CELL

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Abstract - Experimental and computational simulation results for perforated SiC reformer design were presented for high temperature fuel cell system using excess enthalpy flame. Feasibility of non catalytic reformer with perforated SiC tube was verified through the computational simulation and experimental study and applicability of this non catalytic reformer to production of hydrogen and carbon monoxide rich gas was confirmed in this study.

I. INTRODUCTION

The fuel cell is energy inverter which can change chemical energy directly to electrical energy using the potential difference between hydrogen and oxygen. Its features, such as high power density, simple construction and fast start-up make it suitable for domestic appliances. Also, the efficiency of the process in a fuel cell system is not limited by the Carnot cycle efficiency.

The increasing interest in more efficient and low pollution energy conversion systems is the driving force for the ongoing developments in the fuel cell sector. In MCFC and SOFC hydrogen as well as carbon monoxide can be utilized as fuel. Thus, synthesis gas, which can be produced from hydrocarbon fuels, can be directly utilized in such high temperature fuel cells.[1]

For the projected demand in hydrogen, simple and efficient processes of hydrogen generation from various feed stock should be engineered. One of such solutions is a direct partial oxidation of hydrocarbon by excess enthalpy flame under rich and ultra-rich condition without catalyst.

Combustion in stationary porous media occurs inside the voids of the porous matrix. Energy is transferred to the solid by convection from the product gases. Conduction and radiation through the solid porous medium, which has much higher thermal conductivity than the gas mixture and additionally radiates significantly, distributes some of this energy to the region upstream of the flame. This in turn transfers energy via convection to the incoming reactants. The porous matrix acts in essence as an integral preheater. This preheating allows for higher combustion temperatures and increased stability compared to a free premixed laminar flame. Locally, the flame zone may reach temperatures higher than the adiabatic flame temperature of the unburnt mixture, which gives the name “superadiabatic or excess enthalpy flame” to this combustion technology.[2]

In this paper, we present computational simulation and experimental results for perforated SiC(Silicon Carbide) reformer design for SOFC using excess enthalpy flame. All experimental and computational simulation cases use methane as fuel, and results possibility of non catalytic reforming of hydrocarbon fuels using excess enthalpy flame.

II. EXPERIMENTAL APPARATUS

Commercial perforated SiC(Silicon Carbide) reformer is 100mm long, 50mm diameter and 31 holes separated by SiC walls. The flow holes have a radius of 4mm each and are divided by 2mm thick SiC walls.

Fig. 1. Schematics of experimental apparatus

Fig. 1 shows the schematics of experimental apparatus. The experimental apparatus consists of three main parts: the air and fuel flow system, perforated SiC tube reformer and data...
acquisition system.

Reformer system diagnostics were required to assess the temperature profile on the SiC wall and the synthesis gas composition of the exhaust gases. The SiC wall temperature distribution of perforated SiC tube reformer is measured by eight K-type thermocouple. The composition of the synthesis gases is analyzed using a HP 6890 series Gas Chromatography (GC).

### III. SIMULATION APPARATUS

In this simulation model, meso scale reforming process in the perforated SiC tube using a two dimensional approaches with GRI mechanism 1.2 was numerically investigated. GRI 1.2 mechanism contains 104 reactions and 22 species. The numerical simulation model is based on SIMPLE consistent algorithm using segregated solver of Ansys Fluent. The conservation equations of mass, momentum, energy and species are written as:

- **Mass**: \( (\partial / \partial x)(\rho \nu) = 0 \)
- **Momentum**: \( \nabla \cdot (\rho \nabla) = - \nabla p + \nabla \cdot (\rho \tau) + \rho g \)
- **Energy**: \( \nabla \cdot (\rho h + p) = \nabla (k \nabla T) - \sum h J_j + S_k \)
- **Species**: \( \nabla \cdot (\rho h Y_i) = - \nabla \cdot j_i + R_i \)

Commercial SiC tube is 100mm long, 4mm inner diameter and 6mm outer diameter is composed of a SiC cylinder. Fig.2 shows the computational mesh structure for the meso scale SiC tube. The computational mesh structure which were divided into 140X25 and adaption mesh mechanism.

### IV. RESULTS AND DISCUSSION

Fig. 3 presents the temperature curve for perforated SiC tube under equivalence ratio of 1.0 and inlet mixture gas velocity of 40cm/s was simulated. The temperature on this peak was roughly 48K higher than the adiabatic flame temperature of 2,223K for a free laminar flame at these same conditions.

Fig. 4 presents the comparison of experimental and computational simulation temperature curve for reformer under ultra rich equivalence ratio and different inlet mixture gas velocity. The SiC wall temperature is determined by the inlet mixture velocity and equivalence ratio. Computational simulation and experimental results follow similar trends, although experiments predict temperatures that are lower than the ones observed in computational simulation results.

Fig. 5 shows experimental and computational simulation results of hydrogen and carbon monoxide yield versus the different equivalence ratio and inlet mixture gas velocity. The percent hydrogen and carbon monoxide yield increases with increasing equivalence ratio.

### V. CONCLUSION

Feasibility of non catalytic reformer with perforated SiC tube was verified through the numerical and experimental study and applicability of this non catalytic reformer to production of synthesis gas was confirmed in this study.

### ACKNOWLEDGMENT

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### REFERENCES

THE CATALYTIC ACTIVITY OF SPITTERED COBALT LINKED WITH GRAPHITE ON CARBON PAPER IN PEMFC

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Abstract - A Cobalt (Co)-based electrocatalysts were fabricated by sputter deposition on graphene layered carbon paper (G/CP) and heat treatment in an ammonia (NH3) environment for oxygen reduction reaction (ORR) in polymer electrolyte membrane fuel cells (PEMFCs). A sample of 0.4 mg scattered graphene on CP showed highest current density among the samples having 0.2, 0.4 and 0.6 mg amount of graphene layer. However, it could not be inferred from the study whether 0.4mg was the optimal scattered of graphene in the Co/N/G/CP to facilitate high current density. As a result, further investigation needs to be performed to study the morphology and catalytic activity of Co/N/G/CP with different loading of graphene. Although the current density obtained for Co-based electrocatalyst was not as high as that for a Pt based electrocatalyst, the present study suggests that Co/N/G/CP could be a suitable electrocatalyst to introduce non-precious metal electrodes in the PEMFC.

Index Terms - Sputtering, Cobalt, cyclic voltammograms, Graphite, EIS

I. INTRODUCTION

Fuel cells are considered as the next generation devices that generate energy from abundant fuel with the flexibility of manufacturing high efficiency cells in various sizes.[1,2] In 1964, Jasinsky discovered that Cobalt prophyrin showed catalytic activity for oxygen reduction reaction (ORR). [3] As a result, non-precious metal based catalysts of the type M/N/C, where M is Fe or Co, stood out as the novel and low-cost electrocatalyst as a potential alternative of Pt-based catalysts. Numerous studies have been going on in order to improve the catalytic properties of M/N/C towards ORR in PEMFC [4-5]. In most of these studies, the catalysts were fabricated by non-precious transition metals in the presence of nitrogen precursor with a source of carbon at high temperatures. The source of transition metal is generally either salt or N4 metal complexes[6-7].

Since the sputter deposition is in principle an atomistic process, i.e., the atoms form a film or deposit by condensing on the substrate and migrating sites, where nucleation and growth occurs [8], one might expect that the transition metal electrode could be synthesized by this process with more precise control of metal content, film thickness, and even morphological feature [9]. Thus, our recent works focused on applying a sputtering process for fabrication of transition metal electrode [10]. Graphene is composed of pure carbon, with atoms arranged in a regular hexagonal pattern similar to graphite [11].
In this study, Co-based electrocatalysts were fabricated by sputter deposition on graphene layered carbon paper (G/CP) and heat treatment in an ammonia (NH₃) environment. The prepared Co on G/CP (Co/N/G/CP) was investigated as an electrocatalyst for oxygen reduction reaction (ORR) in PEMFC using cyclic voltammetry (CV), method and electrochemical Impedance spectroscopy (EIS).

II. EXPERIMENT

The samples was cut to a round shape with 0.5cm in diameter, and then attached to a glassy carbon disk by carbon tape, which was mounted on a RDE holder (Pine Instruments, USA). A Pt counter electrode and a saturated Hg/HgSO₄ reference electrode were used in a standard three electrodes configuration. The catalytic activity was investigated by cyclic voltammetry (CV) in 0.5M H₂SO₄ at room temperature with a voltage sweep rate of 20mV/s.

III. RESULT AND CONCLUSION

A Co-based electrocatalysts for PEMFCs were fabricated by sputter deposition on graphene layered carbon paper followed by heat treatment in an NH₃ environment, where graphene were impregnated on carbon paper by spray coating method. A sample of Co/N/G/CP with 0.4 mg scattered graphene showed the highest current density compared with samples with 0.2 and 0.6 mg scattered graphene. Even though the above result is not conclusive about the optimized amount of graphene for catalyzing ORR, the result indicates that Co/N/G/CP could be used as electrocatalyst for ORR in PEMFCs. Furthermore, we assume that the formation of ligands between Co and graphene/CP through nitrogen might play an important role in catalyzing the ORR, which needs further investigation.

Fig. 1. Cyclic voltammograms of Co/N/G/CP in O₂-saturated 0.5 M H₂SO₄ solution. Sweep rate = 20 mV/s. Normalized in reference to the geometric area of a RDE (0.196 cm²).

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REFERENCES

OBSERVING PROTON MOTION ON THE NANOSCALE IN POLYMERIC ELECTROLYTE MEMBRANES WITH QUASIELASTIC NEUTRON SCATTERING

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Abstract – We investigate the proton conductivity in high temperature polymer electrolyte fuel cells (HT-PEFCs) with a polybenzimidazole membrane doped with phosphoric acid to achieve the desired proton conductivity. Inelastic neutron scattering methods are applied to get insight into the proton mobility on a nanometer length scale.

Index Terms – Proton conductivity, high temperature polymer electrolyte fuel cells, neutron scattering, diffusion

I. INTRODUCTION

A promising material for the proton conducting membrane in high temperature polymer electrolyte fuel cells (HT-PEFCs) is polybenzimidazole (PBI) doped with phosphoric acid (PA)[1]. Such cells are well suited for medium power applications (up to ~ 5 kW), e.g. in small stationary units or for electrically driven devices. With working temperatures of 140-200°C the produced water evaporates and makes a complicated water management in the cell obsolete. The proton conductivity of PBI-PA is linked to the amount of acid in the membrane. A rather high PA content in the PBI membrane of > 400 wt% is needed to provide an adequate conductivity [2].

PBI membranes show a good chemical resistance and have a high glass transition temperature (~ 700 K). Although this kind of material has already been studied macroscopically (conductivity, rheology etc.), the microscopic dynamics have not been investigated in detail except from some molecular dynamic simulations [3][4].

The neutron scattering techniques offer a new window to reveal the microscopic processes, which are related to electrical ion conduction, and allow studying the dynamics of protons and the polymer matrix separately. Different components can be highlighted with isotopic labeling (exchange of normal with heavy hydrogen). The amount of the scattering vector q provides additional information about the length scales in the system. Recent backscattering and neutron spin-echo (NSE) results will be presented.

II. PROTON DYNAMICS IN PBI MEMBRANES

A. Samples

We studied PBI membranes doped with phosphoric acid. The membranes from Danish Power Systems were used as received and doped with protonated or deuterated phosphoric acid (85wt%) which has been purchased from Sigma Aldrich.

B. Neutron scattering

All neutron scattering experiments were performed at the FRM II research reactor at the Heinz Maier-Leibnitz Zentrum (MLZ) in Garching. Real space distance d and the length of the
scattering vector \( q \) are connected by \( d = \frac{2\pi}{q} \). Cold neutrons with a wavelength of \( \sim 5\text{-}10\ \text{Å} \) probe length scales in the nanometer range, and high resolution techniques like neutron spin echo (NSE) spectroscopy and backscattering spectroscopy provide the appropriate sub-\( \mu \text{eV} \) energy scale (or nanosecond time scale). The instruments J-NSE and SPHERES have been used for these two techniques. Both techniques allow studying the diffusive motion of the protons.

NSE measurements of a PBI membrane with a deuterated PA loading of \( \sim 500 \text{ wt\%} \) reveal the coherent scattering from the polymer network. The normalized scattering function is almost constant in the \( q \)-range of \( 0.05\text{-}0.11\ \text{Å}^{-1} \) and time range up to 40 ns, indicating that the PBI polymer chains do not show fluctuations on these length- and time scales but are rather rigid. An incoherent scattering contribution (from proton diffusion) can be observed. Further experiments are needed for a quantitative analysis of the incoherent scattering with NSE.

The proton diffusion has been studied with the backscattering spectrometer SPHERES. Elastic scans provide the mean square displacement of the protons as a function of temperature. The influence of the phosphoric acid protons has been studied by measuring a sample with a lower amount of phosphoric acid (170 wt\%), once protonated and once deuterated. The difference provides the mean square displacement of the PA protons alone (Fig. 1).

At temperatures below \( \sim 350 \text{ K} \) both samples showed a very similar behaviour, displaying mainly local (e.g. vibrational) motions of the protons which do not contribute to conductivity (inset of Fig. 1). At higher temperatures, diffusion dominates. The proton diffusion coefficient at 450 K is calculated from \( \left< u^2 \right> \) to be \( D_H = 5.3 \times 10^{-13} \text{ m}^2/\text{s} \) [5], much lower than that measured with the higher PA loading with NSE. With the Nernst-Einstein equation \( D_H \) translates into a conductivity from the diffusion of protons of \( \sigma = 0.07 \text{ S/m} \) (assuming a proton density of \( 3\times10^{28} \text{ m}^{-3} \)). An activation energy can be calculated from an Arrhenius plot (Fig. 2) \( \ln(D_H) \) vs \( 1/T \) for \( T > 350 \text{ K} \) (with \( D_H \sim \sigma T \)) and leads to an activation energy of 13 kJ/mol.

**Fig. 1.** Root mean square displacement of protons as a function of temperature (in K) determined with elastic scans at SPHERES. The inset shows the two contributions from PBI loaded with deuterated and protonated PA.

**Fig. 2.** Arrhenius plot of the conductivity above 350 K. The slope yields an activation energy of 13 kJ/mol.

### III. CONCLUSION

HT-PEFCs have been investigated with inelastic neutron scattering techniques. NSE showed that the polymer network is very rigid, while the diffusion of hydrogen could be measured on the appropriate time- and length scales of nanoseconds and nanometers respectively with backscattering spectroscopy. The conductivity associated to this microscopic process has been deduced.

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MORPHOLOGY AND WETTABILITY OF DIFFERENT GAS DIFFUSION LAYERS AND THEIR IMPACT ON FUEL CELL OPERATION

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Abstract – GDL design is still an important field within fuel cell research. State-of-the-art GDLs contain two layers: fiber substrate and MPL. The morphology of the layers is strongly dependent on the manufacturing process. The characteristics of three different MPL compositions were investigated using multiple methods. Some results of the performed research methods were presented. The surface contact angles were determined to assess the hydrophobicity of the MPL surface, which directly faces the catalyst layer within a fuel cell. Mercury porosimetry served as an indicator for the inner morphology. Furthermore, the vapor sorption properties of the materials were investigated and the minimum pressures for water breakthrough (hydro head) were measured to characterize water inventory. In addition, polarization curves with varying gas humidity were performed to investigate fuel cell performance.

Index Terms – contact angle, differential water vapor sorption, hydro head, micro porous layer

I. INTRODUCTION

To balance the water distribution for a suitable membrane humidification and at the same time to prevent blockage of gas diffusion layer (GDL) pores or gas channels is still a key issue in fuel cell research. Depending on the range of operating conditions needed, different GDLs can be selected each with a certain combination of characteristics. One preparation often used is the coating of the fiber substrate with a micro porous layer (MPL). A broad consensus exists that the MPL has a positive effect on fuel cell performance as it changes electrical and mechanical contact. The morphology of the MPL depends on the slurry and the preparation method. Cracks in the MPL can be considered as starting points for water paths through the fiber structure of the GDL [1]. Chun et al. found a corrupted surface around the MPL cracks due to water flow during accelerated aging [2]. Within the presented study, MPLs with hardly any cracks are investigated to compare the slurry composition.

II. EXEMPLARY RESEARCH METHODS

Table I shows the surface wettability of the investigated MPLs. The substrate side is marked with an *.

A. Surface Wettability

B. Water inventory
applying pressure of a water column on the GDL from the MPL-side. The GDL with hydrophobic MPL shows the highest barrier against water breakthrough (hydro head pressure over 150 mbar). Additional investigations during fuel cell operation employing synchrotron radiography showed eruptive water transport at low currents and even water removal at high currents. By the plasma-treatment, the hydro head is lowered to 109 mbar. The partly-hydrophilic MPL results in a hydro head of 77 mbar; this indicates that the hydrophilic fraction of this MPL can initiate water paths through the GDL.

Differential water vapor sorption (DVS) is used to investigate water content during a stepwise increase of the surrounding steam humidity. At each step, mass uptake after reaching equilibrium relative to the dry mass of the sample is plotted (see figure 1). The mass uptake of the GDL with partly-hydrophilic MPL differs from the beginning and reaches a considerably higher maximum value. The curves of the GDLs including hydrophobic and plasma-treated MPL, respectively, are similar until a value of around 40 % r.h. Above this value, the GDL with hydrophobic MPL adsorbs more water in monolayer because of a higher specific inner surface (BET value 7.5 m²/g measured with octane) shown by the more flat slope of mass uptake. The BET values of the hydrophobic and the partly-hydrophilic MPL amount to 5.6 and 4.2 m²/g.

C. GDL Morphology

The morphology was investigated using mercury porosimetry. The maximum in pore size distribution of the substrate without any equipment is 16.0 µm. By MPL coating, the maximum is decreased to roughly 13.2 µm for all three samples because the areal coating weight is almost identical. Additional investigations employing µ-computer tomography showed only an intrusion of the hydrophobic MPL of a few µm into the substrate, but a uniformly coverage.

In addition, mercury porosimetry also reveals the pore size distribution at nm-scale which can be assigned to the inner-MPL porosity. Hydrophobic and plasma-treated MPL feature almost the same maximum at around 32 nm as the plasma only affects the surface. In contrast, the local maximum for the partly-hydrophilic MPL is located at a much higher value of 107 nm.

D. Fuel Cell Operation

Single fuel cells, each one built up with one of the MPL variations on the cathode and all with the same anode GDL (featuring the hydrophobic MPL), have an overall good performance at state-of-the-art operating conditions. As the gas humidity is increased from 50 to 100 % r.h., the power of the fuel cell containing the hydrophobic MPL on the cathode increased. Synchrotron radiography showed a simultaneous rise of membrane water content. Performing the same step, the voltages of the other two fuel cells decreased slightly at high currents and remained stationary at medium currents. Synchrotron radiography showed relatively high water content inside the layers of the GDL with partly-hydrophilic MPL.

III. CONCLUSION

Understanding the role of the MPL in fuel cell operation is still an important research topic. Concluding the experiments performed here, the GDL with hydrophobic MPL (high contact angles, high hydro head pressure) is preferred for a stable performance at fairly humid operating conditions. In contrast, a higher water content stored within the MPL can be advantageous for a rather dry operation. At such conditions, especially the GDL including a partly-hydrophilic MPL (high amount of water vapour adsorption, larger MPL pores) appears preferable.

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DESIGN & MODELING OF DISTRIBUTED BENTHIC ENERGY HARVESTING MICROBIAL FUEL CELL SYSTEM

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Abstract - Developing novel underwater MFCs to provide stable power supply for sensor networks is critical for ocean exploration, environmental monitoring, and national security. In this study, a new distributed benthic energy harvesting MFC (BMFC) utilizing multiple arrays of anodes and cathodes was developed. The major advantage for this multi-electrode configuration is to avert bioturbation from diverse aquatic organisms in the natural environment. The novel distributed BMFC (DBMFC) developed in this study well targeted the stability and robustness of the underwater MFCs. The DBMFCs with multi-anode/cathode configuration well exhibited the higher stability than those with single anode/cathode. The results showed that the DBMFC system achieved peak power and current densities of 190 mW/m² and 125 mA/m² respectively. A computational model simulation was developed which well corresponded with the experimental results, and confirmed the hypothesis that using a multi anode/cathode MFC configuration results in reliable and robust power generation.

Index Terms – active power management, microbial fuel cell, underwater energy harvesting

I. NOMENCLATURE

Microbial Fuel Cell (MFC), Benthic Microbial Fuel Cell (BMFC), Distributed Benthic Microbial Fuel Cell (DBMFC)

II. INTRODUCTION

Benthic environment monitoring, ocean disaster deterrence, and coastal security surveillance are some of the many aspects of aquatic exploration, which have garnered enormous attention and established a critical need for development of autonomous underwater sensor networks [1]. Currently, battery delivered power is the most widely used source, but is expensive and unsustainable. This could be addressed using MFCs which will provide reliable and scalable power supply [2, 3]. A new distributed benthic energy harvesting microbial fuel cell (DBMFC) utilizing multiple arrays of electrodes was developed (Fig. 1). The major advantage for this multi-electrode configuration is to avert bioturbation from diverse aquatic organisms in the natural environment. This prevents electrode reverse reactions and subsequent failure of the system. In the DBMFC system, if one pair of anode/cathode is damaged, the problem only occurs locally without affecting other pairs of anode/cathode. This substantially enhances the stability and reliability of energy harvesting under harsh ocean environment. The DBMFC system also features a compact structure, small footprint, high durability, and high power efficiency.

III. METHODS

The DBMFC system consists of a stacked column of 3 anode casings and an cylindrical expanded metal frame structure that were made of stainless steel. Each casing contained 9 anodes made by carbon fiber brush (fiber stack diameter: 3.8 cm, and fiber stack height: 6.25 cm). A total of 27 anodes were installed in the whole DMFC system, among which every 3 anodes were connected in series to one cathode (total of 9 cathodes, platinum doped, 10% 58 cm²/cathode). The casing was protected by a stainless steel cylindrical frame. Anaerobic sediments with diverse microbial consortium and organic substrates were used as inoculum and the overlying water collected from the Mirror Lake was used to provide the benthic environment for the cathodes, operated at 25 °C. A computational model was developed as per (Eq. 1) to describe the bio-electrochemical reactions in the DBMFC system. Employing this model, the electrical behaviors of the unique distributed multi anode/cathode configuration was investigated.

\[ P/V/Itotal = \sigma(n, I_{cell}) \times n \times P_{cell} \] (1)

IV. RESULTS & DISCUSSION

To evaluate the stability and power efficiency of the DBMFC system in the natural environment, performance was examined by deliberately decoupling anode/cathode pairs from the electrode arrays (1-9). The power and current outputs of the BMFC were measured as a function of the number of working

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anode/cathode pairs (arrays 1-9 implied eight anodes/cathodes pairs were disconnected sequentially, as represented in Fig. 2). Under the context of nine working electrode arrays (with all 9 cathodes coupled to 27 anodes), simulated the best case scenario (no bioturbation), the measured peak power density was 154 mW/m² at the current density of 125 mA/m² (normalized by the cathode surface area). When different anode/cathode arrays were disconnected (representing varying levels of bioturbation), the power generation (Fig. 2(a)) decreased correspondingly. As the electrode arrays were connected in parallel circuit mode, the voltage remained constant about 0.35 V. The overall power of the DBMFC system increased from about 0.01 mW/m² for a single anode/cathode array to 0.10 mW/m² for five anode/cathode arrays, and finally to 0.15 mW/m² for nine anode/cathode arrays (Fig. 2(a)). The current density increased from 0.2 A/m² for one array, to 1 A/m² for five arrays and finally to 2 A/m² for nine arrays. Previous studies [4], [5] showed that simple sediment MFC systems obtained peak power density of 30-60 mW/m² and current density of 50-100 mA/m², which were close to the BMFC system with only one working pair of anode/cathode. In the event of a fault with one or more electrode pairs being damaged, presented as electrode reversal in this study, the conventional MFC would stop functioning and no power would be produced, while the DMFC system could still attain good power output in a relative stable operation.

With all the parameters of the developed model estimated, the voltage is calculated based on cell current measured under different load resistance. The simulated V-I results for the DBMFC system with multiple anode/cathode settings (1, 3, 5, 7 and 9 arrays) are shown in (Fig. 2b). It demonstrated that the simulated data from the computational model is in good agreement with the experimental result, which further validated the model for the unique multi-anode/cathode configuration in the DBMFC system.

V. CONCLUSION

A new underwater MFC system with the unique distributed multi-electrode configuration (DBMFC) was designed and tested in this study. The overall performance in terms of power and current generation was greatly improved over previously reported BMFCs with single electrode set up. Experimental results demonstrated the potential of using this DMFC system to power lower energy microelectronic devices like sensors for underwater applications. A computational model had also been established for understanding the bio-electrochemical reactions of the DBMFC system in order to make it a reliable energy harvesting technique. Ongoing work which will be further discussed is directed towards testing activated carbon electrodes in different reactor configurations to compare the performance with conventional electrodes. Active power management circuit system is being developed to address the non-ideal issues in the DBMFC system.

REFERENCES


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DEVELOPMENT OF ELECTRODEPOSITED IrO2 ELECTRODE AND ITS CATALYTIC ACTIVITY TOWARDS OXYGEN EVOLUTION REACTION IN POLYMER ELECTROLYTE MEMBRANE BASED WATER ELECTROLYSIS


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Abstract – In order to decrease the loading amount of novel catalysts, IrO2 anodes were fabricated by electrodeposition method on carbon paper, and the water electrolysis performances were evaluated. The IrO2 loading amount gradually increased, with deposition time, up to 0.464 mg/cm². When single cells of polymer electrolyte membrane based water electrolysis (PEMWE) were operated, the cell performance was comparable to conventional cells with high novel metal loadings.

Index Terms – electrodeposition; iridium oxides; polymer electrolyte membrane based water electrolysis

I. INTRODUCTION

Among several technologies to produce hydrogen fuels, the polymer electrolyte membrane based water electrolysis (PEMWE) has many advantages, including high purity of hydrogen gas and high production rate. However, large amount of novel metals are utilized as catalysts towards hydrogen and oxygen evolution reactions. In this study, as an approach to reduce the material cost, the IrO2 anodes were prepared by electrodeposition technique and their electrochemical performances were evaluated with various loading amounts.

II. EXPERIMENTAL

By anodic electrodeposition technique, IrO2 were deposited on carbon paper (Autolab, PGSTAT302N). A three electrode cell was utilized with a glassy carbon electrode and SCE as counter and reference electrodes, respectively. The deposition voltage and time were varied to control the loading amount and surface morphology. As cathodes, commercial Pt/C (Tanaka, 45.9 wt%) were sprayed on carbon paper (Pt loading: 0.8 mg/cm²). The commercial Nafion 212 membranes were placed between prepared anodes (IrO2) and cathodes (Pt/C), and the water electrolysis performances were evaluated at 90°C.

III. RESULTS AND DISCUSSION

The IrO2 loading amount was analyzed to gradually increase with deposition time: 0.007~0.464 mg/cm². Fig. 1 shows the surface morphologies after electrodeposition in various deposition times. At large loadings (deposition time > 10 min), delamination of IrO2 deposits were observed.

Fig. 1. SEM images of IrO2 electrodes prepared by electrodeposition at 0.7 V. The deposition time is (a) 1 min, (b) 10 min, (c) 20 min, and (d) 30 min.

In Fig. 2, the polarization curves for water electrolysis are
compared for IrO₂ anodes prepared by electrodeposition with various time. The single cell with very low IrO₂ loading (1 min) showed abnormal behavior at cell voltages above 1.7 V, probably due to the severe carbon corrosion. However, as the deposition amount increased with deposition time up to 10 min, the polarization curves became stable and water electrolysis performances was enhanced. When deposition time was more than 10 min, the performance gradually decreased, which seems to be related to the carbon surface exposure with IrO₂ delamination. Therefore, the highest performance was achieved with the deposition time of 10 min, where uniform IrO₂ deposition is available. It could be confirmed that the water electrolysis characteristics were comparable to previous reports with larger amount of novel catalysts [1~6].

Fig. 2. Polarization curves for water electrolysis with IrO₂ anodes prepared by electrodeposition with various deposition times.

IV. CONCLUSION
By electrodeposition technique, IrO₂ electrodes were prepared with various loading amount (0.007~0.464 mg/cm²). The highest performance for water electrolysis was achieved with IrO₂ anodes with a deposition time of 10 min (0.09 mg/cm²), which was comparable to the previous reports with much larger novel metal loading (1.0~4.0 mg/cm²).

ACKNOWLEDGMENT
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References
THERMODYNAMIC ANALYSIS OF THE USE OF SYNGAS FROM COAL AND BIOMASS TO FEED SOFC SYSTEMS INTEGRATED WITH CO2 SEPARATION PROCESSES

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Abstract – This work investigates the energy performance of industrial processes and power plants for the conversion via gasification of biomass and coal into electricity with carbon capture. In order to define the most efficient utilization of syngas together with an effective separation of carbon dioxide from the exhaust gas, several options were investigated. We analysed different plant scenarios for integrated syngas solid oxide fuel cell (SOFC) plants, with either fuel decarbonisation before its use in stack or carbon dioxide (CO\textsubscript{2}) separation from the anode off-gas. Among the different scenarios for decarbonisation, particular care has been devoted to a process de-carbonizing syngas upstream of the SOFC stack. Through chemical looping with Fe-oxides, C-based components are separated from the original fuel, leaving an H-based fuel only. Overall plant performances have been evaluated for each plant and the best system configuration was found.

Keywords – Syngas, CO\textsubscript{2} separation, chemical looping, SOFC.

I. INTRODUCTION

This work analyses the energy performance of industrial processes and power plants for the conversion of coal via gasification into electricity with carbon capture. We studied different plant scenarios with syngas feeding an SOFC and either fuel decarbonisation before its use in the stack or downstream CO\textsubscript{2} separation from the anode off-gas (essentially via oxy-combustion of residual H\textsubscript{2} and CO and subsequent H\textsubscript{2}O separation/condensation).

To this purpose several plant lay-outs have been compared from a thermodynamic point of view, taking into account all the constraints arising from the integration of the different system components. Among the different scenarios for decarbonisation available, particular care has been devoted to a process able to de-carbonize through chemical looping with Fe-oxides: C-based components are in fact separated from the inlet fuel yielding an H-based fuel only.

The various scenario investigated are listed below:
- Case 1: Integrated Gasification Fuel Cell Hybrid System (IGHS) without carbon capture;
- Case 1-a: Integrated Gasification Fuel Cell Hybrid system with upstream CO\textsubscript{2} separation;
- Case 1-b: IGHS with CO\textsubscript{2} separation after combustion;
- Case 2: IGHS with water gas shifting reactor and CO\textsubscript{2} separation at the anode inlet;
- Case 3: IGHS with syngas decarbonisation through chemical looping with Fe-oxides.

A reference case is also included which refers to the Fuel Cell Hybrid system fed with natural gas. The gasifier is fed with air and a chemical sorbent process is utilized in cases 1-a,1-b and 2.

Since pressurised operation yield better plant performance than atmospheric, only pressurized cases are presented and discussed in this work.
Table 1: Anode inlet gas composition after recycle

<table>
<thead>
<tr>
<th>Molar Fraction</th>
<th>Reference case</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.453</td>
<td>0.2</td>
<td>0.3756</td>
<td>0.9</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.356</td>
<td>0.09</td>
<td>0.065</td>
<td>0</td>
</tr>
<tr>
<td>CO</td>
<td>0.708</td>
<td>0.18</td>
<td>0.04</td>
<td>0</td>
</tr>
<tr>
<td>N₂</td>
<td>0.032</td>
<td>0.41</td>
<td>0.0576</td>
<td>0</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.0277</td>
<td>0.10</td>
<td>0.39</td>
<td>0.1</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.0064</td>
<td>0.02</td>
<td>0.0218</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 1 provides the anode inlet gas composition after anode exhaust recycle for the reference case (methane) and for the cases in study. The recycle factor has been adjusted in order to comply with the SOFC requirements in terms of steam-to-carbon ratio, fuel utilisation factor and inlet temperature.

II. METHODOLOGY

The designated fuel is syngas from coal/biomass gasification. For reference, a syngas composition from the atmospheric up-draft fixed bed gasifier of Sotacaro (Sardinia, IT) was used. The comparisons have been carried out using a simulation tool developed by the University of Genoa called W-TEMP [1]. The installed hybrid SOFC power is ~2MWe.

The code is a modular program capable of simulating several types of energy from conventional systems (e.g., combined cycle) to advanced concepts (humid air cycle, fuel cell hybrid system, biomass gasification integrated plant, etc.), automatically provides the user with detailed thermodynamic, exergetic, economic data about both the internal structure of the layout and the plant as a whole. In Figure 1 is shown the plant layout in one of the scenarios considered (coal gasification and pre-combustion shift reaction with CO₂ capture). In order to investigate the performance of the SOFC subsystem and of the overall plants fed with different syngas compositions, a detailed investigation has been carried out with the aim to defining the optimal fuel utilization factor for each case study.

III. RESULTS AND DISCUSSION

Figure 2 depicts the overall plant electrical performance (fuel cell and micro gas turbine) for pressurised plants. The optimum micro gas turbine compression ratio (β), that represents also the operating pressure of the SOFC, and fuel utilization factor (U_f) are also given for each system configuration. As Figure 2 clearly shows, from the SOFC and Hybrid system point of view the best option is pure hydrogen feeding (Case 3). It is useful to note that both system options 1-a and 1-b do not affect the SOFC inlet gas composition which remains equal to Case 1. Looking at the global plant performance, which takes into account also the gasifier and chemical looping combustion efficiencies that are 81.5% and 60% respectively, the best carbon capture option is represented by Case 2, as summarized in Figure 3.

IV. CONCLUSIONS

The best system configuration has been defined for the coal gasification leading to the choice of the plant lay-out, depicted in Figure 1, with the shifting reactor and the CO₂ capture section inserted before the fuel cell.

In this case, a 2.2 MWe plant fed with coal reaches a global efficiency of 54%, reducing the CO₂ emissions by 90% compared to the reference plant fed by natural gas. Similar performance have been obtained with a 1.5 MWe system fed by biomass.

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CREEP BEHAVIOR OF POROUS SUPPORTS IN METAL-SUPPORT SOLID OXIDE FUEL CELLS
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Abstract -
Creep is the inelastic deformation of a material at high temperatures over long periods of time. It can be defined as time-dependent deformation at absolute temperatures greater than one half the absolute melting. Creep resistance is a key parameter for high temperature steel components, e.g. SOFC metal supports, where high corrosion resistance is a major design requirement. The four variables affecting creep rate are strain, time, temperature, and stress level and make creep difficult to quantify. In this work, the creep parameters of a SOFC metal support have been determined for the first time by means of a thermo mechanical analyzer (TMA) for stresses in the range of 1-17 MPa and temperatures between 650-750 °C. The creep parameters of Crofer® 22 APU were also acquired and compared with values obtained from literature to validate the technique.

Index Terms – metal supports, creep, high-temperature ferritic stainless steel, solid oxide fuel cells

I. INTRODUCTION
Metal supported solid oxide fuel cells are regarded as possible next generation fuel cells. In this application, the use of stainless steel allows to achieve an improved durability. Creep behaviour is of high importance for the performance of materials and designs that can withstand the severe operational requirements of high temperature and long service lifetimes, and thus it needs to be characterized. The ideal creep curve consists of three distinct stages, which are the transient (I), the steady state (II) and the fracture stage regions (III). Typical experimental data contains “creep curves” (strain vs. time) for a constant temperature and different stress levels referred to the rate in the secondary stage of the steady state rate, where competing mechanisms of strain hardening and recovery may be present.

In this work thermo-mechanical analysis was performed to acquire the creep parameters for the porous metal support (similar to the support reported in [1]) and that of Crofer® 22 APU (taken as reference material to validate the technique). Measurements were performed in air and in reducing atmosphere for samples in as-sintered state to assess the influence of scale formation during creep. Furthermore, tests were also carried out in reducing atmosphere on 24 hours previously corroded samples for the assessment of scale thickness and creep resistance correlation. Data processing of these isothermal and iso-stress tests led to the assessment of the stress exponents and the activation energies of the investigated materials.

II. EXPERIMENTAL

Materials and sample preparation
The porous ferritic stainless steel (Fe22Cr) metal support investigated here was fabricated using the same methods as described in [2]. The chemical composition of commercially available ferritic steel Crofer® 22 APU can be obtained from the technical data sheets of the manufacturer and also in ref.[3].

Samples were laser cut with dimensions (0.5x0.3x20) mm from the home-made 300 µm thick porous metal support tapes and also from the commercially available 300 µm thick Crofer® 22 APU metal sheets. Microstructural investigations were performed to verify if laser cutting could damage the microstructure of the samples. Figure 1 shows that the pore dimensions, shape and distribution did not change after the laser cutting procedure.

Methods
A thermo-mechanical analyser (TMA) (NETZSCH, TMA 402 F1/F3 Hyperion) was used to perform the isothermal and iso-stress tests required for the determination of the creep parameters. The reducing atmosphere used during the tests had a composition of 9% H2/N2. The isothermal tests were performed at 700 °C for 72 h applying different loads to cover the stress range from 3 to 17 MPa. The isothermal tests were conducted at 650-700-750-800 °C at 15 MPa for the determination of the activation energy of the considered materials.

III. RESULTS

Typical strain-time plots obtained for the metal supports subjected to different stresses at 700°C are shown in Figure 2. All the creep curves show similar behavior with three
characteristic regions: region (I) transient or initial stage of creep with decreasing creep strain rate; region (II) steady state creep in which competing mechanisms of strain hardening and recovery may be present and finally the increasing creep strain rate region (III) in which necking under constant load or consolidation of failure mechanism occur prior to failure of the test piece.

![Fig. 2. Creep curves of the metal support investigated for different applied loads at 700°C](image)

The minimum strain rate was extrapolated from the steady-state strain rate region (II) and double logarithmic plots of minimum strain rate vs applied stress were made (see Figure 3). The minimum steady-state strain rate (\(\varepsilon_{\text{ss}}\)) is typically correlated to the applied stress (\(\sigma\)) by the Norton’s power law:

\[
\frac{\partial \varepsilon}{\partial t} = A_{II} \sigma^n,
\]

where \(n\) is called the stress exponent and \(A_{II}\) represents a material constant [2].

![Fig. 3. Norton plots (secondary creep rate vs. stress)](image)

The activation energy of the materials was determined from the iso-stress tests performed at 650-700-750-800 °C at 15 MPa. The analysis of the Arrhenius plots obtained (not reported here) led to the attainment of the corresponding activation energy values, reported in Table 1. Table 1 also reports all the experimental creep parameters determined in this study together with the creep parameters values of Crofer® 22 APU taken from literature [3].

**Table 1: Creep Parameters of Porous Metal Support and Crofer 22 APU in Different Atmospheres**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Stress range (MPa)</th>
<th>Creep parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(A_{II})</td>
<td>(n)</td>
</tr>
<tr>
<td>Metal support H₂</td>
<td>0-15</td>
<td>5.36E-12</td>
</tr>
<tr>
<td>Metal support O₂</td>
<td>0-15</td>
<td>8.54E-10</td>
</tr>
<tr>
<td>Metal support H₂ (corroded 24 h)</td>
<td>0-15</td>
<td>8.383E-14</td>
</tr>
<tr>
<td>Crofer 22 APU H₂</td>
<td>0-15</td>
<td>3.02E-12</td>
</tr>
<tr>
<td>Crofer 22 APU[2]</td>
<td>&lt;10</td>
<td>5.00E-10</td>
</tr>
<tr>
<td>Crofer 22 APU[2]</td>
<td>10-17</td>
<td>9.00E-15</td>
</tr>
</tbody>
</table>

The obtained Norton Creep Power law exponent (\(n\)) and \(A_{II}\) constant for Crofer® 22 APU corresponds very well with that from literature [3]. In the case of the metal support, creep rates in air are higher than in reducing conditions, while the stress exponent decreases. In the case of the 24 hours previously corroded metal support samples, the strain rates are the lowest for all the investigated conditions, whereas the stress exponent (\(n\)) increases in comparison with the test performed in reducing conditions. Further studies are being developed for a complete understating of the influence of scale formation into the creep behavior of metal supports.

**IV. CONCLUSION**

The creep parameters of a porous ferritic stainless steel SOFC metal support are reported in this work. The metal supports tested in oxidizing atmosphere show the highest while the 24 h previously oxidised samples show the lowest strain rates.

**ACKNOWLEDGMENT**

The research leading to these results has received funding from EU’s Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement nº 278257 (METSAPP) and from Energinet.dk under the project ForskEL 2012-1-10806.

**REFERENCES**


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RESOLVING CONSTRAINTS IN GLOBAL ENERGY SUPPLY WITH COGENERATIVE, POLYGENERATIVE, AND FAST RAMPING FUEL CELLS

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Abstract – This research focuses on resolving constraints in our global energy supply chains with next generation stationary fuel cell systems (FCSs). Within the present-day electricity supply chain, a primary energy efficiency constraint is the process of electricity generation; a primary air pollution constraint is with power plants under fast ramping conditions. To address these constraints, this research work examines the thermodynamics, chemical engineering process plant design, economics, and environmental impacts of combined heat and power (CHP), combined cooling, heating and electric power (CCHP), and fast ramping stationary FCSs.

Model results indicate that the marginal increase in CHP FCS costs from adding heat recovery capability is moderate for capital costs but significant for installation costs. CCHP FCSs coupled with absorption chillers produce higher net electrical and cooling efficiencies than competing technologies. The marginal cost increase from an inability to electrically ramp quickly is estimated as ~$2,000/kilowatt-electric (kWe) for a 1 kWe FCSs.

Index Terms – electrical ramping capability, energy supply chains, polygeneration, stationary fuel cell systems (FCSs)

I. INTRODUCTION

The fields of management science and engineering, operations research, and business espouse the Theory of Constraints, popularized by Eliyahu M. Goldratt in his book The Goal. Goldratt states: “The throughput of any system is determined by one constraint (bottleneck);” and “An hour saved at a non-bottleneck [process] is a mirage.” The primary tenant of the Theory of Constraints is that time and money are being wasted if one does not focus all of one’s efforts on fixing the least efficient process, i.e. the ‘weakest link’, in a manufacturing supply chain. The efficiency of the entire manufacturing supply chain can improve only when the slowest process in that chain is actively improved. To enhance the effectiveness of any system, the constraint must be identified and worked on until it is no longer the constraint; attention should then be refocused on the new constraint, and so on. The Theory of Constraints has been widely applied to manufacturing supply chains; this work uniquely applies this theory to energy supply chains.

II. METHOD

An energy supply chain spans all of the processes from primary feedstock energy extraction to ultimate end-use. For example, a conventional electricity supply chain often includes the following sequential processes: primary fuel exploration, fuel extraction, fuel transport, fuel storage, consumption of fuel in a power plant for electricity generation, transmission of electricity at high voltage, distribution of electricity at low voltage, and end use of electricity in devices.

Applying the same ethos as the Theory of Constraints, this research uniquely defines a constraint within an energy supply chain as the main process within an energy supply chain that has the highest energy losses, greenhouse gas emissions, air pollution emissions, energy costs, lack of security of supply, or other negative impacts or costs. This work then analyzes the constraints in detail.

III. RESULTS

Within electricity supply chains, the process that is typically least energy efficient and dissipates the greatest amount of energy to the environment as heat is the generation of electricity at power plants. For example, according to U.S. Department of Energy (DOE) Energy Information Administration (EIA) data and Sankey diagrams of energy flows by Lawrence Livermore National Laboratories (LLNL), the U.S. loses about 1/5th of its total annual primary feedstock fuel energy (~21 Exajoules (EJ)) as heat at power plants. Importantly, the U.S. then re-generates about the same amount of heat downstream to heat residential, commercial, and industrial buildings and processes (including building space heating and cooling, hot water heating, and processing heating). The same approximate one-to-one ratio of heat dissipated at power plants to heat re-
generated in buildings holds for different regional areas, including, for example, the state of California.

This research focuses on addressing these kinds of energy supply chain constraints with advanced stationary FCSs. With respect to this last energy efficiency constraint identified, stationary CHP FCSs have the potential to collectively displace both the heat losses at power plants and the heat re-generated within buildings (~21 EJ), at high electrical efficiencies (~60%) and high overall efficiencies (~90%).

Moreover, CHP FCSs can be coupled with absorption chillers, which convert heat into cooling power. For example, lithium bromide (LiBr) absorption chillers can recover heat at temperatures as low as 80°C and convert every one unit of that heat to cooling power at a rate of between 0.5 and 1.5 units of cooling output. This range depends on the chiller’s design and number of effects. CHP FCSs coupled with absorption chillers are often referred to as CCHP generators. CCHP FCSs are polygenerators, i.e. devices that produce three or more useful outputs. When displacing conventional generation, CCHP FCSs can reduce primary fuel consumption for electricity, heating, and cooling by approximately half.

To address energy efficiency and other constraints, this research work shares insights into the thermodynamics, chemical engineering process plant design, economics, and environmental impacts of CHP and CCHP FCSs. Chemical engineering process plant models analyze the thermal integration of CHP FCS and recovering CHP FCS heat for upstream heating of biogas production processes. Roughly 13% of the input biogas lower heating value (LHV) energy is estimated to be needed for biogas production, and this heat demand is at low enough temperatures to be supplied by high temperature (HT) FCS exhaust streams. Techno-economic models indicate that the marginal increase in CHP FCS capital costs from adding on heat recovery equipment can be moderate [1]. However, the marginal increase in CHP FCS installation costs from installing heat recovery capability can be significant [2].

With respect to CCHP FCSs, HT FCSs connected with absorption chillers are compared with HT FCSs connected with traditional vapor compression electric chillers. Model results indicate that, over a range of flow rates and other parameters evaluated, CCHP FCSs coupled with absorption chillers produce higher net electrical efficiencies and higher net cooling efficiencies, compared with the CCHP FCSs coupled with electric chillers. By contrast, CCHP FCSs coupled with absorption chillers produce lower levels of recoverable heat, compared with CCHP FCSs coupled with electric chillers.

Within the electricity supply chain, another supply chain constraint can be identified when applying the lens of air pollution emissions. Some of the highest air pollution emissions in the electricity supply chain are seen at fossil fuel power plants under fast ramping conditions. Natural gas, oil, and coal combustion plants are all deployed for fast ramping, under different conditions, in different regions. Fast ramping power plants are also a segment of the electricity market where the highest growth is expected. Renewables such as solar and wind are expected to provide an increased percentage of market share for electricity; yet their supply is variable and their use must often be coupled with fast ramping power to mitigate their intermittency. Certain types of stationary FCSs in certain design configurations hold the promise of being able to ramp quickly while maintaining high efficiency and low air pollution emissions. This research also explores the value of ramping capability.

Techno-economic models evaluate the financial cost of an ‘inability to ramp.’ Models indicate that the marginal increase in CHP FCS capital and installation cost for a FCS with an inability to ramp its electrically output quickly is approximately $2,000/kWe for 1 kWe FCSs, $1,200/kWe for 5 kWe FCSs, $630/kWe for 25 kWe FCSs and $330/kWe for 100 kWe FCSs [2]. These values are a measure of the ‘cost’ of the inability of FCSs to electrically ramp in a critical back-up power scenario and these values help quantify the financial benefit of investing in a better understanding of fuel cell degradation mechanisms under dynamic conditions.

IV. CONCLUSION
This research focuses on resolving constraints in our global energy supply chains with next generation stationary FCSs. To address energy efficiency and other constraints, this research work shares insights into the thermodynamics, chemical engineering process plant design, economics, and environmental impacts of CHP, CCHP, and fast ramping stationary FCSs. Model results are discussed for the marginal increase in capital and installation costs for adding (1) heat recovery capability for CHP and (2) fast electrical output ramping capability. When displacing conventional generation, CCHP FCSs can reduce primary fuel consumption for electricity, heating, and cooling by approximately half.

ACKNOWLEDGMENT
This work was supported in part by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office.

REFERENCES
REDUCING ENERGY, ENVIRONMENTAL, AND ECONOMIC CONSTRAINTS IN GLOBAL TRANSPORT SUPPLY CHAINS WITH NOVEL FUEL CELL AND HYDROGEN TECHNOLOGIES

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Abstract – This research applies the Theory of Constraints to current and future global energy supply chains. Within conventional automotive supply chains, the greatest constraint to energy efficiency is typically at the point of vehicle use. Within a future transport supply chain based on hydrogen (H₂)-fueled proton exchange membrane (PEM) fuel cell vehicles (FCVs), the energy efficiency constraint shifts to include not only the vehicle but also the process of producing H₂ fuel. To address this constraint, this research analyzes an innovative approach for producing H₂ fuel efficiently: tri-generative stationary high temperature (HT) fuel cell systems (FCSs) that simultaneously produce electricity, heat, and hydrogen fuel (H₂-FCSs). This research discusses H₂-FCS thermodynamics, chemical engineering process plant design, economics, and environmental impacts. Thermodynamic models indicate that H₂-FCSs use ~19% less fuel to produce electricity, compared with standard stationary FCSs, and ~16% less fuel, compared with standalone steam methane reformers (SMRs).

Index Terms – Energy supply chains, fuel cell vehicles (FCVs), stationary high temperature (HT) fuel cell systems (FCSs) for hydrogen (H₂) co-production, tri-generation

I. INTRODUCTION

The fields of management science and engineering, operations research, and business espouse the Theory of Constraints, popularized by Eliyahu M. Goldratt in his book The Goal. Goldratt states: “The throughput of any system is determined by one constraint (bottleneck);” and “An hour saved at a non-bottleneck [process] is a mirage.” The primary tenant of the Theory of Constraints is that time and money are being inefficiently consumed if one does not focus all of one’s efforts on fixing the least efficient process, i.e. the ‘weakest link’, in a manufacturing supply chain. The efficiency of the entire manufacturing supply chain can improve only when the slowest process in that chain is actively improved. To enhance the effectiveness of any system, the constraint must be identified and worked on until it is no longer the constraint; attention should then be refocused on the new constraint, and so on. The Theory of Constraints has been widely applied to manufacturing supply chains; this work uniquely applies this theory to energy supply chains.

II. METHOD

An energy supply chain spans all of the processes from primary feedstock energy extraction to ultimate end-use. For example, a conventional automotive transport supply chain often includes the following sequential processes: petroleum oil exploration, crude oil production from fields, crude oil transport, centralized crude oil processing, gasoline and diesel fuel transport, fuel storage, and on-road fossil fuel vehicle use [1]. Applying the same ethos as the Theory of Constraints, this research uniquely defines a constraint within an energy supply chain as the main process within an energy supply chain that has the highest energy losses, greenhouse gas emissions, air pollution emissions, energy costs, lack of security of supply, or other negative impacts or costs. This work then analyzes that constraint in detail.

III. RESULTS

Within the present-day, conventional, automotive transport supply chain in the United States (U.S.), the highest energy losses, greenhouse gas emissions, air pollution emissions, and energy costs tend to be at the point of use of on-road fossil fuel vehicles. At that point, fuel is converted to motive power of the vehicle and the greatest amount of energy within the supply chain is dissipated as heat to the environment. According to U.S. Department of Energy (DOE) Energy Information Administration (EIA) data and Sankey diagrams of energy flows by Lawrence Livermore National Laboratories (LLNL), U.S. automobiles consume about 16.17 Exajoules (EJ) of primary energy, which translates into about 13.58 EJ of energy dissipated to the environment as heat and 2.59 EJ of useful motive power.
In other words, the U.S. automotive transportation supply chain is about 16% efficient on average, on a well-to-wheels basis (2.59 EJ/16.17 EJ).

A future transport supply chain may be based on H₂-fueled PEM FCVs, which are expected to be two to three times more efficient on a well-to-wheels basis. In such a supply chain, energy losses and energy costs are likely to be high both at the point of vehicle use and at the point of H₂ production. In other words, the locations of some of the bottlenecks shift between a conventional energy supply chain and a H₂-fueled PEM FCV supply chain more towards the fuel production process.

Another important bottleneck to consider is the process with the greatest vulnerability to energy supply security. For the present-day, conventional, automotive transport supply chain in the U.S., the greatest lack of security of energy supply tends to be with the production, transport, and supply of oil. Substitution of gasoline and diesel fuel with H₂ fuel derived from natural gas and renewables can help address this constraint, while also reducing air pollution and greenhouse gas emissions [2].

The supply of H₂ fuel has also been cited as a primary constraint to market deployment of FCVs: FCVs need plentiful H₂ refueling stations across regions to conveniently refuel; H₂ refueling stations need a substantial FCV fleet to attain high capacity utilizations to be economical.

As a result of all of these considerations regarding energy supply chain bottlenecks, this work focuses on analyzing an innovative H₂ production method, that is potentially more efficient, that reuses existing waste energy streams, and that facilitates vehicle refueling: namely, tri-generative stationary HT FCSs that simultaneously produce electricity, heat, and hydrogen fuel (H₂-FCSs). H₂-FCSs use high temperature fuel cells (including solid oxide fuel cells (SOFCs) and molten carbonate fuel cells (MCFCs)) to convert a fuel such as natural gas or renewable methane (which includes biogas) to electricity, recoverable heat, and H₂ in the anode off-gas. An advantage of a HT FCS is that their recoverable heat is at high enough temperature to provide heat for the endothermic steam reforming process to create additional H₂. This electrochemical waste heat from the HT fuel cell stack can be conveyed to an upstream steam reforming reaction to produce additional H₂. At the same time, the same 1 MWe H₂-FCS devotes ~16% less fuel to producing H₂ than does a standalone SMR making the same amount of H₂, because the SMR must combust additional fuel for heating the endothermic steam reforming reaction, while the H₂-FCS reuses waste heat from the stack. When these effects are combined, the H₂-FCS uses between ~16% and ~19% less fuel.

IV. CONCLUSION

Within a future transport supply chain based on H₂-fueled PEM FCVs, a primary energy efficiency constraint is the process of H₂ fuel production. Within the present-day electricity supply chain, a primary energy efficiency constraint is the process of electricity generation. A H₂-FCS can serve both markets at high efficiency, using between ~16% and ~19% less fuel than state-of-the-art competing approaches.

ACKNOWLEDGMENT

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REFERENCES


DESIGN FOR MANUFACTURING AND ASSEMBLY (DFMA) ANALYSIS OF ELECTROCHEMICAL HYDROGEN COMPRESSION (EHC) SYSTEMS

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Abstract - This research analyzes the engineering performance, manufacturing methods, and capital costs of electrochemical hydrogen compression (EHC) systems. EHCs are similar in mechanical structure to low temperature (LT) proton exchange membrane (PEM) fuel cell systems (FCs) and share common operating principles with them. This research applies a design for manufacturing and assembly (DFMA) analysis to EHC. Model results indicate that, at low pressures, the three primary cost drivers for the EHC stack are the membrane electrode assembly (MEA), the stamped bipolar plates, and the expanded titanium (Ti) cell supports. As outlet pressure increases, costs increase non-linearly. Higher operating pressure systems are more expensive due in part to the impact of hydrogen back-diffusion (resulting in more cells per system) and mechanical loads (resulting in more tie rod mass). EHC stack costs are roughly equivalent to EHC balance of plant (BOP) costs, such that total EHC system costs are roughly double stack costs.

Index Terms – cost, design for manufacturing and assembly (DFMA), electrochemical hydrogen compressor (EHC), proton exchange membrane (PEM)

I. INTRODUCTION

EHC systems have been demonstrated in laboratory prototypes but in the future could potentially augment or replace the capabilities of conventional mechanical hydrogen compressors in providing compressed hydrogen fuel (H2) to a future fuel cell vehicle fleet. EHC systems compress H2 by transporting protons (H2 ions (H+)) through a proton-conducting electrolyte through the application of an electric current and also by restricting the volume on the other side of the electrolyte so as to increase the pressure. Compared with mechanical compression, EHC systems may have efficiency, cost, and maintenance advantages, and can compress H2 to higher pressures using fewer stages. While mechanical compression requires multiple stages to achieve high enough pressures for vehicle refueling (up to 103 Megapascals (MPa)) (15,000 pounds per square inch (psi)), EHC laboratory prototypes have achieved outlet pressures of 69 MPa (10,000 psi) in a single stage [1].

II. METHODOLOGY

A DFMA methodology was applied consisting of four primary, sequential stages: (1) System Conceptual Design, (2) System Physical Design, (3) Cost Modeling, and (4) Continuous Improvement to Reduce Cost [2]. The system conceptual design and system physical design were partly based on prior detailed DFMA models for automotive and stationary LT PEM FCs [2, 3]. Laboratory prototype EHC systems are similar to LT PEM FCs in their use of materials and in their mechanical structure, yet their geometries and system designs differ. EHC cells operate at much higher pressures than LT PEM FCs (FCs). High pressure operation requires a greater mass and volume of materials, which tends to increase costs. To bear these high pressures, EHC systems tend to use a circular, planar cell geometry; a larger number of smaller diameter cells per kilogram (kg) of H2 reacted than LT PEM FCs (to reduce the impact of higher mechanical stress and strain on tie rods etc.); thicker electrolytes than LT PEM FCs; electrolyte and cell supports made of porous metal (typically Ti); thicker and more numerous external tie-rods than LT PEM FCs for compression of the cells and end plates; and more robust end plates than LT PEM FCs. Due to the pressure differential across the electrolyte, back diffusion of H2 across the electrolyte can significantly decrease compression efficiency, i.e. the quantity of compressed H2 per unit of energy input; this effect also increases capital costs compared to LT PEM FCs. An important factor reducing the EHC systems capital costs relative to LT PEM FCs is its lower platinum (Pt) catalyst loading. EHC cells need less Pt than LT PEM FCs because the EHC cells do not have to grapple with slow oxygen reaction kinetics at the cathode. In both the LT PEM and EHC cells, the electrolyte requires humidification for proton conduction.
Key model input data was provided by EHC developers, including Giner Inc., Proton Onsite Inc., FuelCell Energy Inc., and H2 Pump LLC. Models were developed for an EHC system operating at a current density of 1 Amp per centimeter squared, a voltage of 0.22-0.26 Volts (depending on operating pressure), an operating temperature of 70 °C, an inlet pressure range of 0.35 to 2 MPa (50 to 300 psi), and an outlet pressure range from 7 to 103 MPa (1,000 to 15,000 psi). DFMA models evaluate the cost to manufacture an EHC system, at varying outlet pressures, system sizes (from 250 to 1,000 kg of H2/day), and production volumes (from 500 to 5,000 EHC systems per year).

III. RESULTS

Characteristic results are described for particular system sizes, outlet pressures, and manufacturing rates. As shown in Figure 1, model results indicate that the major cost driver for low outlet pressure (i.e. 7 MPa) EHC systems is (1) the MEA due to the materials and manufacturing expense, and, in particular, the high cost of Pt. Additional primary cost drivers include (2) the porous metal Ti cell supports; and (3) the stamped stainless steel bipolar plates with proprietary coating. At higher outlet pressures (i.e. 103 MPa), the tie rods also become a primary cost driver because they need to be both thicker and used in higher quantities to manage stress and strain.

Figure 1. EHC stack costs for 250kg/day system size, at 7 MPa (1 kpsi) outlet H2 pressure, at a manufacturing rate of 500 systems/year.

IV. CONCLUSION

For the range of plant sizes, manufacturing volumes, and operating pressures explored in this analysis, EHC stack and BOP capital costs each make up approximately half the cost of the system. Primary contributors to stack capital cost include the MEA, Ti supports, bipolar plates, and, at high pressures, the tie rods. EHC system capital costs increase non-linearly as outlet pressure rises because of design changes needed to overcome the effects of (1) greater H2 back diffusion, (2) higher mechanical loads, (3) higher power draw, and (4) other factors.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office.

REFERENCES


TECHNO-ECONOMIC ANALYSIS OF ADVANCED APPROACHES FOR GENERATING HYDROGEN FUEL FOR VEHICLES

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Abstract – Hydrogen (H₂) production and delivery (P&D) pathways are analyzed to determine the most economical, environmentally-benign, and societally-feasible paths forward for the production and delivery of H₂ fuel for fuel cell vehicles (FCVs). This research identifies key "bottlenecks" to the success of these pathways, primary cost drivers, and remaining Research and Development (R&D) challenges. For each H₂ Pathway, this research effort assesses technical progress, H₂ costs, benefits and limitations, and the potential to meet U.S. Department of Energy (DOE) P&D cost goals of $2 to 4/gasoline gallon equivalent (gge) (dispensed, untaxed) by 2020. For proton exchange membrane (PEM) electrolysis, the primary cost drivers are the cost of electricity and the capital cost of the electrolyzer, within which the balance of plant is expected to be a greater source of cost than the stack. Results are also discussed for photo-electro-chemical (PEC), biological, and solar thermo-chemical production of H₂ (STCH) schemes.

Index Terms – Hydrogen production, photo-electro-chemical (PEC), proton exchange membrane (PEM) electrolysis, solar thermo-chemical production of H₂ (STCH)

I. INTRODUCTION

The H₂ pathway analysis conducted here captures relevant economic, engineering, and societal aspects of specific H₂ P&D pathways; facilitates comprehensive side-by-side comparison of competing pathways; and enables identification of the most promising approaches. This H₂ pathway analysis elucidates the economic, environmental, engineering, societal, energy use and other implications of a particular supply chain design for P&D of H₂. Pathway analysis is conducted using the U.S. DOE’s H2A modeling tools (namely, the H2A Production model and the Hydrogen Delivery Scenario Analysis Model (HDSAM)), which encompass the standard methods of energy, emissions, and cost analysis used by DOE technology teams. This approach identifies performance and cost impacts at each stage of the pathway, as well as the primary cost drivers and key “bottlenecks” to success.

Innovative H₂ P&D pathways analyzed include
1. Advanced electrolysis based on PEM technology;
2. PEC production of H₂ based on both electrode-type and nano-particle suspension-type systems;
3. biological production of H₂ from organisms including photolytic (using genetically engineered bacteria and algae), fermentative (algae as feedstock), and microbial electrolysis; and
4. STCH including both a centralized receiver approach and an approach of multiple decentralized parabolic dishes.

II. METHODOLOGY

A similar methodology is applied to each pathway:
• Literature review on the proposed pathway.
• Process/pathway system definition covering energy efficiency, environmental, and economic estimates.
• Preliminary modeling using relevant software such as Aspen™ chemical engineering process plant software, to assess key engineering performance parameters.
• Conduct further technical interviews to determine the secondary H2A metrics such as land area, personnel required, cooling water, replacement schedule, etc.
• Populate H2A model spreadsheet with the gathered information, carefully noting sources.
• Conduct sensitivity analyses (including Tornado and/or Waterfall Charts) to identify key cost drivers.
• Develop and document case study results.
• Conduct multiple rounds of case vetting with team partners and with others.

H₂ pathways are typically analyzed for (1) a distributed (forecourt/filling station) H₂ production system of 1 to 5 metric tonnes (MT) of H₂ per day, and (2) a central (large plant size) H₂ production system of 50 to 500 MT H₂/day. Pathways are analyzed for a (1) current case, and (2) future case. “Current case” is defined as assuming short-term projections from currently demonstrated technology at production volume. “Future case” is defined as
assuming new materials and systems are developed with increased H₂ production efficiency, longer lifetimes, and reductions in capital and replacement costs.

The PEM electrolysis pathway analysis is based in part on results from a detailed technical and economic survey of four PEM electrolyzer developers. The PEM electrolysis study examines a forecourt size system (1.5 MT/day) and central size system (50 MT/day).

III. RESULTS

H₂A model results indicate that, for the PEM electrolysis H₂ pathway, the most sensitive input parameters include (1) the feedstock costs, and in particular, the cost of electricity input to the electrolyzer, and (2) the capital cost of the electrolyzer equipment, including the stack and balance of plant (BOP). These results are shown in Figure 1, which plots the levelized cost of H₂ on the y-axis for current, future, forecourt, and central cases. Results indicate that the BOP is expected to be a greater source of cost than the stack. Feedstock costs can be reduced through (1) lower electricity prices and (2) higher electrolyzer efficiencies.

### Table I

<table>
<thead>
<tr>
<th>Sensitivity</th>
<th>Current</th>
<th>High Value</th>
<th>Low Value</th>
<th>Future</th>
<th>High Value</th>
<th>Low Value</th>
</tr>
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<tbody>
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<td>Electricity Cost ($/kWh)</td>
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<td>-50%</td>
<td>$0.069</td>
<td>+50%</td>
<td>-50%</td>
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<tr>
<td>Electricity Usage (kWh/kg)</td>
<td>54.6/54.3</td>
<td>65</td>
<td>50</td>
<td>50.3/50.2</td>
<td>55</td>
<td>45</td>
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<tr>
<td>Uninstalled capital Cost ($/kW)</td>
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<td>+20%</td>
<td>-20%</td>
<td>450/400</td>
<td>+20%</td>
<td>-20%</td>
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<tr>
<td>Site Prep (% installed capital)</td>
<td>18.85%/2%</td>
<td>40%</td>
<td>1%</td>
<td>18.85%/2%</td>
<td>40%</td>
<td>1%</td>
</tr>
<tr>
<td>Replacement Interval (yr)</td>
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<td>20</td>
<td>4</td>
<td>10</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>Replacement Costs (% installed costs)</td>
<td>15%</td>
<td>25%</td>
<td>10%</td>
<td>12%</td>
<td>25%</td>
<td>10%</td>
</tr>
</tbody>
</table>

Figure 2. PEM electrolysis tornado chart.

IV. CONCLUSION

Key cost drivers and R&D bottlenecks are discussed for four H₂ production pathways: PEM electrolysis, PEC, biological, and STCH. A primary cost driver for PEM electrolysis is the cost of electricity, which can be reduced through lower electricity prices and/or higher electrolyzer efficiencies. The BOP has a greater cost than the stack.

ACKNOWLEDGMENT

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DESIGNING, MANUFACTURING, AND INSTALLING CO-GENERATIVE FUEL CELL SYSTEMS

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Abstract – This research analyzes the capital costs, electrical subsystem configurations (ESCs), and installation costs for combined heat and power (CHP) fuel cell systems (FCSs). A series of models were developed for these analyses. Model results indicate that for the same global installed capacity, having fewer larger systems appears to be more economical, in terms of both capital and installation costs, compared with installing many smaller systems. Primary capital cost drivers include (1) the fuel cell stack and (2) the fuel processor’s balance of plant (BOP). Primary cost drivers for the ESC equipment include (1) grid-integration design approach, (2) FCS size, and (3) fuel cell type and/or the ability of the FCS to ramp quickly. Primary cost drivers for installation include (1) the costs of installing piping, (2) the costs of trenching conduits for electrical circuits, and (3) contingencies.

Index Terms – capital and installation costs, combined heat and power (CHP), Design-for-Manufacturing-and-Assembly (DFMA), stationary fuel cell system (FCS)

I. INTRODUCTION

This work explores the capital costs, ESCs, and installation costs for natural gas-fueled stationary CHP FCSs. First, this work analyzes the engineering design, manufacturing methods, and capital costs of stationary CHP FCS of different types (low temperature proton exchange membrane (LTPEM), high temperature proton exchange membrane (HTPEM), and solid oxide fuel cell (SOFC), at different sizes (1, 5, 25, and 100 kilowatts-electric (kWe)), and at varying rates of production (100; 1,000; 10,000; and 50,000 systems per year (yr) [1]). Second, this study examines the engineering design, the required equipment, and the associated costs for multiple ESCs linked to the surrounding electrical grid in various ways [2]. Third, this work examines different installation approaches and their associated costs [2].

II. METHODOLOGY

This work pursues three primary tasks: (1) analyze stationary CHP FCS engineering performance and capital costs; (2) examine CHP FCS ESC designs, their linkage to the surrounding electrical grid, and associated costs; and (3) investigate CHP FCS installation approaches and their costs. For each of these three tasks, the methodology applied is summarized below:

Task 1: Performance and Capital Cost Analysis
- Apply a Design-for-Manufacturing-and-Assembly DFMA methodology to the unique components within the FCS that cannot be purchased off-the-shelf, including the fuel cell stacks, the fuel processor, and their assembly.
- Apply price quotes that vary with manufacturing volume to standardized components.
- Delineate specific engineering designs, manufacturing and assembly methods for unique components, and resulting capital costs.

Task 2: ESCs Analysis
- Develop a conceptual framework for ESCs and their linkage to the surrounding electrical grid.
- Delineate design differences and cost impacts, with a focus on ESCs important to commercialization and to FCS life cycle costs (LCCs).
- Analyze different ESC designs.
- Capture trends and key cost drivers.

Task 3: Installation Costs Analysis
- Explore the costs of engineering and design, permitting and inspections, site preparation, base electrical systems, base mechanical systems and other line-item contributors to installation costs.
- Examine existing FCS installations as case studies, where data are available.
- Develop estimates of installation costs for four stationary FCS sizes (1, 5, 25, and 100 kWe) for a base case ESC design.
- Show changes in costs from a base case ESC design for alternative ESC designs.
III. RESULTS

Task 1: Results indicate that, over the ranges evaluated in this study, per unit capital costs ($/kWe) decrease more with increasing system size than with increasing manufacturing volume. For the same global installed capacity (such as 10,000 kWe), per unit capital costs ($/kWe) are lower for larger system sizes produced in smaller quantities (such as one hundred 100 kWe FCSs) than for smaller systems made in larger quantities (for example, ten thousand 1 kWe FCSs). These results are shown in Figure 1 for SOFC systems: 100 kWe FCSs are 13% of the per unit cost of 1 kWe FCSs.

Figure 1. For the same 10,000 kWe global installed capacity, 100 kWe SOFC systems (produced at a rate of one hundred systems/yr) are 13% of the per unit cost of 1 kWe SOFC systems (produced at a rate of ten thousand systems/yr.)

Capital cost drivers vary by system size and annual manufacturing rate. At high power (~100 kWe), the primary capital cost driver is the fuel cell subsystem. At low power (~1 to 5 kWe), cost drivers include both fuel cell and fuel processing subsystems, roughly evenly. The fuel processor subsystem cost does not scale down well at low powers. Within the fuel processor subsystem, the BOP costs dominate at all scales and production levels. By contrast, the reactor is not costly. At low production rates, the fuel processor BOP costs are dominated by compressors, pumps, sensors, and heat exchangers.

An appropriate benchmark for stationary FCS capital costs can include present-day electric power capital costs, which, for example, roughly vary between $500 and $1,000/kWe for combined cycle natural gas turbines. Initial DFMA results indicate that higher power FCSs (25 and 100 kWe FCSs) at production rates of 10,000 FCSs/yr or more, may achieve this cost range [1].

Task 2: A conceptual framework was developed composed of five primary ESCs and eleven sub-configurations. Model results indicate that ESC equipment costs are primarily a function of (1) ECS design type (for example, “Net Metering,” “No Net Metering”, or “Critical Load Capability during Grid Outage”); (2) FCS size, and (3) fuel cell type (LTPEM, HTPEM, SOFC) – and/or the extent of fast ramping capability within the FCS. For example, in a grid outage scenario where the FCS needs to provide power to critical loads via continuous operation, the marginal increase in cost from a FCS’s “inability to ramp” is a key cost driver, particularly for low power (1 and 5 kWe) HTPEM FCSs. The main source of this added cost is an electrically resistive load bank, which is needed for dissipating unused FCS power. In this scenario, the marginal increase in equipment cost for a 1 kWe HTPEM FCS is about $800/kWe. The marginal increase in cost including both installation and capital cost is about $2,000/kWe.

Task 3: Three primary cost contributors to installation costs include (1) base electrical systems external to the FCS; (2) base mechanical systems external to the FCS; and (3) General Conditions (Contingencies). A significant portion of the base electrical and mechanical system costs results from the material, labor, profit, and overhead associated with installing piping and trenching conduits for electrical circuits, respectively. These activities are time, labor, and materials intensive. Finding innovative ways to cut the costs of laying down wires and laying down piping could significantly reduce FCS installation costs.

IV. CONCLUSION

Capital costs of FCSs are lower when manufacturing fewer high power systems than when manufacturing many low power systems, keeping global installed capacity constant. This effect is magnified when considering installation costs as well. Results indicate that larger-sized devices are more economical per unit of electric power, due to reductions in both capital and installation costs with increasing system size. Key cost drivers include the capital cost of the fuel cell stack and the fuel processor BOP; the ability of the FCS to electrically ramp quickly; and the installation costs for piping and for trenching conduits for wire.

ACKNOWLEDGMENT

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DESIGN, MANUFACTURE, AND COST ANALYSIS OF FUEL CELL VEHICLES

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Abstract – Fuel cell vehicles (FCVs) need to compete in a mature vehicle market. Therefore, it is crucial to identify the performance, design, and manufacturing conditions needed to reduce FCV costs to where they can compete. Thus, a design for manufacture and assembly (DFMA) analysis is applied to the cost to manufacture a FCV’s hydrogen-fueled polymer electrolyte membrane (PEM) fuel cell system (FCS). Results of a multi-variable Monte Carlo sensitivity analysis indicate with 90% confidence that the cost of an automotive FCS produced at a production volume of 500,000 FCS/year (yr) is expected to be between $51/kilowatt-electric (kWe) and $65/kWe. Model results also identify a PEM stack design with minimum capital costs, for which values for the following parameters are identified to minimize cost: (1) platinum (Pt) catalyst loading, (2) stack operating pressure, (3) stack operating temperature, and (4) stoichiometric ratio of oxygen. An advanced plate-frame membrane humidifier design is also examined.

Index Terms – cost, design for manufacture and assembly (DFMA), fuel cell vehicle (FCV), polymer electrolyte membrane (PEM)

I. INTRODUCTION

Studies indicate that the use of fuel cells in vehicle transport could reduce primary feedstock fuel consumption and greenhouse gas emissions in transport by a factor of two or more, in addition to significant reductions in air pollution emissions [1] [2]. This research applies a DFMA methodology for estimating the engineering performance, manufacturing methods, and capital costs of FCVs, which include advanced subsystems using novel membrane humidifier technologies and cutting-edge membrane electrode assemblies (MEAs). DFMA is applied to an automotive FCS with a peak net electrical power output of 80 kWe and evaluated at annual manufacturing rates of 1,000 to 500,000 FCVs/yr. The results of this DFMA analysis reveal key cost drivers for FCVs and help compare FCVs with competing technologies based on performance and cost, at similar manufacturing rates and system sizes.

II. METHODOLOGY

The DFMA methodology is composed of four main sequential steps: (1) System Conceptual Design, (2) System Physical Design, (3) Cost Modeling, and (4) Continuous Improvement to Reduce Cost. A key aim of the system conceptual design step (1) is to verify a chemical engineering process plant or other engineering-based models of energy and mass flows with the PEM FCS. In this cost analysis, the automotive FCS is assumed to include a single PEM fuel cell stack producing about 89.4 kWe of gross power, a coolant loop for extracting heat from the stack, and an oxidant delivery system. (Model does not evaluate hydrogen storage and electric vehicle drive train sub-systems.) An essential goal of the system physical design step (2) is to delineate a bill of materials (BOMs) that includes all components. For example, at a broad level, the stack coolant loop equipment includes sensors, thermocouples, valves, a radiator, a coolant reservoir, a pump, and a coolant filter. Furthermore, the oxidant delivery system includes an air filter, an air mass flow sensor, a compressor for pressurizing inlet air, a coolant loop for reducing the temperature of air exiting the compressor, a humidifier for the air upstream of the cathode, and an expander (coupled with the compressor) for capturing energy in the cathode off-gas. A critical aspect of the cost modeling step (3) is to specify and analyze the manufacturing process train, and all related materials, machines, tools, and assembly needs, particularly for any unique equipment that cannot be purchased off-the-shelf (such as the fuel cell stack). For example, in recent years, the average price of Pt catalyst used in the PEM stack was increased from $1,100 per troy ounce (tr.oz.) to $1,500/tr.oz. to reflect historical trends. The purpose of the continuous improvement to reduce cost step (4) is to repeatedly re-evaluate device and manufacturing process designs to further reduce costs. FCV developers and component manufacturers have provided detailed, expert advice at every step of this analysis.
III. RESULTS

FCS capital costs are highly sensitive to (1) Pt catalyst loading, (2) stack operating pressure, (3) stack operating temperature, and (4) the stoichiometric ratio of oxygen. FCS performance and cost were carefully modeled as a function of these parameters. Models included the results from experimental test data for PEM cells and stacks. An optimization was performed to identify the values for these four parameters resulting in the lowest FCS capital cost. The results of this optimization are shown in Table 1, along with additional key parameters. The optimal Pt catalyst loading was 0.153 milligrams (mg) of Pt per centimeter squared (cm\(^2\)); the optimal stack operating pressure was 0.253 Megapascals; the optimal stack operating temperature was 92.3 °C; and the optimal oxygen stoichiometric ratio was 1.5. The resulting stack power density was 692 milliwatts (mW)/cm\(^2\). Results show that the two most influential variables that affect the total FCS capital cost are (1) the fuel cell stack Pt catalyst loading, and (2) the fuel cell stack power density.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Density</td>
<td>mW/cm(^2)</td>
<td>692</td>
</tr>
<tr>
<td>Total Pt loading</td>
<td>mgPt/cm(^2)</td>
<td>0.153</td>
</tr>
<tr>
<td>Gross Power</td>
<td>kWgross</td>
<td>89.4</td>
</tr>
<tr>
<td>Cell Voltage</td>
<td>V</td>
<td>0.695</td>
</tr>
<tr>
<td>Operating Pressure</td>
<td>MPa (atm)</td>
<td>0.253 (2.5)</td>
</tr>
<tr>
<td>Oxygen Stoichiometric Ratio</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>Stack Coolant Exit Temp</td>
<td>°C</td>
<td>92.3</td>
</tr>
<tr>
<td>Active Cells</td>
<td></td>
<td>359</td>
</tr>
</tbody>
</table>

Figure 1 plots the FCS capital costs resulting from the cost minimization analysis. Figure 1 plots the capital cost of the FCS per unit of net electric output ($/kWe) as a function of annual manufacturing rate. Between 1,000 and 500,000 FCS/yr, capital costs decline from an estimated $279.41/FCS to $54.83/FCS. The inflection point in the curve occurs at approximately 10,000 FCS/yr. At 500,000 FCS/yr, the fuel cell stack contributes about 49% of the total FCS capital cost; the fuel cell stacks are estimated to be about $27/kWe, while the FCS is estimated at $55/kWe. The difference between these values is the cost of the balance of plant (BOP) and assembly. (As a point of comparison, automotive gasoline internal combustion engine (ICE) systems cost in the range of $20/kW of mechanical work.)

A multi-variable Monte Carlo sensitivity analysis was conducted based on varying key input parameters over a range of values that were vetted by the FCV industry. The results of the analysis indicate that, at 500,000 FCS/yr, with a 90% confidence, the cost of the FCS is expected to be between $51/kWe and $65/kWe. FCS capital costs are expected to decrease by a factor of five between production rates of 1,000 and 500,000 FCS/yr. An innovative plate-frame membrane humidifier design was analyzed.

IV. CONCLUSION

A multi-variable Monte Carlo sensitivity simulation showed with 90% confidence that the cost of an automotive FCS produced at a production volume of at 500,000 FCS/yr is expected to be between $51/kWe and $65/kWe. FCS capital costs are expected to decrease by a factor of five between production rates of 1,000 and 500,000 FCS/yr. A multi-variable Monte Carlo sensitivity simulation showed with 90% confidence that the cost of an automotive FCS produced at a production volume of at 500,000 FCS/yr is expected to be between $51/kWe and $65/kWe. FCS capital costs are expected to decrease by a factor of five between production rates of 1,000 and 500,000 FCS/yr. An innovative plate-frame membrane humidifier design was analyzed.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office.

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CONDUCTIVITY OF GD-DOPED BACEO$_3$ PROTONIC CONDUCTOR

IN H$_2$-H$_2$O-O$_2$ ATMOSPHERES

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Abstract - This work proposes a radically new simple method of evaluation of the proton conductivity based on measurement of the conductivity of ceramic materials depending on the oxygen partial pressure (pO$_2$) at a gradual transition from the atmosphere of pure oxygen to one of wet hydrogen: O$_2$ $\rightarrow$ O$_2$ (H$_2$O) $\rightarrow$ H$_2$O (H$_2$O) $\rightarrow$ H$_2$O $\rightarrow$ H$_2$O (H$_2$O) $\rightarrow$ H$_2$ (H$_2$O). Experimental data for the solid electrolyte BaCe$_{0.9}$Gd$_{0.1}$O$_3$-$\delta$ have been fitted in accordance with the defect chemistry model. Experimental and theoretical relationships correlate well with each other, which indicate the success of the proposed model description. Analysis of the relationships allowed us to estimate the level of oxygen-ion, proton and electron components and their contribution to the overall conductivity at elevated temperature.

Keywords - BaCeO$_3$, proton conductor, solid electrolytes.

I. INTRODUCTION

Transport characteristics of proton solid oxide materials repeatedly studied various methods: 4-probe DC, impedance spectroscopy, EMF, etc. Assessing the contribution of proton conductivity in general one is usually carried out by comparing the conductivity obtained in dry and wet atmospheres, or determining the proton transfer number using a steam concentration electrochemical cell with separated gas spaces. These methods make a mistake in identifying the contribution of proton conductivity because of in the first method the difference in ionic conductivity obtained in a wet and dry atmosphere is generally not equal to the proton one and in the second method the proton conductivity is calculated based on EMF data obtained for not specific values of pH$_2$O and pO$_2$, but its gradients. In this work the new method of estimation of partial conductivity of Gd-dioed BaCeO$_3$ materials was proposed.

EXPERIMENTAL

The electrical conductivity of the Gd-doped BaCeO$_3$ materials was measured in gas mixtures of H$_2$/H$_2$O and H$_2$O/O$_2$ with the application of a Zirconia equipment by employing the four-point dc technique at 600, 750 and 900 °C. The cell with the sample under investigation was heated to the required temperature and the inside part of the cell was purged by pure oxygen. Thereafter, oxygen was passed through the evaporator. The evaporator was designed as a glass vessel of the original design and was filled by 2/3 with quartz sand in the lower part. The sand provides uniform heating and large surface evaporation. The evaporator was gradually heated from room temperature (water partial pressure (pH$_2$O) corresponds to 0.02–0.03 atm) to 100 °C (pH$_2$O=1 atm). Afterward, the gates of the cell were blocked and further changes in the composition of the atmosphere inside the cell were carried out by an electrochemical oxygen pump.

At the beginning of the experiment the atmosphere inside the cell corresponded to pure oxygen (pO$_2$=1 atm). When the evaporator was heated, oxygen was slowly saturated by water vapor (with fulfilling condition pO$_2$+pH$_2$O=1 atm), and after heating the evaporator to 100 °C, the atmosphere in the interior of the cells corresponded to water vapor containing traces of oxygen. Thereafter, the cell’s valves were blocked and the further changes in the composition of the atmosphere inside the cells were performed by pumping initially the residual oxygen, and then – bound oxygen (with fulfilling condition pH$_2$O+pH$_3$=1 atm). The final state of the atmosphere corresponded to wet hydrogen. Values of water vapor partial pressure under this experiment according as a function of oxygen partial pressure are shown in Fig. 1.

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The obtained logσ/logpO₂ dependences were fitted by theoretical model (Fig. 2) including external equilibrium with pO₂ and pH₂O, electroneutrality condition of main charge carrier defects and balance of anionic sublattice:

\[
K_b = \frac{p^2}{[V'_0] [pO_2]^{1/2}}, \\
K_w = \frac{[OH^\cdot]^2}{[V'_O] [PH_2O]}, \\
[R_{Ce}] = 2[VO'^\cdot] + [OH^\cdot], \\
[VO'^\cdot] + [OH^\cdot] + [O_2^\cdot] = 3.
\]

Fig. 1. Oxygen partial dependences of water partial pressure at different temperatures.

Maximum conductivity at high pO₂ related to the difference in the rates of change of the proton and the p-type electronic conductivity with decreasing pO₂. In the coordinates of logσ/logpO₂ hole conductivity decreases linearly with decreasing pO₂, whereas the growth of proton conductivity (associated with an increase in pH₂O) first occurs at a faster pace than the decrease of σp, then slows down with decreasing pO₂ and reaches a constant value. Therefore, the overall conductivity (Fig. 3) first increases, passes through a maximum and starts to decrease and reaches a plateau. Within the plateau the conductivity is purely ionic.

Fig. 2. Experimental data and model dependences of conductivity for BaCe₀.₉Gd₀.₁O₃₋δ ceramic at 900°C.

Reducing the total conductivity in the second region (region of low oxygen partial pressure) with decreasing pO₂ attributed with decline of proton conductivity. This follows from equation \(\sigma_{H} = \sigma_{H,o}(pH_2O)^{1/2}\) with the data of Fig. 1. According to Fig. 1, the reduction of the oxygen partial pressure from 10⁻¹⁴ to 10⁻¹⁸ atm at 900 °C leads to a change in the water vapor partial pressure from 0.93 to 0.12 atm.

On the base of new proposed method of conductivity measurements and defect model the partial conductivities and its part to total conductivity were calculated at given value of pO₂ and pH₂O.

II. CONCLUSION

A method for measuring the conductivity of protonic materials with varying the partial pressure of oxygen and water vapor was developed. Analysis of dependences of the total conductivity as a function of pO₂ with simultaneous change of pO₂ and pH₂O allows to estimate the contribution of the partial conductivities (protonic, oxygen ionic, electronic) in general. This procedure was applied for estimation of partial conductivities of Gd-doped BaCeO₃ ceramic at 600, 750 and 900°C

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NEW MIXED IONIC-ELECTRONIC COMPOSITE MATERIALS BASED ON SRTI₀.₅FE₀.₅O₃₋Δ AND CE₀.₈(SM₀.₈SR₀.₂)₀.₂O₂₋Δ

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Abstract – The crystal, electrical and electrochemical properties of the new composite materials of (1-x)SrTi₀.₅Fe₀.₅O₃₋Δ–xCe₀.₈(Sm₀.₈Sr₀.₂)₀.₂O₂₋Δ (0 ≤ x ≤ 1, ∆x = 0.25) prepared by solid phase method. Composites have no phase interaction. The increase of the fluorite phase conductivity increased in the reducing atmosphere, and decreased in the oxidation atmosphere. The oxygen permeability was 3×10⁻⁷ mol/(cm² s) at 1173 K and log(p¹O₂/p²O₂)=1. The value of the effective ambipolar conductivity calculated from the obtained data of the oxygen permeability (10.7 mS/cm) is lower with the average ambipolar conductivity obtained from its log σ = log pO₂-dependence (67.6 mS/cm) for the sample 0.5SrTi₀.₅Fe₀.₅O₃₋Δ–0.5 Ce₀.₈(Sm₀.₈Sr₀.₂)₀.₂O₂₋Δ.

Index Terms – composite materials, MIEC, permeability, perovskites.

I. INTRODUCTION

Materials with mixed oxygen ionic and electronic conductivity (MIEC) are increasingly attracting research interest because of their possible use as membranes in the partial oxidation of primary organic fuel to synthesis gas and hydrogen production by electrochemical conversion. Materials based on cerium oxide are widely used in solid oxide electrochemical devices due to the high ionic conductivity [1]. It should be noted that under conditions of low pO₂ and high temperatures, the partial restoration ions Ce⁴⁺→Ce³⁺, accompanied by an increase of the unit cell parameters due to the larger ionic radius of Ce³⁺ than Ce⁴⁺ and size of ceramics in general [2]. This leads to the chemical instability of solid solutions and mechanical destruction of the ceramics. In a series of MIEC materials in the reduction atmospheres, the SrTi₁₋ₓFeₓO₃₋Δ system well established [3]. These materials have higher thermodynamic stability at low pO₂, but lower overall conductivity than systems based on CeO₂. Following the global trends in the development of functional materials for solid oxide electrochemical devices we obtained and studied the transport properties of new (1-x)SrTi₀.₅Fe₀.₅O₃₋Δ–xCe₀.₈(Sm₀.₈Sr₀.₂)₀.₂O₂₋Δ (x=0, 0.25, 0.5, 0.75 and 1) composite materials as the MIEC membrane to produce hydrogen.

II. RESULTS AND DISCUSSION

A. XRD analysis

The materials Ce₀.₈(Sm₀.₈Sr₀.₂)₀.₂O₂₋Δ crystallizes in a cubic fluorite-type structure whereas SrTi₀.₅Fe₀.₅O₃₋Δ have a cubic perovskite-type structure. For composites (x = 0.25, 0.5 and 0.75) two different phases where found, the characteristic reflections which correspond to the fluorite and perovskite structures. The XRD patterns show that no additional reflections related to the impurity phases and phases of the interaction were detected for the composites. For composite system the unit cell parameters of fluorite and perovskite phases vary slightly in comparison with the basic compounds indicating to their high chemical compatibility.

B. Electrical properties

All materials have a semiconducting type of conductivity in the studied temperature range. Conductivity samples decreases monotonically with increasing concentration of fluorite phase system from 0.588 to 0.004 S/cm at 773 K and from 2.443 to 0.147 S/cm at 1173 K for x = 0 and x = 1 respectively. This behavior of conductivity indicates that the transport processes take place mainly through the phase whose content in the composite is predominant (partial effect of conductivities). Transport properties were also measured with change of the oxygen partial pressure (Fig. 1). Despite the fact that the increase of fluorite phase resulted in a decrease of conductivity in an oxidizing atmosphere, in case of intermediate and low...
pO2 values this trend changes. It is known that materials based on cerium oxide are ionic conductors at $1 \times 10^{-10} \leq pO_2/\text{atm} \leq 0.21$, therefore the conductivity of composites and strontium titanate-ferrite in this region is higher due to the presence of the electronic (p-type) conductivity. The ion conductivity of cerium oxide does not change with the gradual decrease of the oxygen partial pressure while the hole conductivity of $(1-x)\text{SrTi}_0.5\text{Fe}_0.5\text{O}_3-\delta-x\text{Ce}_0.8(\text{Sm}_{0.8}\text{Sr}_{0.2})_{0.2}\text{O}_2-\delta$ $(0 \leq x \leq 0.75)$ decreased. Therefore, in the intermediate region of pO2 the conductivity of the sample with $x=1$ becomes higher than SrTi0.5Fe0.5O3-δ-containing samples. Subsequent reduction of pO2 resulted in enhanced conductivity of all samples due to increase in the electronic (n-type) conductivity. Moreover, total conductivity of ceramics increases with increasing x due to higher ionic conductivity of fluorite phase. The ambipolar conductivity calculated from the data of electroconductivity grows with i) decreasing pO2 due to increasing the contribution of the electronic component occurring in strontium titanate, and the material based on cerium oxide and ii) with increasing x in $(1-x)\text{SrTi}_0.5\text{Fe}_0.5\text{O}_3-\delta-x\text{Ce}_0.8(\text{Sm}_{0.8}\text{Sr}_{0.2})_{0.2}\text{O}_2-\delta$ system.

C. Oxygen permeability

Fig. 2 shows the dependence of the permeation current as a function of emf values for the $(1-x)\text{SrTi}_0.5\text{Fe}_0.5\text{O}_3-\delta-x\text{Ce}_0.8(\text{Sm}_{0.8}\text{Sr}_{0.2})_{0.2}\text{O}_2-\delta$ membranes at thickness of 0.05 cm, $T = 900^\circ\text{C}$. The graph shows that at the same emf values (for, example 0.01 V), the current increases with increasing x. Perhaps this is due to the fact that increasing fluorite phase leads to an increase of ionic and electronic conductivity and, consequently, to increase the oxygen permeability. It was found that increasing x in $(1-x)\text{SrTi}_0.5\text{Fe}_0.5\text{O}_3-\delta-x\text{Ce}_0.8(\text{Sm}_{0.8}\text{Sr}_{0.2})_{0.2}\text{O}_2-\delta$ hydrogen flow increased and equal 0.051, 0.092, 0.115, 0.173 and 0.176 ml cm$^{-2}$ min$^{-1}$ for x = 0, 0.25, 0.5, 0.75 and 1, respectively. It is clear that for $\text{Ce}_0.8(\text{Sm}_{0.8}\text{Sr}_{0.2})_{0.2}\text{O}_2-\delta$ ceramics hydrogen flux has a maximum value due to the high ambipolar conductivity compared to other materials.

III. CONCLUSION

In this work transport properties of new $(1-x)\text{SrTi}_0.5\text{Fe}_0.5\text{O}_3-\delta-x\text{Ce}_0.8(\text{Sm}_{0.8}\text{Sr}_{0.2})_{0.2}\text{O}_2-\delta$ composite mixed ionic-electronic conductors were investigated. The electrical properties have strong dependence on the chemical composition and the environmental conditions. We found that with the increase in the fluorite phase in composites conductivity increased under reducing atmospheres and decreased in oxidation one. The results of long-term tests show that composite materials possess high thermodynamic and kinetic stability as compared with the basic oxides.

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DEVELOPMENT OF AN AMMONIA BORANE-BASED POWER PACK: AN APPLICATION TO AN UNMANNED AERIAL VEHICLE

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Abstract – A hydrogen generator fueled by ammonia borane (AB) was newly designed to continuously power an unmanned aerial vehicle (UAV) for 57 min using a 200-Wₑ polymer electrolyte membrane fuel cell (PEMFC). The developed generator was demonstrated to produce 3.8 L(H₂) min⁻¹ autothermally employing tetraethylene glycol dimethyl ether (T4EGDE) as an additive. The H₂-generator was integrated with a commercial PEMFC to construct a power-pack. Upon flight tests, a hybridized power management system (PMS) possessing the fuel cell and an auxiliary lithium-ion battery initially provided 500 Wₑ for take-off while the fuel cell supplied 150 – 200 Wₑ upon cruising. The effluents containing H₂ were further purified using solid absorbents. To evaluate the remaining filter capacity of the absorbents, a real-time monitoring system was utilized. On the basis of these results, a viable reactor concept was discussed for long-term fuel cell implementations.

Keyword: Ammonia Borane, Hydrogen Power-Pack, Unmanned Aerial Vehicle

I. INTRODUCTION

Due to its high hydrogen storage capacity (19.6 wt%), and potential regenerability, ammonia borane (NH₃BH₃, AB) has been explored as a promising hydrogen storage material. The AB material can release hydrogen on demand via various methods, and among them, thermolysis of AB at < 250 °C proved to generate large amounts of hydrogen with high H₂ storage density of > 13 wt% (material-based). However, the slow kinetics for AB dehydrogenation makes this material less attractive for fuel cell applications. In this context, many strategies have been employed to improve the slow rate of AB dehydrogenation. In particular, various types of chemical additives were used to accelerate H₂-release from AB.

From an engineering point of view, utilization of AB as a solid fuel needs to resolve a number of technical challenges including continuous feeding of AB, efficient removal of gaseous byproducts, and facile discharge of liquid/solid spent-fuels. Significant efforts have been made to construct an AB-based hydrogen generator that ensures reliable feeding of AB with highly capable H₂ purification equipment. For example, DOE’s Hydrogen Storage Engineering Center of Excellence (HSECoE) has been focusing on developing relevant reactors using the mixture of AB with either silicon oil [1] or ionic liquid [2]. In parallel with these works, we recently developed a new, continuous reactor fueled by AB pellets, which demonstrated its capability to continually power a 200-Wₑ polymer electrolyte fuel cell (PEMFC) [3].

We report here on an AB-based portable hydrogen power-pack, which comprises a hydrogen generator, a hybridized power management system (PMS) equipped with a 200-Wₑ PEMFC, an auxiliary battery, and a control unit. The developed hydrogen power-pack was applied to an unmanned aerial vehicle (UAV) platform under collaboration with the Korea Aerospace Research Institute (KARI). To the best of our knowledge, no direct demonstration using the AB fuel for a practical application has previously been made to date. The power-pack was verified to drive a UAV for 57 min with fast load-following ability and rapid response time. Possible strategies for improving the efficiency of the hydrogen generator are further discussed.
II. EXPERIMENTAL

The AB-based H₂ generator was integrated with a commercial PEMFC stack (AEROPAK [4]) into a UAV (Ucon System, RemoEye-006) which consists of a platform, sensors, data links, and ground control stations. The UAV have been employed for reconnaissance, and it has limitations in the dimensions and weight for the desired H₂ generator. The allowed space for the AB-based hydrogen generator in the UAV fuselage was limited to 610 mm × 120 mm × 120 mm. The permissible weight for the fuel cell system including the AB-based H₂ generator and 200 -W PEMFC stack is restricted to 2,800 g in the UAV platform. The weight of the commercial stack is 470 g, and the AB-based H₂ generator was designed to have a weight of 1,706 g. The weights of AB pellets, T4EGDE, and filter materials (activated carbon materials; 3M 6001 & 6006) were designed to have 110 g, 120 g, and 260 g, respectively.

In the present PMS, a fuel cell and a lithium-ion battery were hybridized in parallel. Upon a sudden increase of load and for emergency landings, the lithium battery in the PMS is designed to provide supplemental power. In the flight test, both fuel cell and battery were initially employed to supply the necessary power of 500 W_e for take-off while the fuel cell alone provided a sufficient power of 180 - 200 W_e and further recharged the battery during cruising and maneuvering. The flight tests were performed at the Goheung Aviation Center at the Korea Aerospace Research Institute.

III. RESULTS AND DISCUSSION

![Image](310)

Fig. 1. (a) The developed H₂ power-pack and (b) an UAV platform.

![Image](34x154)

Fig. 2. Results for a flight test: the evolution of (a) the flight attitude (roll and pitch) and (b) flight speed and altitude.

This developed H₂ generator and a UAV platform were depicted in (Fig. 1). During cruising, flight data were automatically collected at a ground control system through RF communication with the UAV.

The flight test results including flight trajectories, aircraft movement (angles of roll and pitch), altitudes, and speeds of the aircraft are depicted in Fig. 2. The roll and pitch angles were recorded in the range of -30° to 20° and -5° to 10°, respectively (Fig. 2a). This result suggests that the AB-based power pack can be employed for various types of aircrafts under normal flight conditions. The UAV was maneuvered at an altitude of 150 - 200 m with a speed of 60 km/h upon cruising (Fig. 2b). In this flight test, the AB pellets proved to be continuously fed into the reactor with a rate of ca. 2.5 g min⁻¹ (30 ea. min⁻¹) for a total feeding time of 57 min (ca. 142 g).

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PREPARATION OF Ni-AL ALLOY UNDER LOW TEMPERATURE AND METHANE STEAM REFORMING FOR FUEL CELL APPLICATIONS

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Abstract - The new alloying method has been suggested to synthesis Ni-Al alloy powder using AlCl₃ as an activator at relatively low 500~600 ℃ under vacuum condition. The used AlCl₃ served as the catalyst, promoting the reaction between Ni and Al powder and lowering the fabrication temperature by 900~1,000 ℃ compared with that of the conventional process. Ni-Al alloy properties prepared by varying parameters were investigated and the as prepared Ni-Al alloys were alkali leached by NaOH solution for surface modification to enhance the specific surface area. The methane steam reforming activity tests were performed at temperature range of 600~850 ℃ to investigate the possibility in fuel cell system as the catalysts. As results, it was confirmed that leached Ni₅₀Al alloy shows as good methane conversion and long term stability as that of commercial catalyst and superior H₂ yield at low temperature of 600 ~ 750 ℃.

Key Words - aluminum leaching, low temperature gas-solid reaction, methane steam reforming, nickel-aluminum alloy

I. INTRODUCTION

The mainly used Ni-based catalysts for methane steam reforming have several types of deactivations. Reactivity and deactivation can be enhanced by modifying Ni surfaces with a second metal to form alloy or compound. Ni-Al alloys are known as a promising high temperature material and reported to have good catalytic selectivity and activity. The general method of preparation of the Ni-Al alloy requires approximately 1,400~1,500 ℃. This high temperature process sharply increases the cost of fabrication of the Ni-Al alloy material. Moreover, large Ni-Al alloy lump is obtained. Regarding this, our group has already reported a new low temperature gas-solid process for the fabrication of Ni-Al alloy powder [1]. In this study, we have modified our suggested process to reduce the amount of AlCl₃ and to avoid using H₂ gas. The Ni-50 mass% Al (hereinafter Ni₅₀Al) is used as a precursor like Raney nickel catalysts produced from the precursor alloy by leaching aluminum to form a Ni-enriched surface layer leading to an improvement of its catalytic properties. In addition, the catalytic hydrogen production experiments were carried out.

II. EXPERIMENTAL

Ni-Al alloy powders were prepared according to the same way we previously reported [2]. The as-prepared alloy powders were subsequently alkali leached. The powder was stored in a stirred 5M aqueous NaOH solution, and then rinsed in deionized water to dry at oven. The phases and morphologies of as-prepared Ni-Al alloy powder were characterized by XRD, and SEM. The BET surface area and pore size distribution were measured by nitrogen adsorption method.

Methane steam reforming experiments were carried out in a conventional fixed-bed flow reactor. Prior to the reaction, the catalysts were pretreated. The temperature was then increased from 600 to 850 ℃ and kept constant at these temperatures for reaction. The reactant mixture of CH₄ and H₂O stream (mole ratio of H₂O/CH₄ = 2) was introduced into the quartz tube with nitrogen carrier gas (mole ratio of N₂/CH₄ = 2.5) at GHSV of 22,000 h⁻¹.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD profiles patterns of the as-prepared Ni-Al alloy powder heat-treated at the temperatures of 400 ℃, 500 ℃ and 600 ℃ for 10 h. As shown in figure, with the heat-treated at 400 ℃, both Ni and Al peaks as well as Ni₂Al₃ and NiAl₃ crystalline, were detected demonstrating that the Ni-Al alloy can be formed
at 400 °C. At 500 and 600 °C, the only Ni$_2$Al$_3$ and NiAl$_3$ peaks were observed without any other pure Ni and Al peaks, showing that Al contained in the original mixture was completely consumed to form Ni-Al alloy powder and these XRD results is correspondent with that of other reports[3].

Ni-Al alloy powder could be formed at the condition of time over 10 h and only as small amounts as of 0.2 wt% AlCl$_3$ activator even though not shown here and this is showing that a small amount of AlCl$_3$ is sufficient to activate the reaction between Ni and Al because AlCl$_3$ acts as a catalyst.

The XRD patterns for the Ni50Al and Alfa Raney alloy powder before and after leaching. All the diffraction peaks observed in the profiles of two alloys are assigned to those of Ni$_2$Al$_3$ and NiAl$_3$, having no significant difference between them before alkali leaching. But, after leaching process, both pure small intensity Ni and Al peaks were observed in case of Alfa-Raney alloy. These results are consisted with the SEM images, BET surface area and pore size distribution profiles (not shown here). After alkali leaching, BET surface area increased approximately from 0.92 to 31.7 m$^2$/g over 30 times and around 0.1 $\mu$m pores were mainly formed on the alloy powder surface.

The catalytic performances of the alkali leached as-pretreated Ni50Al alloy and reference leached Alfa-Raney alloy for MSR were investigated at temperatures from 600 to 850 °C with 50 °C interval. Figure 2 shows the gaseous products distribution of H$_2$, CO, CO$_2$, and inlet CH$_4$ conversion of each alloys were plotted, respectively as a function of reaction temperature. As shown in figure, the methane conversion with time depends strongly on the reaction temperature and two leached alloy shows similarity, over 95% conversion of methane at the temperature of 750 °C.

In addition, the production rate profiles on temperature shows that more amount of H$_2$ was produced per unit leached NiAl alloy gram than leached Alfa-Raney alloy and this might be related with the results of alkali leaching process, selectively leached Al from the Ni$_3$Al only in the outer surface, forming the fine Ni particles on the surface.

The long term activity test over 200h results show that the leached Ni50Al could have good catalytic properties and stability in the methane steam reforming process even though now shown here.

![Fig. 1. XRD patterns of Ni-Al alloy powder heat-treated with several temperatures of 400-600 °C for 10h.](image)

![Fig. 2. Steam reforming product distribution and Methane conversion of (a) leached Ni50Al (b) leached Alfa-Raney alloys, respectively at 750 °C.](image)

**IV. CONCLUSION**

The above experimental results show that successfully lump-free Ni-Al alloy powders were prepared using AlCl$_3$ activator at a relatively low 400 – 600 °C. In addition, we could confirm that alkali leaching of aluminum significantly affects the surface structure of the NiAl alloy to enhance specific surface area and properties. The leached Ni50Al alloys showed good CH$_4$ conversion, superior H$_2$ yield at low reaction temperature below 750 °C and the long term catalytic stability for carried-out methane steam reforming by isothermal tests.

**ACKNOWLEDGMENT**

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AMMONIA BORANE-BASED SOLID FUELS FOR PEMFC APPLICATIONS

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Abstract – In this study, ammonia borane (AB) based solid fuels were screened utilizing 18-crown-6 (18C6) and its derivatives as promoters, and their dehydrogenation properties at 125 °C were examined for fuel cell applications. Among promoters employed, dibenzo-18C6 molecule showed excellent activity for the desired H2 production, with > 2 equiv. of H2 being released in 30 min. FT-IR and solid-state 11B NMR spectroscopic studies revealed that spent-fuels containing B=N bonds (e.g., borazine) were formed. Density functional Theory (DFT) method was further employed to elucidate the role of the solid promoters.

Keywords: Ammonia Borane, Dehydrogenation, Hydrogen Bonding Interaction, Fuel Cell

I. INTRODUCTION

Hydrogen-based economy has attracted considerable attention for last decade in parallel with growing concerns about global warming. One of the key technological issues for achieving hydrogen economy is to develop reliable hydrogen storage systems that store high quantities of hydrogen in a safe manner. For instance, US Department of Energy (DOE) offers a guideline of > 5.5 wt% of system-based hydrogen storage capacity in 2015 for transportation applications. In this context, various types of hydrogen storage materials such as metal hydrides, complex hydrides, and chemical hydrides have extensively been studied, but only limited materials could potentially meet the DOE target to date. Owing to its reasonable stability under ambient conditions, high potential hydrogen storage density (19.7 wt%, material-based) and possible regenerability, ammonia borane (NH3BH3, AB) has recognized as one of the most promising hydrogen storage materials for polymer electrolyte membrane fuel cell (PEMFC) applications. To achieve high hydrogen storage density for long-term uses, production of hydrogen from AB via thermolytic decomposition is generally preferred over hydrolysis-based processes since the latter method not only provides a limited hydrogen density, but it also produces ammonia that is detrimental to Pt catalysts at a PEMFC. Thermolysis of AB, however, has shown slow H2-release kinetics at < 100 °C, insufficient for practical applications. Considerable efforts have been made to accelerate the rate and extent of H2-release from AB using transition metal catalysts, scaffolds, chemical promoters, and ionic liquids.

In the course of developing an efficient AB-based hydrogen storage system, we have recently found that a series of polyetheral promoters can activate B-H bonds of AB partially by hydrogen bonding interactions between a promoter and AB to facilitate the formation of the reactive intermediate, diammoniate of diborane (DADB), ultimately enhancing the rate of dehydrogenation from mixtures of AB and the promoters [1]. In addition, this discovery has been extended to apply to a continuous hydrogen generator utilizing spherical-shaped AB pellets as fuels with one of the polyethers, tetraethylene glycol dimethyl ether (T4EGDE) as a promoter for powering an UAV equipped with a 200 W polymer electrolyte membrane fuel cell (PEMFC) [2].

We report here on AB-based solid fuels containing 18-crown-6 derivatives as promoters for PEMFC applications. Compared to those of pristine AB, extents and rates of H2-release properties from the AB-based fuels containing 18-crown-6 derivatives were enhanced at temperatures in a range of 95 °C – 125 °C. Consistent with the previous results,13 density functional theory (DFT) methods suggest that the 18-crown-6 molecule can interact with AB via hydrogen bonding interaction. Solid-state magic angle spinning (MAS) 11B NMR spectroscopy was employed to characterize spent-fuels.

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II. RESULTS AND DISCUSSION

Fig. 1. H$_2$-releases from AB in the presence of different amounts of T4EGDE and 18C6 at 125 °C: (■) pristine AB, (●) 18C6 = 10 (wt%), (▲) 18C6 = 15 (wt%), (▼) 18C6 = 20 (wt%), (○) 18C6 = 25 (wt%), and (●) 18C6 = 30 (wt%).

To explore the influence of added 18C6 on AB dehydrogenation at 125 °C, various quantities of 18C6 was initially employed. Rate and extent of H$_2$-release increased with an increase in the amount of added 18C6, as depicted in Fig. 1. Utilization of 0, 10, 15, 20, 25, and 30 wt% of 18C6 afforded ca. 1.2, 1.1, 1.5, 1.8, 1.8, and 2.0 equiv. of H$_2$ within 30 min, respectively. In the presence of ≥ 20 wt% of 18C6, the rate and extent of dehydrogenation from AB were found to be nearly identical to produce > 2 equiv. of H$_2$ over 60 min (Fig. 1). The determined H$_2$ yields, defined as [weight of H$_2$/weight of (AB + 18C6)] × 100, indicate that an optimized quantity of 18C6 for AB dehydrogenation at 125 °C is 20 wt%, and this mixture of AB and 18C6 (80:20, wt%) yielded a material-based hydrogen storage capacity of 10.3 wt% within 60 min.

Fig. 2. In-situ FT-IR spectra of borazine produced during dehydrogenation at 125 °C: (black) pristine AB, (red) AB/T4EGDE (75:25, wt%), and (blue) AB/18C6 (75:25, wt%).

In-situ FT-IR spectroscopy was employed to characterize gaseous byproducts formed during dehydrogenation from the following three mixtures at 125 °C (Fig. 2): (i) AB, (ii) AB/T4EGDE (75:25, wt%), and AB/18C6 (75:25, wt%). In all cases, characteristic N-H and B-H stretching frequencies corresponding to borazine were found as a major gaseous byproduct in the FT-IR spectra.

Fig. 3. H$_2$-releases from AB at 125 °C in the presence of: (■) pristine AB, (●) AB:18C6=75:25 (wt%), (▲) AB:Benzo-18C6=75:25 (wt%), (▼) AB:Dibenzo-18C6=75:25 (wt%).

Variation of substituents within the 18-crown-6 molecules could potentially influence the extent and rate of AB dehydrogenation electronically and sterically. To validate the hypothesis above, other 18C6 derivatives, monobenzo-18C6 and dibenzo-18C6 were utilized for AB dehydrogenation at 125 °C. The monobenzo-18C6 promoter exhibits better activity than any other additives, as depicted in Fig. 3. The H$_2$-release from AB with dibenzo-18C6 molecule exhibited even lower activity for AB dehydrogenation than that without any promoters.

We will further discuss about the possible roles of these additives in promoting AB dehydrogenation, based on DFT studies.

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A NOVEL, IN SITU ANALYTICAL TECHNIQUE: PROBING OXYGEN TRANSPORT PHENOMENA OF VARIOUS METAL OXIDES FOR SOLID OXIDE FUEL CELLS

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Abstract - Metal oxides with perovskite or fluorite structure have been widely used for anode, cathode and electrolyte for solid oxide fuel cells (SOFCs). Understanding of defect chemistry occurred at a SOFC component is of great importance because physical properties of these materials depend on their non-stoichiometry. In this context, a real-time monitoring technique to probe oxygen transport phenomena is beneficial to design next-generation SOFC materials. In this contribution, we developed a combined system utilizing thermogravimetric analyzer and a 4 probe electrical conductivity measurement, which provides useful information about changes in weight of a material (e.g., Ceria and a perovskite) simultaneously along with its electrical conductivity. Applicability of this newly developed monitoring system for a number of SOFC materials will be discussed.

Keyword: Thermalgravimetric analysis, Electrical conductivity, Metal oxide, Perovskite

I. INTRODUCTION

In recent years, metal oxide materials have extensively been studied for a number of catalytic applications. Among these materials, metal oxides with fluorite structure and perovskite structure have particularly attracted significant attention since they possess high oxygen conducting ability and/or high electron conductivity. In this regard, these materials have been employed as electrodes and/or electrolyte especially for solid oxide fuel cells (SOFCs).

SOFCs are one of the promising candidates as an alternative energy technology. In the SOFCs, fluorite structured materials such as yittria stabilized-zirconia (YSZ) and gadolinium doped-ceria (GDC) have widely been used for electrolyte. In addition, perovskite structured materials including lanthanum strontium manganite (LSM) and lanthanum strontium cobalt ferrite (LSCF) are employed for electrode. To fabricate SOFCs for high performance, the characterization of these materials is essential.

Various techniques such as dilatometer, thermo-gravimetric analysis (TGA), and conductivity measurement have been developed to analyze the characteristics of metal oxide materials in terms of temperature and oxygen partial pressure. Firstly, dilatometer measures thermal expansion of a desired material and its thermal property is mainly associated with fabrication issue. Secondly, TGA is a method to detect the changes in properties of materials with temperature and time. Thirdly, conductivity measurement as a function of oxygen partial pressure at a target temperature is directly related to the performance of SOFCs, which helps understand the relationship between oxygen defect and conductivity.

To elucidate the correlation between oxygen stoichiometry and electrical property in metal oxides, two major physical properties of a sample are usually measured in separate systems.

A: electrical measurement (electric charge concentration)
B: weight measurement (oxygen ion concentration)

To determine the stoichiometry of a metal oxide accurately, the results obtained in situ by both measurements A and B should be combined in an equilibrium state following changes in oxygen partial pressure. In general, the previously studied methods measured electrical conductivity with an assumption that the used material was in an equilibrium state. If the material did not reach to the equilibrium quickly, however, one would obtain inaccurate information. In this context, clarification of the correlation between oxygen ion concentration and electrical charge concentration in metal oxides is critical. In this study, a combined system utilizing...
weight measurement and electrical measurement is developed, and its applicability is discussed.

II. EXPERIMENTAL

The combined system was made up of weighing sensor and resistance sensor, and the structure and design of two sensors were modified and optimized. Mass change was detected using commercial balance measurement (CUX620H, CAS), and electrical conductivity was also sensed using commercial resistance meter (RM3544, HIOKI). The two kinds of data were collected at the same time, and temperature and oxygen partial pressure were also controlled. The conceptual diagram and developed equipment of the combined system were shown in Fig. 1. The samples were prepared as rectangular bar, which was pelletized and sintered and 4-probe method was used to measure total electrical conductivity.

![Fig. 1. Conceptual diagram of the developed equipment (left) and its photograph (right)](image)

III. RESULTS AND DISCUSSION

The changes of mass and conductivity sample are monitored as function of temperature and oxygen partial pressure. Cathode material as an example, which is perovskite structured, is measured using the invented system. The sample is heated to temperature of 600°C and maintained, and the oxygen partial pressure is controlled to observe the oxygen transport phenomenon.

\[ \frac{1}{2} O_2 + V_{O^\bullet} \leftrightarrow O_{O^\bullet}^6 + 2h^\bullet \]  

The relationship between oxygen transport and conductivity are shown in Fig 2. The mass change indicates the oxygen transport in the perovskite structure defined by equation (1). As the oxygen partial pressure changes, the mass and the conductivity shows differences at the same time. This result shows that the invented system is able to observe the oxygen transport phenomenon through changes of electrical conductivity and mass in terms of oxygen partial pressure and temperature.

![Fig. 2. Changes of conductivity and mass in terms of oxygen partial pressure](image)

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DEVELOPMENT OF A 2 KW DIRECT METHANOL FUEL CELL SYSTEM FOR BACKUP POWER

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Abstract – This paper describes recent results in developing durable and cost efficient direct methanol fuel cell systems (DMFCs) for uninterruptible emergency power supply (UPS). Based on a DMFC system with an average power output of 1 kW for the replacement of batteries in small fork lift trucks – this system was continuously operated for 20,000 h – the economic and technical challenges to achieve competitiveness to other already existing UPS technologies are described. Especially the further cost reductions due to a reduced number of sensors and the durability during the long standby phases are in the focus of the research work. In spite of a reduced number of sensors the efficient and secure operation of the system must be guaranteed. To achieve long term stability the right treatment of the stack during the standby will be identified by analysing the behaviour of short stacks equipped with MEAs from different manufactures.

Index Terms – Direct Methanol Fuel Cells (DMFC), durability, uninterruptible power supply (UPS)

I. INTRODUCTION

The DMFC is the type of fuel cell that is already commercially available in the power range from several Watts up to a few hundred Watt. Today, systems in the kW power range are not commercially available due to the high investment costs for the fuel cell stack. But the benefit of this technique is in the methanol - in particular its high energy density and easy handling. The liquid energy carrier allows long runtimes without refilling and no rent has to be paid for compressed gas cylinder. These advantages can overcome the higher investment costs for the fuel cell. It is possible to achieve operating costs that are lower than with batteries or other fuel cell backup systems. Especially for security related backup stations runtimes of several days without refilling are necessary.

II. ECONOMIC ASPECTS OF UPS SYSTEMS

Besides battery replacement in light traction applications [1, 2], backup power systems with DMFCs are an economically interesting option for telecommunication systems, electronic data processing centres or other infrastructure important to safety. The advantages of such DMFC systems are the energy density (4.4 kWh/L), the easy storing and handling of methanol, compared to hydrogen (0.9 kWh/L @ 700 bar incl. tank) and lead acid batteries (0.08 kWh/L). Therefore it is possible to achieve low costs of electric energy generation (see in Fig. 1). For calculation the specific costs of the electric energy generation it was assumed that the number of sensors in the DMFC system is reduced and that all systems have a lifetime of 10 years with 5,000 h of operation.

Fig. 1. Costs of electric energy generation with different techniques; PEFC: polymer electrolyte fuel cell, DMFC: Direct methanol fuel cell
The energy generation with the DMFC is more favourable than with other fuel cell techniques or batteries, but it is still higher than with a diesel gen set. But in comparison to the diesel gen set the fuel cell persuades with its reliability and with low emission of noise, sound and vibrations.

III. DURABILITY ESPECIALLY DURING STANDBY

At Forschungszentrum Jülich a 1 kW DMFC system was continuously operated for more than 20,000 h with a highly dynamical load profile. This system was developed as a battery replacement which enables small fork lift trucks to operate 24/7 without any downtime due to charging the batteries. The degradation rate at 0.1 A/cm² is less than 9 µV/h.

To achieve this, the fuel cell system’s components were optimized to be inert and the operating media was filtered so only a low amount of contaminations with ions or other impurities could influence the durability of the membrane electrode assembly (MEA). On the other hand the operating conditions, the electrical hybridisation and the control of the DMFC system are designed in a manner for enhancing the life time.

The demands for backup power are different from conventional applications. Such systems will be in standby mode during most of their lifetime and only a few thousand hours in operation. The typical lifetime of professional backup systems is ten years; this means such systems are more than 80,000 h in standby and only about 5,000 h in operation. Together with users and manufactures of backup systems a more detailed identification of these demands is on-going and the results will be presented at the conference.

To achieve the lifetime of ten years the degradation rate during standby should not exceed 1 µV/h based on a current density of 0.1 A/cm² for the characterisation. To achieve this degradation rate, different conditions for standby will be tested, especially in terms of catalyst corrosion. The focus is on controlling the corrosion of Ruthenium in the anodic catalyst layer. This can be done by feeding the anode with a low methanol concentration or by drying the whole stack and by other temporally limited processes during standby. These tests are always accompanied with chemical analysis of the operating media to identify possible traces of impurities.

IV. CONCLUSION

The results are promising; they show that DMFC systems could be an economical advantageous alternative for an emergency power supply system, due to the low maintenance costs. And the durability tests also show that it will be possible to operate such systems for ten years or more if the right standby-operation method is identified.

ACKNOWLEDGMENT

This work is founded by the Helmholtz Validierungsfonds, a special fond to promote techniques that have a status near to commercialization.

REFERENCES

List only one reference per reference number according to the following examples:

A GUIDELINE FOR DESIGNING MORE DURABLE CATALYSTS BASED ON THE COHESIVE CHARACTERISTICS OF 3D, 4D AND 5D METALS

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Abstract – Analogical trends were found in the intra metallic bond energy of the 3d, 4d and 5d metals. The intra metallic bond energies increase from Ca, Sr, and Ba to near the center of the series and then decrease toward Zn, Cd, and Hg. The shape was like a volcano at the maximum at the half-filled d-electrons, and at the minimum at the no or full-filled d-electrons.

Index Terms - Sinterability, Diffusivity, 3d, 4d, 5d

I. INTRODUCTION

The d-orbital metal elements such as the typical novel metals; Pt, Rh, Ru, Pd serve many industrially important catalytic functions such as the three-way catalysts of automobiles, the oxygen reduction reaction (ORR) of a polymer electrolyte membrane fuel cell (PEMFC). Besides, it is used in the hydrogen reforming reaction which is essential to practical use of PEMFC. However, it is not limited only the novel metals, but also any supported metals to have serious problems such as the decrease of specific surface area due to the duration under the continuity of reaction. Therefore the supported metals were designated to be highly dispersed in order to maintain clustered nanoparticle condition over a long period. It is important to theoretically evaluate the cohesive property of metallic elements instead of only depending on the trial-and-error experimental inspection such as the long-term duration tests. Actually, composite oxides have been developed for the practical catalyst, rather than the monoxide. The each ratio of monoxide is designated to satisfy the activity and durability to form composite oxide. Even in such a composite metal oxide support, diffusivity of the each metallic cation becomes prominent under the high temperature. Therefore, it is important to understand the characteristics of metallic elements in the same way as the case of supported metals. This study investigates the intra-metallic bond strength of 3d, 4d and 5d metals and investigates the relevance with the experimental basis on the various cohesive characteristics of metallic elements. Substitution of noble metals by other metals like core shell catalysts has been applied for the catalysts in the PEMFC to reduce the cost. In the hope that a combination of different metals would have improved catalytic activity and stability relative to those of a pure metal, the ORR has been studied on numerous bi- or multimetallic alloys [1]. Rather than use a trial-and-error or combinatorial approach, fundamental features of 3d, 4d and 5d metallic elements were concluded in this study.

II. METHOD

The elements of Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn belong to the 3d group metals. The elements of Sr, Y, Zr, Nb, Mo, Te, Ru, Rh, Pd, Ag, and Cd belong to the 4d group metals. The elements of Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, and Hg belong to the 5d group metals. The crystal bulk models of all 3d, 4d and 5d group metals were quantum chemically calculated by the tight binding quantum chemical (TBQC) calculation [2]. The data were also compared with the other theoretical method, density functional theory (DFT) [3] calculation. Besides, computed intra metallic binding energies were compared with experimentally measured heat of formation divided by the bond numbers in respective metal crystallites [4].
III. RESULTS

As shown in Figure 1, the intra metallic binding energies of 3d, 4d, and 5d metals obtained from TBQC calculation were agreed well with those of DFT and experimentally measured values. These two computed results and experimentally measured values were periodically arrayed along with the occupation number of 3d, 4d and 5d orbitals. The values of intra metallic binding energy were ranged from about 5 to 35 kcal/mol. The Ca and Zn in 3d metallic elements, Sr and Cd in 4d metallic elements, and Ba and Hg in 5d metallic elements showed the smallest values. There has no d electrons in the Ca, Sr and Ba, respectively. On the contrary, there are full 3d, 4d and 5d electrons in the Zn, Cd and Hg, respectively. The bond strength between the intra metals in the crystallites revealed nearly symmetric at the elements of half-filled d-electrons, such as Mn, Tc and Re, and volcanic shaped plots. Coincidently, the degree of the cohesive energy, surface energy, and Tamman temperature of 3d, 4d and 5d metallic elements also has symmetric properties at the elements of half-filled d-electrons. The results showed that intra-metallic binding energy reveals the correlation with various cohesive properties. When the cohesive energy, surface energy, and Tamman temperature is lower, the binding energy between the atoms in the crystallites becomes weaker, and vice versa. The stability to sintering of the catalyst has much relevance with that order. The experimental observations suggest that the stability to sintering is in the order: Ir > Rh > Pt > Pd [5]. The order was almost same as TBQC and other compared results quantitatively presented the degree of bond strength as following sequence: Ir: 28.4 kcal/mol > Rh: 22 kcal/mol ≒ Pt: 23.7 kcal/mol > Pd: 16.3 kcal/mol.

IV. CONCLUSION

The results of intra metallic binding energies of 3d, 4d, and 5d metals obtained from TBQC calculation were agreed well with that of DFT and experimentally measured values. These two computed results and experimentally measured values were periodically arrayed along with the occupation number of 3d, 4d and 5d orbitals. The experimentally observed order of the stability to sintering was understood well when the degree of intra metallic bond energies were quantitatively evaluated. This could lead a guideline for designing more durable catalysts.

REFERENCES

DEVELOPMENT OF A EXPERIMENTALLY VALIDATED MODEL FOR SOLID STATE HYDROGEN STORAGE DESIGN OF MATERIAL AND TANK


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**MATRES, Via Diaz 21, Treviso (IT)

Abstract – EDen is a European project, supported by FP7 – JTI FCH. It aims to develop an innovative embedded system for the storage of energy, thanks to combination and thermal integration between a SOFC (capable to work like SOE) and an innovative solid state hydrogen storage tank. In the proposed work, the objective is the optimization through modeling of behavior and physical performance for hydrogen storage solution in solid-state material (Mg-based metal hydrides). The candidate material for hydrogen storage, and final pellet (utilized inside tank) have been defined through the identification of best physics, to better describe gas’ diffusion phenomena and thermal exchange inside the storage tank.

Index Terms – Design, Hydrogen storage, Material, Modeling

I. INTRODUCTION

Nowadays, numerical simulations have a considerable importance and impact in R&D processes until industrial developments in order to reduce time development and time to market, by passing some redundant prototyping steps.

Inside EDen project, modeling is a useful step to optimize and define parameters of the system and identify interaction between every component and their magnitude. In particular, the optimization of tank (on both the material side and geometry/shape of pellet) is a critical point, and it requires an accurate study.

In this context, a proper model was developed in order to describe kinetics behavior of magnesium-material. COMSOL Multiphysics commercial software has been used, extended with Fluid Dynamic and Heat Transfer modules. The model has been validated with experimental data to confirm its accuracy. The calibrated tool has been used to perform further numerical simulation about possible material and tank designs.

II. BUILDING MODEL

In order to perform a numerical simulation of a real system, it is necessary to develop a proper physical model. First, physical behavior of a simple geometry of pellet has been described, composed by compressed magnesium powder.

So, some approximations have been considered: hydrogen gas has an ideal behavior, radiative heat transfer is neglected and thermal conductivity of system is calculated by weighted average of components. Moreover, constant volume of pellet during reaction has been assumed.

Next picture is basic geometry on designed numerical tool.

Moreover, some fixed conditions have been considered: constant pressure of hydrogen on above side of pellet, heat flow is normal to bottom and external surfaces of pellet and heat exchange depends by h (coefficient of heat transfer).

Next three main variables have been considered in system:

- **Pressure.** Pressure inside tank and pellet obeys to Darcy’s law,

\[ \overline{\nabla} P = -\frac{\mu}{k} \overline{v} \]  

- **Temperature.** Temperature is given only by conductive heat transport,

\[ \rho_c C_v \frac{\overline{ST}}{\overline{dt}} + \rho_c C_m \frac{\overline{SMT}}{\overline{dt}} + \rho_c C_p \nabla (\overline{T}) = \lambda_c \nabla' (T + \overline{S}) \]

Where, \( S \) is heat source from reaction of de/hydriding:

\[ S = - \left( \frac{\overline{dx}}{\overline{dt}} \frac{\rho_c^m - \rho_{m_h}}{PM} \cdot (1 - \varepsilon) \right) \Delta H \text{ reaction} \]

- **Reacted fraction.** Reacted fraction is the mass ratio between formed...
magnesium and maximum magnesium quantity (or magnesium hydride for dehydriding reaction). We assume that velocity of reaction are subjected to Avrami’s law [1, 2, 3]:

\[
\delta x = \frac{m_1 (1 - x)(- \ln (1 - x))}{\xi} \cdot G (P, P_e) \cdot C \cdot e^{-\frac{E_{Att}}{RT}}
\]

Where G is driving force function of reaction (function of pressure and equilibrium pressure of material). In next table, main parameters of material are reported,

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>MAIN PARAMETERS UTILIZED IN OUR PHYSICAL MODEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>∆H</td>
<td>-71000</td>
</tr>
<tr>
<td>∆S</td>
<td>132</td>
</tr>
<tr>
<td>Arrhenius’s coefficient</td>
<td>7.7 10^6 for Adsorption, 1 10^5 for desorption</td>
</tr>
<tr>
<td>Energy of activation (E_{Att})</td>
<td>110 for Adsorption, 105 for Desorption</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.5</td>
</tr>
<tr>
<td>m (ADS)</td>
<td>1.96</td>
</tr>
<tr>
<td>m(DES)</td>
<td>0.8</td>
</tr>
</tbody>
</table>

III. EMPIRICAL VALIDATION

The numerical tool has been verified in comparison with a real apparatus, indicated in below figure.

![Experimental design and its representation in software (COMSOL) for numerical simulation.](image)

Adsorption and desorption phenomena have been simulated at the same physical condition (temperature and pressure) of experimental apparatus.

![Comparison between numerical simulation and experimental data for ADSsorption phenomenon](image)

![Comparison between numerical simulation and experimental data for DESsorption phenomenon](image)

IV. CONCLUSION

Proper numerical tool has been developed to describe accurately hydrogen’s adsorption and desorption phenomena on pelletized magnesium. The model has been validated from comparison with experimental data and it will be used for optimization of the pellet and tank’s geometry proposed in EDen project.

ACKNOWLEDGMENT

Authors are grateful to MATRES, Alvise Bianchin and Enrico Forlin for experimental data provided.

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Stationary Fuel Cells –
Insights into Commercialisation

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Abstract

Introduction

Fuel cell systems for stationary applications offer the promise of substantial benefits for end users: more power and heat, for the same amount of fuel with lower emissions. These benefits are available across a range of sizes from 1kWe, or even smaller, suitable for domestic Combined Heat and Power (CHP) use, through hundreds of kW to MWe sized units ideal for commercial and industrial CHP and power only uses. The end user and emissions benefits have been explored in a number of reports over the past several years. However, even with these benefits stationary fuel cell systems still face the challenge of commercialisation, of selling products to end users profitably and sustainably over the longer term.

Stationary Fuel Cell Systems

Stationary fuel cell systems have been under development for several decades in the world’s regions, notably USA and Canada, Japan and South Korea, and Europe. Principal developers include Fuel Cell Energy, Bloom Energy and UTC (now ClearEdge) and Ballard in North America, Panasonic, Toshiba and JX in Japan, Posco in South Korea and a number of smaller systems producers in Europe, Topsoe Fuel Cells, Intelligent Energy, Baxi, Hexis, CFCL, Ceres Power and SOFC Power.

Stationary fuel cells have been ‘sold’ for a number of years, often with significant government support, but numbers have been relatively small. However, the move towards commercialisation has accelerated in the past few years. Data from the 2012 Fuel Cell Industry Review points to shipments of 16,000 units in 2011, totalling 81MW of power capacity. These figures represent increases of 94% and 133% respectively over 2010. In particular Japan has seen thousands of small scale domestic units installed over the past few years as part of the Ene.Farm programme, with numbers of larger units, of hundreds kW to MW, being installed in North America, Europe and South Korea.

Challenges

Stationary Fuel Cell Systems potentially offer solutions to the varied energy issues that face Europe, and other regions of the world. The European Union’s 20-20-20 targets for emissions, efficiency and energy sources point to a need to do things differently, and stationary fuel cell systems can be part of the solution.

The stationary fuel cell value proposition is complex. Costs are clearly important, but so are the other benefits of stationary fuel cells: the environmental benefits of lower emissions, the relatively small size and quiet operation and the promise of autonomy from mainstream power suppliers for end user. Such benefits nonetheless need to be matched by three key operational and economic criteria: reliability, durability and affordability.

Fuel cell systems must be able to offer reliability of supply equal to centralised power and gas grids; they should have an operational lifetime equivalent to existing domestic and commercial boilers and generators; and they need to be ‘competitive’ in terms of cost of delivered power and heat (cooling). Over the past decade fuel cell systems have demonstrated their reliability, whilst the lifetime of equipment is also increasing.

Arguably fuel cell systems are making steady progress towards reliability and durability targets and the greatest challenge remains that of cost, but even here progress is being made.

The Cost Challenge

The prospect of wide scale commercialisation of stationary fuel cells will ultimately depend on cost. Evidence available in the market place suggests that the costs of stationary fuel cell systems are currently available for between €25,000 to €40,000 per kW(e). This wide range in costs reflects the size and maturity of the units; with smaller unit costs being considerably more than larger units on a cost/kWe basis.

Larger fuel cell units of 100kW(e) plus in size are currently the cheapest in terms of cost per kW(e) installed. Anecdotal evidence suggest that units produced by Fuel Cell Energy and UTC (now ClearEdge) are increasingly economic without any form of public support. These units are suitable for...
CHP applications for large buildings, for example offices’, with a number of units recently located in Europe, including London.

Smaller fuel cell units in the kW(e) range are more expensive, with cost/price several times those of the larger units. Actual costs are difficult to determine, but numbers announced in the Japanese Ene.Farm project for residential units are in the €20,000 to €25,000 / kW(e) range.

With cumulative sales of larger fuel cell systems in the hundreds and smaller residential units in the thousands (Panasonic reported sales to end of Dec 2012 of 21,000, and Toshiba 11,000 at the end of November 2011) it is clear that there is a market, and a growing market at that, for stationary fuel cell units.

Cost Targets

Actual cost targets to achieve early deployment are perhaps less daunting than might first appear to be the case. With all new technologies and products there are always ‘early adopter’ style customers who are willing to purchase products or services above the prevailing price offered by competitive products or solutions. In addition there are early markets where due to specific local circumstances the proposition of a new product or solution need not be as stringent as in other markets.

Reducing Costs

Experience with other innovative energy technologies shows that costs can be expected to fall as a function of ‘experience curves’ as noted in the IEA and OCED report on Experience Curves for Energy Technology policy. This report, albeit somewhat dated, provides a series of examples of the experience curves for innovative energy technologies such as Solar pv and wind turbines where costs were seen to fall as cumulative sales increased. Cost reductions in technologies could be a function of better technologies, better manufacturing and simply better business processes within technology developers and producers.

Reducing the cost of stationary fuel cells is and will be a function of better technologies and better manufacturing activities, as well as better business processes amongst developers.

Fuel Cell System Cost Reduction in Practice

Identifying real examples of cost reductions in the fuel cell field is difficult given the limited numbers of units in service and the increase in production experience to date. However, evidence from the Japanese Ene.Farm project over the past few years provides an example of what has been achieved by leading businesses in the field. Both Panasonic and Toshiba have made public announcements in the past few years about the costs of their products and progress in reducing these costs alongside product improvements.

Panasonic, with Tokyo Gas, announced in January 2013 that it had reduced the cost (excluding installation) of its domestic PEM fuel cell system to ¥1,995,000 by approximately ¥760,000, a reduction of 27.5%. from its 2011 model, which was a reduction in cost from its 2009 model (selling at ¥3,465,000). A year or so earlier in January 2012 Toshiba with Osaka Gas announced that it had reduced the cost of its SOFC domestic fuel cell system by ¥650,000 to ¥2,604,000, a 25% reduction in cost. In both cases sales increases were anticipated and further cost reductions expected.

The Panasonic announcement also included further information on the performance and other aspects of the unit. The cost reduction was associated with an improvement of lifetime from 50,000 hours to 60,000 hours; a reduction in components by 20%; reduced weight by 10% and reduced size overall. Of significance was a reduction in noble metals in the fuel processing by 50% and platinum catalyst by 50%. Total efficiency, both heat and power, was calculated at 95% LHV.

Toshiba noted that it had reduced costs of its newer unit through, for example, reducing platinum content by 20% and the number of cells by 15%, whilst the number of components was down 40%, achieved by simplifying the system and integrating pipes. Additionally Toshiba stated that the fuel efficiency of its unit both in electrical and heat terms was improved to provide a total efficiency at LHV of 94%.

What is evident from the cases of Panasonic and Toshiba is that cost reductions are possible over time, but that they are not simply a function of numbers of units produced and installed, but a mix of both production increases and technology and product improvements, made by it should be added experienced and capable businesses.

Conclusions

The early commercialisation of Stationary fuel cell systems can be achieved in niche markets able to support a higher than expected price. To be able to offer such prices fuel cell system manufacturers will need to achieve cost reductions which are a function of better technologies and business processes as well as more units produced.

References

[3] Experience Curves for Energy Technology Policy IEA and OECD 2
EFFECT OF HYDROGEN FEEDING SUBSYSTEM ON EFFICIENCY AND DURABILITY OF PEM FUEL CELL SYSTEMS

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Abstract – The hydrogen feeding sub-system is one of balance of plants (BOP) components necessary for the correct operation of a fuel cell system (FCS). In this paper the performance of a 6 kW PEM (Proton Exchange Membrane) FCS, able to work with two fuel feeding procedures (dead-end or flow-through with recirculation), was experimentally analyzed with the aim to verify the effect of the anode operation mode. The FCS operated at low reactant pressure (< 1.5 bara), without external humidification. The experiments were performed in both steady state and dynamic conditions, typical of automotive applications. The results were analysed in terms of total available power, individual cell voltage distribution and efficiency. The performance worsening observed without fuel recirculation in dynamic conditions evidenced the correlation between the fuel feeding method and cell voltage uniformity.

Index Terms – Fuel cell vehicles, Hydrogen feeding sub-system, PEM fuel cells, Fuel cell durability

I. INTRODUCTION

The development of fuel cell electric vehicles requires the appropriate design of the on-board fuel cell system (FCS), i.e. the choice of suitable balance of plants (BOP) components, their integration and optimal management finalized at maximum efficiency and durability [1,2]. In previous works the issues related to air feeding strategies and water management were analyzed, evidencing the role of different devices and methodologies in optimizing the performance of a PEM stack for automotive applications [3].

The aim of the present paper is to evaluate the PEM stack performance for two different hydrogen feeding sub-system designs, i.e. dead-end versus flow-through modes. In the first case hydrogen is loaded to the stack as pressurized gas, and a purge valve normally closed placed at the outlet has the function to drain out the possible excess of nitrogen and water accumulated in the anode side during stack operation. The flow-through option implies the continuous fuel recirculation and requires additional components, such as a hydrogen recycle pump or ejectors. The choice between the two configurations affects the design of the specific sub-system and influences its integration with the other FCS components.

II. EXPERIMENTAL

Table I reports the main technical specifications of the 6 kW PEM fuel cell system used for experimental tests.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stack power</td>
<td>6.2 kW</td>
</tr>
<tr>
<td>Cell number</td>
<td>96</td>
</tr>
<tr>
<td>Stack voltage range</td>
<td>53 - 110 V</td>
</tr>
<tr>
<td>Hydrogen pressure</td>
<td>30 – 40 kPa</td>
</tr>
<tr>
<td>Air pressure</td>
<td>&lt; 40 kPa</td>
</tr>
<tr>
<td>External humidification</td>
<td>Absent</td>
</tr>
<tr>
<td>Water cooling</td>
<td>250-350 kPa</td>
</tr>
<tr>
<td></td>
<td>283-348 K</td>
</tr>
<tr>
<td></td>
<td>20 l/min</td>
</tr>
</tbody>
</table>

The system operated at low pressure and was equipped with a fuel recirculation pump that permitted the flow through operation mode in the anode compartment. The lack of an external humidification system limited the current values in the range 20-130 A, in order to avoid drying-out phenomena in the low load region. The FCS was connected to a DC-DC converter, whose output voltage was in the range 200-290 V. The experimental runs were carried out in both steady state and dynamic conditions, by using 22 Pb battery modules (12 V, 40 Ah) and variable resistances as loads.
III. RESULTS AND DISCUSSION

Figures 1-3 evidence the effect of the two fuel feeding operation modes on individual cell voltages in different working conditions. The cell voltages reported in these figures refer to average values calculated on groups of three cells, except the first and last three ones, which were individually acquired. In Figures 2 and 3 the cell voltage instantaneous acquisitions refer to the end of acceleration phases.

**Fig. 1.** Cell voltage acquisition during a test in stationary conditions: 323 K, 3.3 kW, stoichiometric ratio: 1.7

**Fig. 2.** Cell voltage acquisition during an acceleration phase from 1.2 to 3.8 kW in 12 s: 313 K, 3.6 kW, stoichiometric ratio: 1.8

No significant difference was observed for steady state runs (Figure 1) while some behavior differences between the two fuelling procedures could be observed during acceleration phases (Figure 2). In particular, passing from 1.2 to 3.8 kW in 12 s at 313 K slightly higher individual values of cell voltages and more uniform distribution were detected for flow-through mode. The dynamic behavior was also investigated during cold start phases. Figure 3 shows the results of tests carried out accelerating from 1.2 to 3.1 kW in 16 s at 288 K. In these conditions, that are more susceptible to flooding phenomena, the dead-end procedure required a higher hydrogen purge frequency with respect to the flow-through (about 2.5 times higher) and determined a not optimal cell voltage distribution: higher voltage values were detected for the first 20 cells, while a general diminution was observed for the last 40 cells.

**Fig. 3.** Cell voltage acquisition during an acceleration phase from 1.2 to 3.1 kW in 16 s: 288 K, 2.6 kW, stoichiometric ratio: 2.2

On the other hand, the flow-through mode, thanks to hydrogen recirculation, allowed the stack regular working to be obtained with lower purge frequency. This result suggests that, at least in dynamic conditions here investigated, the fuel recirculation favors a higher cell efficiency and voltage uniformity. This last aspect is very critical as far as durability is concerned, as a scarce cell voltage uniformity can accelerate MEA (Membrane Electrode Assembly) degradation phenomena [4,5].

IV. CONCLUSION

The experimental tests carried out on a 6 kW PEM FCS in both steady state and dynamic conditions evidenced the effect of hydrogen feeding sub-system on cell performance. In particular higher cell efficiency and better voltage uniformity can be obtained in transient phases with hydrogen recirculation, especially at operative conditions that favor stack flooding phenomena (low temperatures and high load).

ACKNOWLEDGMENT

The authors gratefully acknowledge Mr A. Rossi for the cooperation in experimental tests.

REFERENCES

PERFORMANCE OF A BIOGAS-POWERED SOFC PILOT PLANT: DESCRIPTION OF THE BIOGAS TREATMENT AND OPTIMISATION OF THE FUEL CELL OPERATIONAL CONDITIONS


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Abstract – This paper investigates the potential of a biogas-powered 2.8 kW_e SOFC pilot plant constructed and operated in Mataró WWTP (NE Spain) for 18 months within the BIOCELL and the MCFC-CONTEX projects. The biogas treatment was based on a biotrickling filter and a polishing stage, with removal efficiencies greater than 99% and achieving contaminant’s concentration below the fuel cell limit. The SOFC unit consisted of an electrochemical train and an after-burner. Therefore the ratio biogas-to-burner/biogas-to-stack must be optimized. Results showed that this value should be between 25% and 50% in order to optimize the overall electrical efficiency, reaching values of 24-33%, which is a very promising and optimistic result for the SOFC technology.

Index Terms – Biogas treatment, electrical and thermal efficiencies, fuel cell, SOFC

I. INTRODUCTION

Fuel cells (FCs) are progressively becoming a real alternative to conventional cogeneration technologies for a wide range of power generation applications. Their implementation in Waste Water Treatment Plants (WWTP) combines a high-efficient technology for electrical generation with the use of a renewable fuel, thus simultaneously addressing two key environmental impacts: climate change and depletion of resources.

II. METHODOLOGY

A biogas-powered SOFC pilot plant was constructed and operated in Mataró WWTP (NE Spain) for 18 months within the BIOCELL and the MCFC-CONTEX projects. The plant treated around 10 Nm³/h (which corresponded to 1 – 5% of the overall WWTP biogas production) and had a nominal power capacity of 2.8 kW_e (electrical) and 1.2 kW_t (thermal).

Raw biogas analyses showed really high concentrations of H₂S (2.000 – 3.600 ppm), siloxanes (4 – 6 mg Si/Nm³) and linear hydrocarbons (6 – 10 mg/Nm³). Therefore, having a reliable and robust biogas treatment is the major issue that needs to be addressed in order to achieve the stringent inlet requirements for these contaminants in fuel cells (H₂S 1 ppm, siloxanes 0.5 mg Si/Nm³ and hydrocarbons 0.1 mg/Nm³).

Moreover, technical (removal efficiency, elimination capacity and availability), economic (investment and operating expenses) and environmental (climate change due to the use of energy) indicators were assessed for different biogas treatment technologies.

A. Biogas treatment

On one hand, a biotrickling filter was the chosen technology for main H₂S removal because of its low operating costs compared to physical – chemical treatments.

On the other hand, a further polishing stage with adsorption technologies based on iron hydroxides + biogas drying + virgin activated carbon in the case of the BIOCELL project (adsorbent materials provided by a Spanish company: Bioconservación) was used to remove the remaining H₂S and other biogas contaminants.

Within the scope of the MCFC-CONTEX project, different adsorbent materials will be tested and their performances will be compared, focusing on optimising the operational conditions and maximising the adsorption capacity.
B. Fuel cell

A small amount of clean biogas (0.9 – 1.2 Nm³/h) fuelled a fully integrated SOFC unit operating at 850 °C, with a nominal power capacity of 2.8 kW, and equipped with flow-meters and temperature, pressure and voltage sensors to monitor and compare simulation performance to experimental performance (at steady-state conditions).

III. RESULTS AND DISCUSSION

A. Biogas treatment

Removal efficiencies greater than 99% were achieved and the contaminants’ concentration after the entire treatment system never exceeded the fuel cell limit. However, the availability of the biotrickling filter was affected by filter clogging, thus decreasing the availability of the entire SOFC line.

Results showed that the complete biogas treatment had an OPEX of 3.5 – 4.5 €/Nm³, slightly higher than those for classical cogeneration technologies (Internal Combustion Engines and Microturbines) but still a very promising result.

Since 75% - 80% of the OPEX is due to the polishing stage, further investigations need to be carried out in order to test more efficient adsorbent materials and achieve a better performance as well as reducing the costs. Within this context, a benchmarking of different adsorbent materials has been carried out for the MCFC-CONTEX project and the most promising will be tested on pilot scale and their results will be compared.

Table 1. Summary table of some of adsorbent materials

<table>
<thead>
<tr>
<th>Commercial name</th>
<th>Material and composition</th>
<th>Removal strategy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norit RGM 3</td>
<td>Impregnated activated carbon, Cu(I) and Cr(VI)</td>
<td>Chemisorption</td>
</tr>
<tr>
<td>Airpel Ultra DS</td>
<td>Doped activated carbon</td>
<td>H₂S Catalytic reaction</td>
</tr>
<tr>
<td>HCA-R</td>
<td>Iron oxide impregnated onto a ceramic base</td>
<td>H₂S Catalytic reaction</td>
</tr>
<tr>
<td>Sulfatreat</td>
<td>Iron oxide (Fe₂O₃)</td>
<td>H₂S Catalytic reaction</td>
</tr>
<tr>
<td>Norit RB 3</td>
<td>Virgin activated carbon</td>
<td>Siloxanes Physisorption</td>
</tr>
<tr>
<td>Airpel 10</td>
<td>Virgin activated carbon</td>
<td>Siloxanes Physisorption</td>
</tr>
<tr>
<td>TSI</td>
<td>Macroporous silica gel</td>
<td>Siloxanes Physisorption</td>
</tr>
</tbody>
</table>

B. Fuel Cell

The SOFC unit consists of an electrochemical train and an after-burner. Therefore, two different biogas flows are considered, namely biogas-to-stack and biogas-to-burner. The later generates no electricity; hence in order to optimise the overall electric efficiency of a SOFC system, it is necessary to optimise the ratio biogas-to-burner/biogas-to-stack.

The results show that the biogas flow ratio needs to be greater than 25% to guarantee energy self-sufficient operation of the system at 850 °C and smaller than 50% to maximise system’s electrical efficiency (at 24 – 33%).

Notwithstanding, thermal efficiencies are very high (in the range of 31.6 – 43.5%), even when the ratio is lower than 25%, indicating that electrical performance could be further optimized if the thermal integration is improved.

IV. CONCLUSIONS

Biogas treatment technologies are fully capable of reducing the concentration of contaminants to the stringent extent of fuel cell’s specifications. However, it is necessary to keep investigating and assessing which ones are able to reach equilibrium between optimising the operational conditions, maximising the adsorption capacity and minimising the costs.

SOFC stack electrical efficiencies of 56.4 % can be obtained if operated at high fuel utilisation and high temperature. The temperature of the stack plays a major role on the efficiency; i.e.: 10% decrease is observed when temperature drops from 850 to 780 °C.

Finally, the global electrical efficiency of the system is 24 – 33%. These values are still lower compared to Internal Combustion Engines or other fuel cell types (i.e.: MCFC), but the possibilities of improvement are significant.

ACKNOWLEDGEMENTS

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NON-NOBLE ELECTROCATALYST SUPPORTED ON CARBON NANO-NETWORKS FOR OXYGEN REDUCTION REACTION

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Abstract – An iron-nitrogen-containing non-noble metal electrocatalyst, supported on interconnected graphitic structures (CNNs), was synthesized using a wet-impregnation method. The CNNs support was produced in-house by Chemical Vapor Deposition (CVD) of ethene over cobalt nanoparticles that were synthesized in dense microemulsions. The electrocatalyst was characterized by TGA, BET, XPS, EDX, and TEM. Additionally, it was tested at the cathode of a polymer electrolyte membrane (PEM) and a direct methanol (DM) fuel cell (FC) in single-cell experiments showing a performance that was comparable to state-of-the-art non-noble electrocatalysts. Additionally, a discrete tolerance to methanol was observed. The relatively simple synthesis procedure and the cheap precursor materials of catalyst support and electrocatalyst make this a promising material for low temperature fuel cell applications.

Index Terms – Electrocataylst - Iron-nitrogen catalyst – Low Temperature Fuel Cells - ORR

I. INTRODUCTION

Low temperature fuel cells, such as Polymer Electrolyte Membrane (PEM) and Direct Methanol (DM) Fuel Cells (FC), are very promising alternatives for portable applications and as alternative to combustion engines for the automotive market because of their higher efficiency and lower CO₂ emission. However, the main issues preventing mass-scale commercialization of such promising devices are their cost and their durability that are not meeting worldwide requirements. These issues are closely related to the FC electrodes and especially their degradation with time and their cost[1]. Within our group, we developed a novel carbon material that consists of networked carbon nanostructures (CNNs) and is currently produced by the TU Delft spin-off company Minus 9[2]. It shows attractive properties for catalysis of fuel cells such as high surface area, high electrical conductivity, great oxidation resistance, surface defects increasing the material ability to disperse in solution and to simplify integration into polymer matrices. The versatility and simplicity of the synthesis route promises a less costly production than carbon nanotubes (CNTs), which have already been proven to be a more robust support than the presently used carbon black.

In previous work, three different types of CNNs were synthesized by varying the quantity of Co from 0.1 to 1.7% in weight, and used as carbon support for non-noble catalyst production. Electrochemical tests showed that the use of Co in the production of highly active CNNs is crucial, since the best performance was achieved with the higher metal content. Non-noble catalyst on CNNs outperformed non-noble catalyst synthesized according to the same procedure on CNTs, both in activity and in oxidation resistance, resulting in a promising cheaper alternative to catalyst for Oxygen Reduction Reaction in Fuel Cells[3]. In this work, iron-nitrogen containing CNNs performance is evaluated by in-situ electrochemical tests both for PEM and DMFC applications.

II. EXPERIMENTAL

A. Catalyst preparation and characterization

CNNs were synthesized by catalytic CVD, as previously described[2]. Briefly, we performed a fixed-bed thermal catalytic CVD at 700 °C of ethene over cobalt nanoparticles prepared in dense microemulsions. Thermo gravimetric analysis, Raman Spectroscopy, BET and Transmission Electron Spectroscopy (TEM) were carried out to characterize the electrocatalyst. Electrocatalysts were synthesized as previously described[3, 4]. CNNs were impregnated using 2,4,6-tripryidyl-s-triazine as nitrogen source and iron acetate as iron source. Active sites were created by performing pyrolysis on the powder, under nitrogen atmosphere at 1000K for 3 hr. Energy
Dispersive X-ray spectroscopy (EDX), X-ray Photoelectron Spectroscopy (XPS) were carried out to further characterize the electrocatalyst.

**B. Single-cell tests**

The electrodes were prepared according to a procedure described in previous work\(^4\). Catalyst loading was 2.6 mg cm\(^{-2}\) for the cathode and 2.6 mg cm\(^{-2}\) of PtRu (1:1 at., Alfa Aesar) for the anode in single cell tests. The membrane electrode assemblies (MEAs) for single cell studies were prepared by hot-bonding the electrodes on either side of a pretreated Nafion\(^\text{®}\) -115 membrane at 125 °C and 50 kg cm\(^{-2}\). Single cell tests were performed in a fuel cell test fixture of 5 cm\(^2\) active area (Hydrogenics Test Systems). For single cell polarization experiments, H\(_2\) or methanol (at 1, 2, or 10M) and O\(_2\) (RH 100%) were fed respectively to the anode and cathode chamber.

**III. RESULTS AND DISCUSSION**

The non-noble electrocatalyst showed a BET surface area of 80 m\(^2\)/g, a high oxidation resistance, a significant amount of defects in the graphitic structure, and 1.7 % Co and 1.2 % Fe in metal weight content and 5.7% nitrogen, consisting in almost equal amounts of pyridinic, pyrrolic and quaternary-graphite like nitrogen. These results have previously been reported\(^3\). Fig. 1 shows a TEM image of the electrocatalyst.

**Fig. 1 TEM image of CNNs**

In the single-cell tests, the best performance, 121 mW cm\(^{-2}\) corresponding to 47 mW mg CAT\(^{-1}\), was achieved with hydrogen feed at 60°C and 200kPa relative pressure, the corresponding polarization and power density curves are shown in Fig. 2 and compared to the same curves measured at 30°C.

**Fig. 2 Polarization and power density curves in H\(_2\) single cell, □ at 30°C, □ at 60 °C, 0.1 NLPM H\(_2\), and 0.2 NLPM O\(_2\).**

Fig. 3 shows the power density curves at 60 °C for different methanol concentrations. Generally, higher methanol concentrations in the feed decrease the performance but here, at higher pressures, an optimum performance was achieved with 2 M concentration. Most likely the faster kinetics and higher methanol cross over with higher concentration have an opposite effect on performance. The best performance, 15 mW cm\(^{-2}\) corresponding to 6 mW mg CAT\(^{-1}\), was achieved at 90 °C, 2 bar, 0.5 NLPM O\(_2\), 2 mL min\(^{-1}\) MeOH at 2 M.

**Fig. 3 Power density curves at different methanol concentrations as anode feed, 100 ml min\(^{-1}\) O\(_2\) and 60°C.**

**IV. CONCLUSION**

A non-noble electrocatalyst was synthetized using networked graphitic structures as support and tested in both PEMFC and DMFC. The results are comparable to those recently reported for similar systems\(^4\) but at least one order of magnitude lower than state-of-the-art Pt-based electrocatalysts. The simplicity of the synthesis procedure and the low material cost make the present systems an interesting alternative.

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INTEGRATED GAS DIFFUSION AND CATALYST LAYER FOR DIRECT METHANOL FUEL CELLS: ELECTRODEPOSITED BIMETALLIC PtAu NANOCATALYSTS ON CARBON NANOFIBERS

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Abstract - Innovative electrodes have been developed by growing platelet carbon nanofibers directly on graphite paper, and placing bimetallic nanoparticles of platinum and gold on them by electrodeposition. In this way the electrodes consist of a single layer providing both diffusive and catalytic function. Platelet carbon nanofibers were grown on graphite paper by plasma enhanced chemical vapor deposition, using methane and hydrogen as precursors. The electrodeposition was carried out by using a galvanostatic polarization, using precursor salts of platinum and gold. The electrodes were characterized by scanning electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, energy dispersive X-ray analysis and cyclic voltammetry. PtAu/pCNF electrodes show higher electrocatalytic activity for the methanol oxidation reaction than a commercial carbon substrate electrode with electrodeposited Pt nanoparticles.

Index Terms - Carbon nanofibers, catalyst electrodeposition, plasma enhanced chemical vapor deposition, methanol oxidation reaction.

I. INTRODUCTION

Competitive industrial application and wide commercialization of Direct Methanol Fuel Cells (DMFC) is still restricted by the easy poisoning of the platinum anode electrocatalyst by CO-like reaction intermediates and high Pt load in order to obtain reasonable performances. The combination of unconventional methods to deposit the catalyst nanoparticles only on the uppermost surface of the electrode with unconventional carbon supports seems to be very promising [1].

Carbon nanofibers (CNF) have been proved to be a promising substrate for electrocatalyst, especially the platelet morphology (pCNF) [2]. This CNF type has the graphene layers oriented perpendicularly to the fiber axis and, as a consequence, is characterized by high surface area and a great number of plane edges with high energy. Such a structure allows a good dispersion of catalyst nanoparticles, which are strongly anchored to the substrate with negligible coalescence, with a gain in the catalyst utilization and electrocatalytic activity with respect to the commercial electrodes. Our previous papers [3,6] show that electrodes made of platelet carbon nanofibers, directly grown on graphite paper by plasma enhanced chemical vapor deposition (PECVD), as substrate for electrodeposited platinum nanoparticles exhibited good and encouraging results in terms of electrochemical performance and stability.

In order to reduce the platinum load and enhance the poisoning tolerance, instead of the expensive PtRu catalyst it is possible to use a PtAu catalyst [4,5].

II. EXPERIMENTAL

The pCNF were grown on graphite paper, catalysed by electrodeposited nickel clusters. A “home built” original PECVD reactor was used. The gaseous precursors were CH₄ and H₂ in the fixed flow ratio 7:1.

A galvanostatic electrodeposition (GED), at applied charge 300–750 mC for an electrolysis time of 150 s, was carried out in the following electrolytes (in H₂SO₄ 1 M): H₂PtCl₆ 2.5mM+AuCl₃ 2.5mM (2.5Pt1.5Au) and H₂PtCl₆ 4mM+AuCl₃.
The working electrode was a graphite paper disk covered by pCNF and the reference electrode was a saturated calomel Hg/Hg₂Cl₂ electrode (SCE).

The electrodes morphological analysis was performed by field emission gun scanning electron microscopy (FEG-SEM; LEO mod.1530). The catalyst deposit structure was analyzed by X-ray diffraction (XRD). The catalyst nanoparticles stoichiometry was calculated by X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray (EDX) analysis.

The electrocatalytic performance and the stability were studied using cyclic voltammetry (CV) in H₂SO₄ 1M and CH₃OH 0.5M+H₂SO₄ 1M.

The platinum and gold loads were determined by a spectrophotometric method, after metal dissolution in boiling HNO₃/HCl (1:3 v/v). The sample absorption spectra were recorded between 380 and 700 nm and a mathematical method was implemented to determine the metals amount.

III. RESULTS AND DISCUSSION

PECVD allowed to obtain CNF with high density, narrow transversal cross section distribution (average of about 100 nm) and good quality, i.e. high purity walls and controlled morphology (Fig.1 left panel).

The co-electrodeposition of platinum and gold, depending on the electrolyte solution composition and electrodeposition charge, gives raise to Pt/Au ratio between 0.7 and 2, measured by EDX and XPS, and different deposit morphologies from very faceted to more globular nanoparticles, but always with a great nanostructured surface, that increases the metals exposed surface. The deposit is distributed uniformly on the electrode surface, but the nanoparticles have not been deposited even in the nanofibers mat porosity under all tested conditions (Fig.1 right panel).

The electrochemical real surface (ERS) increases with the Pt/Au ratio because gold is not catalytically active towards the hydrogen adsorption/desorption reaction. The most promising electrode is that with low Pt/Au ratio obtained from 4Pt1Au solution that exhibits high ERS with. Its Lₚt is only 11 μg cm⁻², with consequent about 50 m² g⁻¹ of electrochemical active surface (EAS). Moreover, after CV it shows a considerable Au surface enrichment, measured by XPS, enhancing the catalyst long term stability. As a matter of fact the mass specific activity (MSA) of this electrode, even if lower than that of an electrode catalyzed by only Pt, is up to three times higher than that of a commercial carbon black electrode (Fig.2).

![Fig.1 - SEM micrograph of pCNF (left) and PtAu/pCNF (right).](image)

XRD spectra clearly show the specific peaks of the two metals, demonstrating that the obtained deposit is not an alloy but is constituted by bimetallic nanoparticles.

The electrochemical real surface (ERS) increases with the Pt/Au ratio because gold is not catalytically active towards the hydrogen adsorption/desorption reaction. The most promising electrode is that with low Pt/Au ratio obtained from 4Pt1Au solution that exhibits high ERS with. Its Lₚt is only 11 μg cm⁻², with consequent about 50 m² g⁻¹ of electrochemical active surface (EAS). Moreover, after CV it shows a considerable Au surface enrichment, measured by XPS, enhancing the catalyst long term stability. As a matter of fact the mass specific activity (MSA) of this electrode, even if lower than that of an electrode catalyzed by only Pt, is up to three times higher than that of a commercial carbon black electrode (Fig.2).

IV. CONCLUSIONS

PtAu bimetallic nanoparticles were deposited on platelet carbon nanofibers by electrodeposition, which localizes the catalyst nanoparticles only on the exposed surface of the electrode with great catalyst load reduction. The electrocatalytic properties for the methanol oxidation of PtAu/pCNF with different Pt/Au atomic ratio have been investigated and the results showed better performance with respect to an electrode made of a commercial nanometer carbon based substrate (Vulcan XC-72R). The particular morphology of platelet CNF determines a strong anchorage of catalyst nanoparticles to the substrate with reduced coalescence phenomena. Finally, bimetallic catalysts led to an increase in Pt tolerance to poisoning with a gain in terms of long-term stability.

The results highlights a large increase of the mass specific activity, up to three times for the innovative PtAu/pCNF composite electrode, together with a considerable decrease in the catalyst load (about seven times for the same electrode) respect to state of the art Pt (Pt/C electrode), with a great advantage in terms of cost and performance.

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STACK SHUNT PROTOCOL: A SIMPLE AND COST-EFFECTIVE METHOD FOR MITIGATING CATALYST SUPPORT CARBON CORROSION IN PEM FUEL CELL STACKS

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Abstract – A stack shunt able to prevent high cathode potential peaks was evaluated as a way to minimize catalyst carbon support corrosion and its effects on performance and lifetime of PEM fuel cell stacks. During separate stack tests, one with the shunt design and another without, a 24-cell stack was subjected to continuous starts and stops for several months and its performance constantly monitored for voltage decline. With the shunt, there was a 37% reduction in the degradation rate for each startup/shutdown cycle, and a two-fold increase in the number of startup/shutdown cycles before an individual cell reached the specified “End of Life” voltage criteria. Post-analysis revealed cathode catalyst layer thinning was more severe in the unprotected stack. The proposed shunt protocol is very cost-effective and does not require any substantial changes in the system, and is recommended as viable method to decrease the catalyst support carbon corrosion rate.

Index Terms– PEM fuel cell, voltage degradation, start-stop cycles, stack shunt.

I. NOMENCLATURE

FE-SEM – Field Effect Scanning Electron Microscope
MEA – Membrane Electrode Assembly
PEM – Proton Exchange Membrane

II. INTRODUCTION

Automotive and backup applications share a similar operation mode: both will experience many starts and stops during the fuel cell stack’s lifetime. As a result, one degradation mechanism becomes predominant: carbon corrosion, which can lead to a severe loss of catalyst surface area. If no mitigation strategy is applied, the active area loss could be sudden and rapid. Under certain operating conditions, only a few hundred startup/shutdown cycles will be achieved before a dramatic decline in performance occurs, as signified in a characteristic I-V curve. Consequently, many backup power systems are guaranteed for as few as 500 startup/shutdown cycles.

Industrial targets typically specify “End of Life” after a 10% loss in the efficiency of the fuel cell system, and a degradation rate lower than 10 μVh⁻¹[1]. However, several manufacturers report that in order to satisfy durability needs, a decay rate of 1 μV/cycle must be achieved [2]. Resolving carbon corrosion is more critical with respect to other stack issues in order to reach the durability requirements essential for large-scale commercialization, especially in automotive and stationary backup applications.

III. DISCUSSION

The shunt experiment used a 24-cell PEM fuel cell stack designed and assembled by Electro Power Systems SpA. The bipolar plates were made of pure graphite. The reactant flow fields were multi-serpentine design, with a cooling flow field between every cell. The MEA’s were made with carbon paper gas diffusion media, chemically stabilized and mechanically reinforced perfluorosulfonic ionomer membrane, catalyst active area of 200 cm², and Pt/C-based catalyst layers with anode Pt loading of 0.2 mg/cm² and cathode Pt loading of 0.6 mg/cm².

Proprietary management software controlled all phases of the stack’s operation. The software regulated the voltage ramp rate such that the stack gradually reached the current operating point. This avoided rapid potential changes that are well known to accelerate the Pt dissolution rate [3].

A 5-ohm shunt completely discharged the 24-cell stack in about 30–40 s. Figure 1 shows the complete scheme of the system. The shunt protocol includes a relay switch that connects the load during operating mode, and switches to the shunt once the shutdown phase begins.
designed using a DC-DC converter as a "dynamic load" for the stack during shutdowns. This device controls the output voltage of the DC-DC converter during shutdown by transferring a limited amount of electrical energy from the stack to the output, simulating the operation of the shunt resistor. The output voltage is stabilized by connecting a capacitive load to the power system.

Figure 1.

The stack shunt protocol requires three important features to be applied during the shutdown in order to be effective:

**Anode gas recirculation:** This prevents a localized fuel starvation during hydrogen consumption while the shunt is connected to the stack during the shutdown phase [4,5].

**Air flow at the cathode:** Together with the anode recirculation, it ensures equal reactant gas distribution within the entire stack and limits any voltage differences between cells. Otherwise, the gas composition may not be homogeneous in every cell, and the cell voltage can be different from cell to cell when using a unique stack shunt.

**Venting procedure:** This prevents excessive pressure drop in the anode compartment, which can quickly fall below 0.05 MPa (absolute) in seconds. A high-pressure difference between anode and cathode (which is open to ambient air) can damage the membrane, which typically is no more than 25-30 µm thick.

When these three items are combined with the shunt, the high cathode potential excursions due to the co-presence of hydrogen and air in the anode compartment can be avoided, or at least mitigated. The gas recirculation avoids fuel starvation in the outlet area of each cell, which is unavoidable in a dead-end mode [4,5]. In the meantime, the fuel is consumed by the hydrogen oxidation reaction; and when the hydrogen is totally consumed, the cell voltage will drop off.

During the shutdown phase, the stack shunt remains connected until the next startup in order to avoid any possible voltage generation due to residual un-reacted hydrogen. However, the anode gas recirculation system is stopped once the voltage drops to zero volts.

Results obtained with the stack shunt protocol show a decrease in the voltage degradation rate by 37% per startup-shutdown cycle, as compared to unprotected startups and shutdowns. This improvement allowed double the number of cycles before the stack reached a pre-defined "End of Life" operating voltage.

Results obtained with the stack shunt protocol show a decrease in the voltage degradation rate by 37% per startup-shutdown cycle, as compared to unprotected startups and shutdowns. This improvement allowed double the number of cycles before the stack reached a pre-defined "End of Life" operating voltage.

**IV. "ELECTRONIC" STACK SHUNT**

As a further improvement to the dedicated shunt resistor used in the 24-cell stack test, a new device was designed using a DC-DC converter as a "dynamic load" for the stack during shutdowns. The device controls the output voltage of the DC-DC converter during shutdown by transferring a limited amount of electrical energy from the stack to the output, simulating the operation of the shunt resistor. The output voltage is stabilized by connecting a capacitive load to the power system.

This design has several interesting features: (a) the resistor can be eliminated from the balance of plant; (b) the input impedance of the DC-DC converter can be set by modifying the switch’s duty-cycle, allowing precise control of the current during the entire shutdown phase; (c) the current sink is independent from the actual voltage of the fuel cell stack; and (d) the current sink can be lowered in case of high voltage differences between individual cells, which can happen during cell flooding.

**V. CONCLUSION**

The main effect of carbon corrosion observed during the unprotected startups/shutdowns was a reduction of the fuel cell’s voltage output (50 mV at 0.9 A/cm²), attributed to increased wettability/flooding, and leading to high mass transport losses at high current density. See Figure 2.

Incorporation of a stack shunt provided a definite improvement in the MEA’s durability and stack lifetime by mitigating carbon corrosion during startup and shutdown. Since this method does not require a complex or expensive modification in system hardware, it is suitable for commercial fuel cell systems. The stack shunt feature would be particularly useful for automotive and back-up applications, where the number of startup/shutdown cycles is considerably high.

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Abstract - The use of a metallic rather than a ceramic interconnector has become a popular choice in the SOFC technology because of key advantages in terms of electronic and heat conductivity, as well as workability characteristics. However, corrosion problems still remain to be solved with metallic interconnectors, particularly in high temperature applications (HT-SOFC, 800°C and above). High Cr ferritic stainless steels with suitable ceramic protective layers are therefore widely used for their good property balance, including corrosion resistance in HT-SOFC systems. However, recent trends in reducing operational temperatures below 800°C could make it attractive using more cost effective alternatives such as low Cr grades of ferritic stainless steel. Here, we report preliminary results on the long-term corrosion behaviour of a commercial ferritic stainless steel containing 13Cr % (SS405), at 700°C under simulated cathode conditions.

Index Terms – SOFC, Interconnectors, 13Cr stainless steel, Corrosion.

I. INTRODUCTION

Energy technology drives the sustainable development toward the green economy, including energy security, environmental protection, economic growth and social welfare. Fuel cells play a key role in energy sector because they are the most promising future energy conversion systems with high energy efficiency and low environmental impacts. Depending on the type of fuel cells, they can be used in stationary, portable and transport applications. Solid oxide fuel cells (SOFCs) have been getting attention in recent years for efficient, clean and silent distributed power generation. Currently, the primary goal is the reduction of the capital cost of the SOFC systems to effectively compete with traditional power generation technologies.

SOFCs is made of an nickel-based anode, an oxide-based electrolyte typically yttria-stabilized zirconia (YSZ), and a perovskite-based cathode typically LaMnO₃ doped with strontium. The relatively low oxide ion conductivity of the electrolyte dictates the high operating temperature of the fuel cell, around 1000 °C. The high operating temperatures causes problems in the cost-effective SOFC because of the expensive materials able to resist under such temperatures for the whole system life.

Commonly, unit cells are combined in a modular fashion into a stack to achieve the voltage and power output level required for the application. Interconnector are required for electrical connection between two adjacent cells, physical barrier between the anodic and cathodic inlet gases and structural support for the cells. The output performance of the SOFC stack is determined by the resistance of the interconnectors. For stable high temperature operations, interconnectors are made from conductive ceramic materials such as perovskite oxides, that are chemically and structurally stable at 1000°C and above. However, due to recent technology developments, the average operating temperature has been lowered at 800°C with trends to further progressive reductions towards the 500°C limit using more conductive electrolyte such as gadolinium doped ceria (GDC). Under these milder temperature conditions, it is possible to use metallic alloys as interconnectors, such as ferritic stainless steels.

The use of a metallic interconnector rather than ceramic materials has the advantage of a higher electronic conductivity, higher ductility and higher heat conductivity. However, some problems still remain to be solved with the metallic interconnectors. The most important problem is the evaporation of Cr-containing volatile species, that migrate from the chromia passive layer formed on the surface of ferritic stainless steels to the cathode/electrolyte interface forming poor-conductive phases at the triple-phase boundaries and affecting the cell performance.

For SOFC systems operating at intermediate temperatures (IT-SOFC, 600-800°C), the problem can be solved by using ferritic stainless steels with lower Cr content to minimize chromia evaporation and, at the same time, by coating with protective spinel and perovskite oxide layers, that improve the surface electrical properties and further prevents the chromia...
evaporation by entrapping Cr as well. In this context, the aim of this work is to study, under typical cathode IT-SOFC conditions, the long-term degradation of a commercial 13 Cr ferritic stainless steel (SS405) at 700°C.

II. EXPERIMENTAL

A commercial 13 Cr ferritic stainless steel (SS405) plate (1 mm thickness) was treated at 700°C in ambient air. The weight changes due to the oxidation processes were checked up to 5000 hours. The sample was analyzed by SEM-EDX and XRD in order to identify corrosion mechanisms and products. The XRD analysis was performed by means of Rigaku Miniflex diffractometer with Cu-Kα radiation (tube output voltage 30kV and tube output current 15mA) and scanning range from $2\theta = 3°$ to $2\theta = 90°$ (step 0.02° and rate 2°/min). Raw data were submitted on three processes: smoothing process by Savitzky method; background elimination process by Sonnevelt method; Kα2 elimination process.

III. RESULTS AND DISCUSSION

In general, high temperature alloys for SOFC interconnectors, such as ferritic stainless steels, owe their oxidation resistance to the formation of protective scales by the oxidation of the chromium component to Cr2O3. However, a critical minimum Cr content is needed to guarantee the formation of a protective, continuous Cr2O3 scale. Indeed, the comparison between the 13Cr and a typical benchmark 18Cr ferritic steel (SS430), fig.1, demonstrates that SS405 does not produce a diffusion protective oxide scale, even though it undergoes to a slowly growing corrosion process [1]. Indeed, SEM analysis indicated that weight gain should be mainly due to internal oxidation attack effects rather than to scale thickening.

Fig. 1. Weight changes of 13Cr and 18Cr ferritic steels in ambient air, at 700°C and 800°C, respectively.

XRD analysis, fig.2, shows the signs of oxide scale structural and phase evolution over time. At beginning, a spinel oxide phase is the main constituent of the oxide scale being minor amounts of Cr2O3 visible only after 3200 hour. This may be expected because, in alloy with 13 Cr content the formation of the external scale of FeCr2O4 is kinetically favored, while the internal scale of Cr2O3 is thermodynamically favored.

Fig. 2. XRD Analysis of SS405 oxidized at 700°C in ambient air at different exposure time. The circles indicate the 13Cr ferritic steel, the triangles the spinel phase and the squares the chromia phase.

SEM analysis confirmed the time-evolving nature of the external oxide scale showing that the apparently stable dual-layer spinel structure observed after a few thousand hour exposure essentially consists of inner FeCr2O4 spinel layer and a (Mn,Cr)-rich outer spinel layer. More detailed results will be presented and illustrated at the time of the Conference.

IV. CONCLUSION

The long-term corrosion behavior at 700°C in ambient air indicate that a 1 mm-thick SS405 stainless steel plate is not a suitable SOFC interconnector material mainly because of a internal oxidation attack effects that could affect significantly the cell performance.

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COMPUTATIONAL ANALYSES OF SOLID OXIDE FUEL CELL

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Abstract - Mathematical models are important tools for studying complex systems such as fuel cell devices. The aim of this work is to develop electrochemical model for intermediate temperature solid oxide fuel cells (IT-SOFCs) in order to investigate the whole fuel cell processes and the operating condition effects. In this way it is possible to select the optimal conditions leading to the highest cell performances. The investigation is focussed on the main factors affecting the cell performances, such as working temperature, the component thickness and the porosity. In addition, the exergetic analyses provide the contribution of every overpotential on cell voltage degradation.

Index Terms – SOFC, modeling, exergy.

I. NOMENCLATURE

Dp, pore diameter (3µm); Ds, grain size (1.5µm); Di, diffusion coefficient of the species i (i=H2,H2O,O2); Ecell, open circuit voltage (V); Ea,i, activation energy for the electrode i (Ea,a=129400Jmol^{-1}, Ea,c=130900Jmol^{-1} [1]); F, Faraday constant (96487Cmol^{-1}); j_{exi}, exchange current density the electrode i (i=a,c); j_{ion}d, ionic current density (A/m^2); j, current density in external circuit (A/m^2); K, coefficient for exchange current density for the electrode i (K_o=3.2 10^{13}Am^{-2}, K_c=7 10^{11}Am^{-2} [1]); n, mole of electrons transferred per mole of reactant (mol); p_i, total pressure (bar); p_{i,part}, partial pressure of the species i (i=H_2, H_2O, O_2) in the bulk fuel steam (bar); p_{i,surf}, partial pressure of the species i (i=H_2, H_2O, O_2) at the electrode surface (bar); P_{o}, oxygen partial pressure at which ionic and electronic conductivity of GDC electrolyte are equal (bar); R, gas constant (8.314472 JK^{-1}mol^{-1}); T, temperature (K); Vcell, cell voltage (V); V_{cath}, cathode potential (V); x, ratio of length of grain contact neck to grain size (x=0.7[2]); z_i, thickness (m) for the component i (i=a,c,e); βd, transfer coefficient (β=0.5 [3]); ΔGo, standard Geeb’s Free Energy (Jmol^{-1}); ε, porosity (%); ηΩ, ohmic polarization (V) for the component i (i=a,c,e); ηi, concentration polarization (V) for the cell electrode i (i=a,c); ηa, activation polarization (V) for the electrode i (i=a,c); ρ, resistivity (Ω m) for the component i (i=a,c,e); σ, ionic conductivity of the electrolyte (a=anode; c=cathode; e=electrolyte).

II. INTRODUCTION

For IT-SOFC the electrolyte is usually gadolinium doped ceria (GDC), in which the replacement of Ce^{4+} of CeO_2 with Gd^{3+} produce oxygen vacancy promoting the ion conductivity at low temperature. The anode is made of Ni-GDC cermet and the cathode is LaFeO_3 doped with Sr and Co. Typically, IT-SOFC operates at 500-800 °C where the ceramic electrolyte becomes highly conductive to oxygen ions even if GDC is partially conductive to electrons due to the reduction of Ce^{4+} to Ce^{3+} in the anode side. The aim of this work is to develop an electrochemical model for IT-SOFC with a zero-dimensional approach in order to optimize the designs of the fuel cell device and select optimal operation conditions with the highest cell performances. In addition, the exergetic analyses provide the contribution of every overpotential on cell voltage degradation.

III. MATHEMATICAL MODEL

The open-circuit voltage of a fuel cell is calculated using the Nernst equation, eq.1, the Gibbs Free Energy in the JANAF Thermochemical tables and the partial pressure at the reaction zone (tripl-phase-boundary), that are calculated by equations obtained from Fick’s law, eq.2-4:

\[ E_{cell} = -\frac{ΔG^0}{2F} - \frac{RT}{2F} \ln \left( \frac{p_{H_2,O}}{p_{H_2} p_{O_2}} \right) \] (1)

\[ p_{H_2} = p_t \left( \frac{p_{H_2,O}}{p_t} - \frac{j_{ion}RT_{H_2}}{2F p_t e^{1.5D_{H_2}}} \right) \] (2)

\[ p_{H_2,O} = p_t \left( \frac{p_{H_2,O}}{p_t} - \frac{j_{ion}RT_{H_2}}{2F p_t e^{1.5D_{H_2}}} \right) \] (3)

\[ p_{O_2} = p_t \left[ 1 + \frac{p_{O_2}}{p_t} - 1 \right] e^{j_{ion}RT_{O_2}} \] (4)

Under electrical load, the cell voltage is depleted because of the overpotentials, eq.5. The ohmic overpotential, eq.6, is related to opposition of the cell components to the electric current flow.

\[ E_{cell} = \eta_{i} + \eta_{i}c + \eta_{i}e \] (5)

The concentration overpotential, eq.7 and 8, is related to the
mass transport difficulties of the gas species to reach the anode and cathode surfaces.

\[ \eta_{c,a} = \frac{RT}{2FE} \ln \left( \frac{P_{H_2}P_{O_2}^n}{P_{H_2}P_{O_2}} \right) \]  
\[ \eta_{c,c} = \frac{RT}{4F} \ln \left( \frac{D_{O_2}}{D_{O_2}} \right) \]  

(7)  
(8)

The activation overpotential, eq. 9, is related to the kinetic problems of the anodic and cathodic reactions. The exchange current density, eq. 10 and 11, depends heavily on both the operating conditions and the electrode microstructure properties, affecting the triple phase boundary [2,4].

\[ j_{ion,a} = j_{a,a} \left[ \frac{e^{\frac{-F\eta_{a,a}}{RT}}}{1 - e^{\frac{-F\eta_{a,a}}{RT}}} \right] \]  
\[ j_{o,a} = k_{a} \frac{72x\eta_{a,a}}{D_{p}^2(1 - \sqrt{1 - x^2})} \]  
\[ j_{o,c} = k_{c} \frac{72x\eta_{o,c}}{D_{p}^2(1 - \sqrt{1 - x^2})} \]  

(9)  
(10)  
(11)

In all equations it is taken in account the effects of the mixed ionic/electronic conductivity of GDC by calculating the ionic current density from the applied current density and the electronic leakage current density, eq.12 [1].

\[ j_{ion} = \frac{-Fj_{ion}}{RT \sigma_{ion,a}} e^{\frac{-R}{1 - e^{\frac{-F\eta_{a,a}}{RT}}} (e^{\frac{-F\eta_{a,a}}{RT}} - 1)} \]  

(12)

IV. RESULTS AND DISCUSSION

In order to assure the mechanical resistance, the whole thickness of the cell has to be around 1mm. The cell configuration changes with the components relative size to anode-supported cell, cathode-supported cell and electrolyte-supported cell. Figure 1 shows the obtained ternary diagram with anode, cathode and electrolyte thickness ranging from 0.1µm, the minimal size required to form a continuous film, to 1000µm. The electrolyte-supported IT-SOFC shows the worst performance for the high exergetic loss due to the ohmic overpotential. Between the anode and the cathode supported cell, the former shows the best performances because of the lower exergetic loss due to the concentration overpotential. The grey zone in Fig.1 contains the optimum cell configurations. The anode supported IT-SOFC shows the best performance from 800K to 1200K because the electrolyte has not enough ion conductivity at lower temperature and has significant electronic conductivity at higher temperature. For having suitable power density, the current density has to be higher than 300mA/cm². While, for having suitable efficiency the current density has to be lower than 800mA/cm². Fig.2 shows the optimum operating condition within the grey zone.

V. CONCLUSION

The anode supported IT-SOFC shows the best cell performance because of the low exergetic losses. The mild operating conditions, such as 800K and 300mA/cm², not only assure high efficiency and high power density, but also promote the cell endurance against thermal stress and corrosion issues.

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COMPARATIVE ASSESSMENT OF INTEGRATED SYSTEMS FOR BIOENERGY PRODUCTION BY FUEL CELL DEVICES: ENVIRONMENTAL ASPECTS

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Abstract - An environmental impact assessment is reported for the integrated systems for bioenergy production by fuel cell devices. A study of life-cycle assessment (LCA) has been carried out to compare the environmental impact of two different integrated systems of fuel cell. The systems have the same fuel processor plant (an anaerobic digester) and the same clean-up unit for hydrogen sulfide removing (based on conventional porous carbon materials) but have different energy conversion device, which is an high temperature solid oxide fuel cell (HT-SOFC) and an intermediate temperature solid oxide fuel cell (IT-SOFC) respectively.

Index Terms – bioenergy, biogas, SOFC, LCA.

I. INTRODUCTION

Public concern about energy security, global warming and economic recession derive the global governance towards political actions that support the scientific research focused on energy technology development in order to promote the green economy. Currently, the aim of the worldwide research is related to the development of high efficient energy conversion systems exploiting the removable energy sources. In this context, high temperature fuel cell technology plays a key role for developing an integrated system, that is able to convert directly into electricity and cogenerated heat the chemical energy stored in biomass materials. The integrated system includes three main components: the plant for the production of biomass derived gases, such as an anaerobic digester and gasifier; the unit for the biofuel clean-up; the device for the energy conversion, such as a solid oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC). Even though the utilization phase of that integrated systems is environmental sustainable because of the renewable energy source utilization, the high energy conversion efficiency, and the negligible production of noise and air pollution, the manufacture phase can lead to significant environmental impacts due to the need of exotic materials and sophisticated components. The environmental impacts assessment is performed by the LCA analysis, which studies the environmental aspects and potential environmental impacts throughout a product’s life from raw material acquisition through production, use and disposal. The goal of LCA study is to identify the best environmental profile between two fuel cells, to give useful information for decision maker as preliminary fundamental step for the future fuel cell regulation basing not only on the technical performance but also on the potential environmental impacts. LCA procedure is described in ISO 14040 series and ILCD Handbook and for fuel cell also in the Guidance document for performing LCA on fuel cells [1-3]. LCA methodology is iterative and consists of four steps: the goal and scope definition, in which the system boundary, the aim of the study and the methods of analysis are defined; the inventory, in which the input resources and the output emissions are estimated over all life stages of the product (the raw materials extraction, the product manufacturing processes, the transportation, the distribution, the use and the waste management phases); the impact assessment, in which specific life cycle impact assessment methods are applied in order to evaluate the magnitude of the potential damage of the product
on environment and human health; the interpretation that could be include final consideration and reporting, sensitivity analysis, uncertainties evaluations.

II. RESULT AND DISCUSSION
The objective of this study is to compare the environmental impact of two different integrated systems having the same fuel processor plant, which is an anaerobic digester, and the same clean-up unit for hydrogen sulfide removing, which is based on conventional porous carbon materials, but having different energy conversion device, which is an high temperature solid oxide fuel cell (HT-SOFC) and an intermediate temperature solid oxide fuel cell (IT-SOFC) respectively, fig.1. The components of HT-SOFC working at 1000°C include the anode of Ni-YSZ cermet, the cathode of LaMnO3 doped with Sr, and the electrolyte of yttria-stabilized zirconia (YSZ) [4]. The components of IT-SOFC working at 700°C include the anode of Ni-GDC cermet, the cathode of LaFeO3 doped with Sr and Co, and the electrolyte of gadolinium doped ceria (GDC) [5]. Concerning the LCA comparative study, preliminary analysis is gate to gate and the functional unit is 1kW, the power of the fuel cell system. Data concerning IT-SOFC are obtained from laboratory tests, simulation and estimation, data for HT-SOFC are derived from industrial process found in literature. This difference in data scaling influence the results; indeed the optimization of industrial process shows better value of energy and material consumption than IT-SOFC. The methods selected for the environmental evaluation is IMPACT 2002+, that allows the grouping of all the potential environmental impacts (Midpoint categories) into four damage impacts categories. The damage categories are: human health, taking into account respiratory and carcinogenic effects, ozone layer depletion greenhouse gas and ionizing radiation impacts (expressed in DALY, Disability Adjusted Life Years); ecosystem quality, related to ecotoxicity, acidification, eutrophication and land use impacts (expressed in PAF, Potentially Affected Fraction); climate change, related to the total gaseous emissions with global warming potentials (expressed in kg of CO2);resources, related to the total non-renewable energy consumption for mineral extractions (expressed in MJ). The IT-SOFC shows the highest damage related to human health and ecosystem quality categories (fig.2) due to the highest amount of nickel as electrocatalyst (fig.3). Vice versa the IT-SOFC shows the lowest damage related to climate change and resources categories (fig.2).

III. CONCLUSION
Technological advantage of SOFC that works at low temperature is related to the utilization of metal interconnectors instead of ceramic one, the higher thermodynamic conversion efficiency, the easier technique for sealing and the heat management with lower radiation heat loss. In addition, the preliminary LCA study shows that the integrated system with IT-SOFC has lower damage related to the climate change and the utilisations of non-renewable energy resources over all life stages. However, challenges on IT-SOFC components arise from its significant negative effects on human health and ecosystem quality.

REFERENCES
Abstract – Lignite and char derived from lignite were tested as fuels for direct carbon solid oxide fuel cells (DC-SOFC). Experiments were performed with a pulverized solid fuel directly fed to DC-SOFC anode compartment. The maximum power density of 143 mW/cm² was achieved with a char derived from lignite, much higher than 93 mW/cm² obtained with a pulverized, raw lignite fuel. Pre-processing of as received lignite, to form a char, increases power density generated in DC-SOFC. Reloading of DC-SOFC anode compartments with fresh fuel leads to a similar cell performance. Additional series of experiments were performed with CO/CO₂ gas mixtures, supplied as a fuel to solid oxide fuel cell (SOFC). The SOFC cell operated with 92% CO-8% CO₂ gas mixture generated power density of 342 mW/cm².

Index Terms – direct carbon fuel cell, solid oxide fuel cell, lignite, electric power generation

I. INTRODUCTION

Direct carbon fuel cells [1] based on solid oxide fuel cell technology (DC-SOFC) are promising electrochemical devices enabling high efficiency electric power generation using pulverized coal, biomass, and other solid fuels with high content of elemental carbon [2, 3]. Lignite, also known as brown coal, is commonly used for stationary electric power generation. There are several approaches to implement high efficiency electric current generation with lignite as a fuel:
(a) lignite received from a coal mine, dried and milled, can be directly fed to anode compartment of the DC-SOFC,
(b) lignite derived char can also be directly fed to anode compartment of DC-SOFC cell as a pulverized solid,
(c) fuel mixture of CO and CO₂, derived from lignite or lignite char in a dry gasification process can be used, as a gas fuel, in a SOFC cell.

Directly fed to DC-SOFC anode compartment as lignite or lignite char, carbon reacts with oxide ions at the anode surface while CO₂, formed as a product of reactions (1) or (4), reacts with a carbon in a Boudouard reaction (3):

\[
\begin{align*}
\text{anode:} & \quad C + 2O^2- \rightarrow CO_2 + 4e^- \quad (1) \\
\text{anode:} & \quad C + O^2- \rightarrow CO + 2e^- \quad (2) \\
\text{bulk:} & \quad CO_2 + C \rightarrow 2 CO \quad (3) \\
\text{anode:} & \quad CO + O^2- \rightarrow CO_2 + 2e^- \quad (4)
\end{align*}
\]

II. EXPERIMENTAL

All three alternative fuels: lignite, char derived from lignite and simulated CO+CO₂ gas mixtures, have been tested as fuels for DC-SOFC cells and SOFC cells. The results have been compared with performance of SOFC cell fuelled with a reference hydrogen fuel (97%H₂+3%H₂O).

A. Fuel Preparation

The lignite sample, received from the Belchatow (Poland) coal mine was dried at 378 K for 2 hours and milled for 40 min. Part of the sample was used as a fuel in a DC-SOFC experiment (“lignite”). Lignite, also known as brown coal, is commonly used for stationary electric power generation. There are several approaches to implement high efficiency electric current generation with lignite as a fuel:
(a) lignite received from a coal mine, dried and milled, can be directly fed to anode compartment of the DC-SOFC,
(b) lignite derived char can also be directly fed to anode compartment of DC-SOFC cell as a pulverized solid,
(c) fuel mixture of CO and CO₂, derived from lignite or lignite char in a dry gasification process can be used, as a gas fuel, in a SOFC cell.

The resulting char was used as a solid pulverized fuel in a consecutive DC-SOFC experiment (“lignite char”). Both lignite and lignite char samples were analyzed (SEM, EDS, BET, LHV, proximate and ultimate analysis). The low heating value (LHV) of 18478 kJ/kg and 21621 kJ/kg was measured for lignite and lignite char, respectively.

In order to simulate gaseous fuels (CO+CO₂) derived from a dry gasification of lignite or lignite char with CO₂, mixtures of CO and CO₂ were supplied to SOFC cell.
B. Experimental Setup

All tests have been performed with electrolyte supported planar SOFC cell (Ni-YSZ|Ni-GDC|YSZ|LSM-GDC|LSM, electrolyte thickness 150 μm, 5x5 cm², Fuel Cell Materials). The active area of the cell was 16 cm² in both SOFC and DC-SOFC housing configurations. The cathode compartment setup was identical in both configurations. The anode compartment in a DC-SOFC configuration was constructed to allow for a batch supply of ca. 30 cm³ of carbonaceous fuel, forming a pulverized carbon fixed bed over the anode surface.

C. Experimental Results

In a typical SOFC cell configuration, anode was reduced in a humidified H₂/N₂ mixture. The cathode air flow was kept at 0.2 liters/min. Following the anode reduction process, fuel mixtures of CO+CO₂ with a varying CO content were supplied to anode of SOFC cell operated at temperatures ranging from 1023 K to 1123 K. After this part of experiment was completed, SOFC cell was cooled down, disassembled and mounted in a DC-SOFC housing. The anode compartment of DC-SOFC cell housing was filled with either lignite or lignite char, to form a pulverized fixed bed above the anode surface. The DC-SOFC cell housing was then heated up to operating temperature and operated without any gas flow over the anode compartment. For lignite fuel, in-situ pyrolysis takes place during heat-up, leading to a char formation. In this process, the anode remains in direct contact with lignite derived volatiles possibly affecting cell performance. The overview of performance measurements at 1123 K for both SOFC and DC-SOFC cells is summarized in Table I. The results of cell polarization measurements with lignite char as a fuel are shown in Fig. 1 for DC-SOFC operated at temperatures in the range between 1023 K and 1123 K.

III. CONCLUSION

Three different fuels: raw lignite, char derived from a raw lignite and CO+CO₂ fuel gas mixture, represent different approaches to electric power generation from lignite. At the current stage of SOFC and DC-SOFC technology development, the maximum power density generated in the fuel cell increases in the following fuel order: raw lignite (DC-SOFC), lignite char (DC-SOFC) and CO+CO₂ gas mixture (SOFC). In the fuel batch mode (DC-SOFC), electric current is generated until fuel is completely used-up in the anode compartment. Reloading of pulverized fuel in fixed bed of DC-SOFC anode compartment only slightly lowered the cell performance.

REFERENCES

A REDUCED-ORDER APPROACH TO ALKALINE ELECTROLYSIS MODELING

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Abstract - In this work two models of electrolysis devices are proposed. The first one is based on the sum of voltage losses due to different phenomena; this is the classical approach currently available in literature and adopted in both fuel cells and electrolysis simulations. The second model is based on a lumped and equivalent circuit approach. Compared to the first one, this model requires less parameters that depend just on thermodynamics and geometries. This makes the alternative suitable for complex systems simulations. After a calibration of the parameters, a comparison with available literature data is set up. The differences between the models result negligible and both of them are suitable for the description of the device.

Index Terms - Electrolysis, modeling

I. NOMENCLATURE

E \( V \) external applied voltage
i \( A/cm^2 \) current density

II. INTRODUCTION

Alkaline electrolysis is one of the commercial technologies for hydrogen production. Considering that the share of renewable energy sources is worldwide increasing, the use of electricity in water splitting process becomes more sustainable than in the past. Moreover, this could be an efficient way to store the exceeding renewable energy and solve some issues related to unpredictable power flows \[1\]. Hydrogen can be than locally stored and reconverted in electricity through a fuel-cell when the demand is higher; as an alternative, it can be stored as fuel for other applications or, according to recent opinion, mixed with natural gas in the existing gas infrastructure.

In order to describe this kind of system, an accurate modeling of the main device (i.e. the electrolyser) is required; furthermore, unsteady operation must be taken into account. In literature, a large effort is made to model transient behavior of hydrogen storage systems. In this work two models, a traditional and an innovative one, are compared in order to check if they are suitable for the simulation of medium scale electrolysis stack.

III. MODELS

The first considered model describes the polarization curve of the electrolytic cell as a sum of voltage contribution that increases the minimum thermodynamic voltage required for water dissociation reaction. This is the classical loss-estimate approach to both fuel cells and electrolysis modeling and is based on a combination of thermodynamics, heat and mass transfer theory and empirical electrochemical correlations; it is currently adopted in order to describe the electrolysis device in complex unsteady systems that couple intermittent energy sources (i.e. solar or wind plants) with electrolysis/fuel cell storage systems. The second one is based on a completely different reduced-order approach lumping all the effects through an equivalent electric circuit; thus, it’s possible to avoid the explicit description of the electrochemical behavior of the cell.

A. Loss-estimate approach

The polarization curve is obtained as sum of different contributions; in particular reversible voltage, electrochemical overpotential, ohmic losses and mass transport resistances are usually included. Different models based on this approach are published in literature; among the most recent and detailed, the one proposed by Hammoudi \[2\] is adopted. The analytical formulation of the model can be summarized in the expression

\[
E = E(i) = E_{rev} + E_{act}(i) + E_{ohm}(i)
\]

where the reversible contribution \( E_{rev} \) can be calculated.
from thermodynamics, the activation one \( E_{\text{act}} \) is described by Butler-Volmer equation [2] and the ohmic losses \( E_{\text{ohm}} \) include different resistance effects (electrolyte resistance [3], bubbles influence [4]). The influence of temperature on each term is considered. This model is based on a detailed analysis of each effect and involves several parameters related to geometries and materials as well as to electrochemical interactions and kinetics, which are strongly case-dependent.

### B. Reduced-order approach

This approach describes the electric behavior of the electrolyser by means of an equivalent circuit that is shown in Fig. 1.

![Reduced-order model equivalent circuit](image)

From Ohm’s and Kirchhoff’s laws applied to the circuit, the following equation can be obtained

\[
E = \frac{E_{\text{max}} + \eta_w \cdot i_{\text{max}} \cdot r_1}{r_2 (1 - \eta_w)} + 1
\]  

(2)

where the reversible potential \( E_{\text{max}} \) can be estimated by thermodynamics, the maximum current \( i_{\text{max}} \) is the current that allows the complete consumption of the fed water, the water utilization factor \( \eta_w \) is related to the real consumption and therefore to the applied current \( i \); \( r_1 \) and \( r_2 \) are the ionic and electronic internal resistances of the system. In this case all the parameters are related to physical properties; the main issue is the estimation of the maximum current. In this case we assume the chemical equilibrium in the outlet stream as constraining condition.

### C. Comparison against literature data

In Fig. 2 the results given by the two models are compared with available literature data [5-7]. Although the polarization curves are different due to temperatures and experimental facilities setup, results are all comparable and therefore we can conclude that both models yield reasonable predictions; anyhow each system can be described more accurately after a case by case adjustment of the single device characteristics (i.e. geometries) and of the parameters. The models have been also compared with some preliminary data of an electrolyser operated at the Energy Department of Politecnico di Milano, with encouraging results (average fitting error of about 6 % for both models).

### IV. CONCLUSION

Both the models can describe the general behavior of an electrolysis device and the fitting on a specific device can give accurate results, very similar for the two approaches. They differ just in the very low current density zone that is not interesting for practical applications due to safety issues. Therefore the evaluation of an equivalent electrical circuit and a reduced order or lumped description of the involved phenomena is an interesting alternative to the classical approach. Moreover the number of required parameters has been reduced to the minimum and the models are suitable for use in integrated hydrogen energy system simulations. Further investigations can be focused on the application of this approach to unsteady applications modeling.

### REFERENCES


HIGH YIELD SYNTHESIS OF A DURABLE PLATINUM CATALYST IN BICONTINUOUS MICROEMULSION FOR PEMFC APPLICATIONS

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Abstract – The price of the electrical energy produced by state of the art PEMFC is high, which hampers their full commercialization. One of the most expensive components is the catalyst material directly followed by its production method. Here we report on a high yield and relatively cheap synthesis of monodisperse platinum nanoparticles using bicontinuous microemulsion. Small nanoparticles of 2-4 nm in size have been synthesized. Process rate is controlled by the reducing agent and surfactants control the size of the resulting nanoparticles. The catalyst produced in the sodium AOT/water/heptane microemulsion showed higher durability compared to commercial catalysts. In addition, all nanoparticles produced by this procedure had a higher electrochemical surface area (ECSA) compared to commercial catalyst.

Durability, microemulsion, PEMFC, platinum catalyst

I. INTRODUCTION

Various techniques (liquid-phase, gas- phase or vapor-phase) have been proposed for the production of the platinum nanoparticles, however obtaining monodisperse nanoparticles of a small size at a high yield remains still an issue [1]. In contrast, here we report on the synthesis of monodisperse and small nanoparticles (2-4 nm) at high yield using bicontinuous microemulsions. These particles are subsequently tested as a catalyst for PEMFCs. The bicontinuous microemulsion, consisting of continuous water and oil nanostructures, acts as a template for the catalyst synthesis [2]. Previously in our group the synthesis route in a bicontinuous microemulsion of sodium AOT/water/heptane has been reported [2]. In this work we study the catalytic activity for the oxygen reduction reaction (ORR) and the durability of synthesized catalyst, and extended the study to other dense microemulsion systems, such as Triton X-100/water/toluene.

II. RESULTS AND DISCUSSION

Two microemulsion systems have been studied: sodium AOT/water/heptane and Triton X-100/water/toluene. The synthesis procedure is cheap, at ambient conditions and with high yield due to high water content (up to 40%). The general procedure for the synthesis is as follows: two microemulsion are prepared, where the first one contains a platinum precursor (H₂PtCl₆) in aqueous phase, and the second one contains one of the possible reducing agents N₂H₄, NaBH₄, or CH₂O. Afterwards, the stabilized microemulsions are mixed and the reduction reaction of platinum occurs in the confined aqueous channels of the bicontinuous microemulsion. A change of the microemulsion color from yellow to black during 1-2 hours, depending on the strength of the reducing agent, is observed evidencing formation of platinum nanoparticles. After the completion of the reaction, the carbon support-Vulcan XC-72 is added to the microemulsion to serve as substrate for the platinum nanoparticles. Subsequently, the mixture is washed with THF, 0.1M HClO₄ and demineralized water in order to remove the surfactant.

In Figure 1 the resulting particles of 2-4 nanometers synthesized in sodium AOT (54 wt%)/water (20wt%)/heptane (26wt%) using different reducing agents are given. It is clear, that varying the strength of the reducing agents the rate of the platinum reaction could be tuned.

Platinum nanoparticles were also synthesized in a dense microemulsion formed with the surfactant Triton X-100, which is less strongly adsorbed on a platinum surface, to avoid poisoning of the catalyst, see Figure 2 for results.
Both methods, synthesis in a microemulsion of strongly and in a weakly adsorbing surfactants, yield nanoparticles with similar crystal structures as confirmed by X-ray diffraction studies.

Figure 2. Pt nanoparticles synthesized in Triton X-100/water/toluene microemulsion.

Catalyst materials produced in the microemulsions of Triton X-100/water/toluene and Na-AOT/water/heptane showed high ECSA of 86 and 132 m$^2$/g respectively. The durability of both catalyst materials was tested by potential cycling between 50-1100 mV in 0.1 M HClO$_4$ and compared to the commercial catalyst. The platinum nanoparticles synthesized using a microemulsion formed by sodium AOT showed the highest resistance to degradation, see Figure 3. This was mainly caused by the monodispersity of the catalyst and to the presence of traces of the surfactant, which stabilize platinum nanoparticles and reduces agglomeration tendency.

Figure 3. Durability studies of the synthesized catalyst compared to the commercially available JM HiSPEC 9100.

III. CONCLUSION

In this work bicontinuous microemulsions were employed for the synthesis of platinum nanoparticles. This method provides a cheap way to produce platinum nanoparticles with a higher yield compared to other microemulsion based synthesis techniques. The size and morphology of the nanoparticles, as well as reactions rates can be tuned. As a result small and monodisperse nanoparticles are synthesized which show higher activity and stability than commercial catalyst.

REFERENCES


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SYNTHESIS AND CHARACTERIZATION OF SULFONATED POLY(PHENYLENE KETONE) FOR PROTON EXCHANGE MEMBRANE APPLICATION

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Abstract - Poly(phenylene ketone)s without ether linkage in the main chain were synthesized via nickel-catalyzed carbon-carbon coupling polymerization of 1,2-bis(4-chlorobenzoyl)-3,6-diphenylbenzene and 2,5-dichlorobenzophenone. Post-sulfonation process was carried out to add sulfonic acid group by using chlorosulfuric acid. The number of sulfonic acid groups were controlled by varying the mole ratio of ketone monomers in synthesized poly(phenylene ketone) copolymers. The copolymer membranes were identified by 1H NMR spectroscopy and thermogravimetric analysis (TGA). Sorption experiments were conducted to observe the interaction of sulfonated polymer with water. Ion exchange capacity (IEC) and proton conductivity were evaluated with the increasing degree of sulfonation. Moreover, membrane’s durability will be assessed by Fenton’s reagent.

Index Terms - Poly(phenylene ketone), Nickel catalyst, proton conductivity, Sulfonation.

I. INTRODUCTION
Polymer electrolyte membrane fuel cells (PEMFCs) which convert chemical energy to electrical energy offer many advantages, such as high efficiency, high energy density, quiet operation, and environmental friendliness [1]. The perfluorinated proton exchange membranes, such as Nafion, Flemion, and Aciplex, are widely used as PEM materials due to their high proton conductivity with good chemical and physical stability. However, these membranes still have some disadvantages, such as high methanol permeability, poor performance at temperatures above 80 °C, and high cost for extensive applications [2]. These problems are connected to the development of sulfonated aromatic polymers as an alternative proton exchange membrane. But hydrocarbon membranes suffer chemical degradation by nucleophiles generated by the PEMFC operating systems [3]. We focused on polyphenylene structure without ether linkage and pendant phenyl diketone. Pendant benzoyl groups has a great of advantages, such as good durability and thermooxidative stability [4]. Di-ketone monomer has selective sulfonation on phenyl rings of polymer side chain.

II. EXPERIMENTAL
A. Materials
Dimethylacetamide (DMAc), nickel bromide, zinc powder, triphenylphosphine, and chlorosulfuric acid were purchased from Sigma-Aldrich. Nickel bromide, zinc powder and triphenylphosphine were stored under nitrogen condition. 1,2-Bis(4-chlorobenzoyl)-3,6-diphenylbenzene was prepared as follows the previous procedure [5]. 2,5-Dichlorobenzophenone was purchased from IS Chem Co., Korea.

B. Synthesis of polymer
To a 100 mL three-necked flask was added Nickel bromide, zinc powder, and triphenylphosphine and also, in another round-bottomed flask, ketone monomers- 1,2-bis(4-chlorobenzoyl)-3,6-diphenylbenzene and 2,5-dichlorobenzophenone were taken. The mixtures of catalysts and monomers were prepared in glove box under nitrogen atmosphere. DMAc was added via syringe in catalyst flask and stirred at 80 °C. After 30 min, monomers dissolved in DMAc and injected by syringe into the catalyst flask. The reaction was proceeded for 5 h before precipitation into water containing 30% hydrochloric acid. After stirring for 1 h, the yellow solid was filtered and washed twice with methanol and water before drying in oven at 60 °C.
C. Sulfonation of polymer

Polymer was dissolved in dichloromethane and a solution of chlorosulfuric acid in dichloromethane was added dropwise to the polymer. After 6 h, the reaction mixture was decanted into water and filtered. The polymer washed thoroughly with deionized water and then dried in a vacuum oven at 80 °C.

III. RESULTS AND DISCUSSION

The sulfonated polymer was prepared as follows in Scheme 1. In figure 1, IEC (meq/g) is an indication of the mole content of sulfonic acid groups in the polymer membrane. Ion exchange capacities of sulfonated diketone polymers (SKPs) were in the range of 1.53-2.34 meq/g, and the corresponding water uptakes are 28.4-69.5% at 80 °C, whereas the IEC of the Nafion 211® was 0.91 meq/g and water uptake 28%.

Proton conductivities of the SKPs were measured as a function of the mole fraction of sulfonic acid groups. The conductivity of the polymers increases with the greater degree of sulfonation. The proton conductivities of SKP 20, 30, and 40 were 79.42, 95.38 and 109.12 mS/cm, respectively. This result is comparable with 104.3 mS/cm of Nafion 211® at 80 °C under 90% relative humidity.

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INVESTIGATION AND MEASUREMENTS OF DURABILITY & CATALYST DEGRADATION OF LOW TEMPERATURE PEM FUEL CELLS

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Abstract - The current-voltage curve, also called polarization curve is a specific characteristic of the fuel cell, which describes generally the overall performance of the fuel cell. Polarization curve is a special characterization of the fuel cell which shows relationship between cell potential and current density under a set of constant operating conditions. This paper presents the diagnostic results of single polymer electrolyte membrane fuel cell assemblies characterized by polarization curves. Single PEM fuel cell assemblies were investing through accelerated voltage cycling test at different values of relative humidity.

Key Words–Catalyst, degradation, polarization, humidity.

I. INTRODUCTION

Ever increasing population of the world, diminishing size of fossil fuel resources and rapid change in global climate due to the utilization effects of the fossil fuels have moved the world in burgeoning the demand for clean and sustainable energy. Fuel cell technology is fulfilling this demand by using renewable produced hydrogen as a fuel instead of the fossil fuels [1].

Among different types of fuel cells, the Polymer Electrolyte Membrane (PEM) fuel cells have the capability to convert the chemical energy of the fuel (hydrogen), effectively into electrical energy with the formation of pure water as the only byproduct. Their significant features of high power density, low operating temperature, easy and fast start-up/shut-down processes make PEM fuel cells a promising candidate to the next generation power source for transportation, portable and stationary applications d[1]. Factors like durability and cost are still the main hurdles to overcome before commercialization.

II. EXPERIMENTAL

Eleven fuel cells, each of area 5cm2 were assembled. In eight fuel cells (G, G1, G2, G3, G4, G5, G6, & G8) MEA (membrane electrode assembly)-micro reinforced composite expanded polytetrafluoroethylene polymer electrolyte membrane were used while in other cell was characterize cells F, F1 and F2 MEA (Y) a perfluorinated sulfonic acid membrane was used. MEA (X) has catalyst loading of 0.4mg Pt/cm2 on both anode and cathode side and MEA (Y) has catalyst loading, 0.6mg Pt/cm2 on cathode and 0.3mg Pt/cm2 on anode . MEAs were activated at 0.6V (15min) and 0.4V (30min) and OCV (1min) for 6-8 cycles. The cells were examined through the Accelerated Voltage Cycling Test. Before starting the potential cycling experiment each cell was characterized by recording the reference characterization curves [2].

The activation of the MEA and the characterisation curves (Polarisation Curve, EIS, Cyclic Voltammogram and Hydrogen Diffusion Measurement) of the cell are recorded by connecting the fuel cell to the characterisation test stand. All the characterisation curves were recorded by using cathode as working electrode and anode as counter electrode. The pressure of the gases was maintained between 1 and 2 bar, almost (1.5 bar) with stoichiometric coefficients of 1.5 for H2, 2 for O2 and 2.2 for air respectively. The fuel cell was operated at 70°C. The temperature of the humidifier was set at 68°C. Thus the value of relative humidity (RH) applied for all characterization curves was 90%. The fuel cell was purged both on anode and cathode sides with dry and wet nitrogen before starting the experiment and after finishing the experiment.
III. RESULTS AND DISCUSSION

Electrochemical Analysis
Three fuel cells F, F1 and F2 were assembled by using MEA of type H25-F. The fuel cell F was tested at 92% RH, F1 was operated at 80% RH and F2 was investigated at 90% RH. During the test series, after the completion of 1000, 3000, 5000, 7500, 10000 and 15000 voltage cycles the accelerated voltage cycling test was stopped and the fuel cells were characterised by polarization curves, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The fuel cell F worked till 10,000 voltage cycles, F1 and F2 worked longer and stopped working after 12,570 voltage cycles and 17,536 voltage cycles respectively.

<table>
<thead>
<tr>
<th>Fuel Cell</th>
<th>% RH</th>
<th>Voltage Cycles Completed</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>92%</td>
<td>10,000</td>
</tr>
<tr>
<td>F1</td>
<td>80%</td>
<td>12,570</td>
</tr>
<tr>
<td>F2</td>
<td>90%</td>
<td>17,536</td>
</tr>
</tbody>
</table>

Figure 1 illustrates the comparison of all polarization curves with oxygen at cathode for the fuel cell F. The graph indicates that the limiting current density with the fresh MEA is less than its value after 1000 voltage cycles but afterward the maximum current density decreases with the increase in the number of voltage cycles. The current density versus voltage curve at 10,000 voltage cycles shows the effect of mass transport limitation due to poor water balance.

It is also visible from that the current density versus potential curves, till 3,000 voltage cycles show large linear region of ohmic drop but the curves after 5000, 7500 and 10,000 voltage cycles exhibit a short region of ohmic losses with less values of limiting current densities. Figure 1 shows the power density curves for the fuel cell F with oxygen supply at its cathode. It is visible from the figure that the power density increased in the beginning from zero cycles to 1,000 voltage cycles. It might be due to proper humidification of the fuel cell at 1,000 VC. After that, the power density decreased until 7,500 VC.

Since polarization curve and power density curve are two different expressive ways for showing the same behaviour of the fuel cell, therefore, for all other cells investigated by accelerated voltage cycling tests [3], only polarization curves were plotted and discussed. Details results and discussion will be provided in Final paper submission.

Figure 1: Comparison of all Polarization Curves and Power Density with Oxygen supply at cathode of the fuel cell F (92% RH), Stoichiometry (H2=1.5, O2=2.0, Air=2.2), Cell Temp.<80°C, Area cell=5cm², Relative Humidity=92%, Pressure=Ambient (1.013 bar)

IV. CONCLUSION

Eight fuel cells assembled with same G type of MEA were investigated at different values of relative humidity. The different fuel cells were operated at 81%, 70%, 60% and 33% relative humidity respectively whereas the fuel cells G1, G3, G4 and G5 were tested at 90% RH. On the whole the fuel cells tested at 90% RH show better performance except G4 as compare to other cells. Among them G1 and G3 has maximum lifetime, more than seven thousand voltage cycles i.e., 7500 and 7350 VC respectively and G8 exhibited minimum lifespan just 1500 VC. The reason of bad performance of fuel cell G4 is starvation of gases during recording of characterization curves after 1,500 voltage cycles. This caused the deterioration of electro-catalyst and performance degradation of the cell.

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EFFECTS OF VARIOUS BIOGAS CONTAMINANTS ON THE PERFORMANCE OF AN SOFC SHORT STACK


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Abstract - The effect of sulfur, chlorine, hydrocarbon and siloxanes compounds on the performance of SOFC short-stacks is presented. These contaminants are typical of biogas from anaerobic digestion in waste-water treatment plants and landfill. Some of them can be also found in bio-syngas from biomass gasification.

Even though a properly designed cleaning section should take care of their removal, from sub-ppm(v) to few ppm(v) concentration levels can still breakthrough toward the Solid Oxide Fuel Cell (SOFC) under certain circumstances (e.g., the presence of humidity in the gas feed, which reduces the adsorption capacity of the adsorbent material, or simply a saturated catalyst condition).

In this study, several experiments were performed on short-stacks to better understand the chemical and electrochemical stability of Ni-SOFC anodes when interacting with selected contaminants. Observed deactivation and/or degradation trends are also motivated according to contaminant-specific interaction mechanisms with Ni.

Keywords - biogas, contaminants, sulfur, chlorine, siloxanes.

I. INTRODUCTION

The presence of contaminants can hamper the operation of prime powers that convert the biogas into electricity. Especially, the presence of several compounds with a certain seasonal variability makes the task difficult of designing a cleaning section for providing a clean gas. For instance, moisture and/or traces of hydrocarbons in the biogas feed not detrimental for a high temperature fuel cell or the upstream reformer, can drastically reduce the removal efficiency of activated carbons generally used as adsorbents due to competitive adsorption processes.

The typology and amount of contaminants, mostly Volatile Organic Compounds (VOCs), must be determined accurately in order to properly design a section for removal of those compounds that can affect the operation of the power system.

Especially when high-efficiency high-temperature fuel cell generators are used, stringent fuel requirements in term of ppm(v), or even ppb(v), of selected contaminants apply.

Concerning biogas from primary and secondary sludge of waste-water treatment plants, sulfur, chlorine and siloxanes compounds can be found at the ppm level, along with traces of other VOCs, e.g., light hydrocarbons such as CH4, aromatics (mostly benzene and toluene), alkanes and alcohols. Also halocarbons (halogen carbon compounds) can be found.

In Figure 1, organosilicon compounds measured monthly at the SMAT S.p.a plant in Torino (IT) are given. The most abundant compound observed was D5 (C10H30O5Si5, Decamethylcyclopentasiloxane).

![Fig. 1. Siloxane compounds in the as produced anaerobic digestion biogas from the SMAT WWTP plant. (The highest value for D5 observed on month 4, corresponded to a concentration value of 1.14 ppm(v) in the as-produced biogas.)](image-url)

II. EXPERIMENTAL

Commercial SOFC stacks were used for the experiments. The stack is generally operated at a fixed nominal operating...
point corresponding to a current of 20 A and a fuel utilization (FU) of 60%. The feeding gas is the simulated mixture of a reformate from biogas from anaerobic digestion under the following assumptions:

- the starting biogas composition is taken as CH4-CO2 60-40 vol. %;
- the reformate composition is calculated assuming biogas steam-reforming (steam-to-carbon (S/C) ratio of 2) in an equilibrium reactor operating at 750°C. The resulting gas composition is CH4 0.3%, CO2 10.0%, CO 19.3%, H2 50.6% and H2O 19.9% on a molar basis.
- Contaminants analyzed in this work are only H2S, C2H4 and the combined effect of C2H4 plus COS. Further results on the effect of COS, C2Cl4, HCl and D4 will be available in the future as part of the research activities of the SOFCOM project (see Acknowledgments for further detail on this project).

III. RESULTS AND DISCUSSION

In Figs. 2 and 3 the effect of H2S and C2H4 and C2H4+COS on the stack performance are shown respectively. No permanent degradation is observed when feeding H2S up to 25 ppm, however sulfur blocks active sites thus temporarily increasing ASR. Ethylene is well tolerated by the stack and converted as a fuel. No carbon deposition was observed with post-mortem analysis of the stack tested in Fig.3. When co-feeding an organic sulfur compound (COS) in addition to C2H4, an initial degradation was observed, that was recovered during operation without removing the contaminants.

Results show that hydrocarbons are well tolerated being converted as fuel within the SOFC anode. Up to 1,000 ppm of C2H4 was fed in the anode stream with no apparent voltage drop during 200 hr of test. Sulfur causes a deactivation of the anode electrode due to dissociative chemisorption on the Ni electrode. H2S dissociates into hydrogen and elemental sulfur, S strongly adsorbs on the nickel surface and thus blocks the active sites for electrochemical reactions, thus causing a slight temporary and partially reversible reduction of electrochemical active sites, which translates in an increased Area Specific Resistance (ASR). In fact, a protracted exposure to ppb or ppm levels of H2S (or other organic sulfur compounds, such as COS) may eventually cause an irreversible degradation of the Ni electro-catalyst due to micro-structural reconstruction processes that are thought to promote Ni agglomeration [2].

IV. CONCLUSIONS

Several trace compounds present in AD biogas can affect the performance of the SOFC if not captured in the cleaning section. In this work, the effect of H2S and C2H4 was analyzed. Future work will show the effect of chlorine compounds, whose interaction with Ni-SOFC should be even weaker than sulfur, and siloxanes, expected to be highly detrimental for the SOFC operation.

ACKNOWLEDGMENTS

This work was partly funded by the European Union (Project number 278798, http://areeweb.polito.it/ricerca/sofcom), with contributions from the partners involved: POLITO, SMAT, IEN, TUM, MATGAS, CNR, VTT and TOPSOE.

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EXERGY ANALYSIS OF A HYDROGEN-BASED RESIDUAL LOAD MANAGEMENT SYSTEM CONSISTING OF PROTON EXCHANGE MEMBRANE ELECTROLYSER AND SOLID OXIDE FUEL CELL UNITS

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Abstract – In this work exergy analyses for different process chains of hydrogen storage systems are conducted. The excess power produced by wind and solar power plants in Germany is used in PEM electrolyzers (PEMEL) to generate hydrogen which is stored under high pressure and then used in different intermediate temperature SOFC and SOFC-GT systems.

It is shown that the whole chains maximum exergy efficiency over one year of part-load operation ranges between 33 % and 39 %. Furthermore the increase in efficiency by using waste heat from the fuel cells in an open Brayton cycle is very small due to the low operating temperature. Thus new process combinations are proposed which will be examined in a next step.

Index Terms – exergy analysis, PEMEL, SOFC, SOFC-GT

I. INTRODUCTION

The German power supply is being transformed from nuclear and fossil sources towards mainly wind and solar sources. Due to their intermittent supply, long term high capacity storage systems will be required. Hydrogen created through electrolysis appears to be a favorable energy carrier for this application.

In this work an energy storage system is investigated concerning its full and part-load exergy efficiency. The hydrogen is generated by proton exchange membrane electrolyzers (PEMEL) and stored under high pressure in salt-caverns. It is then distributed by a pipeline grid and reconverted to power and heat by either solid oxide fuel cells (SOFC) or combined solid oxide fuel cell gas turbine systems (SOFC-GT).

II. SIMULATION

The simulation is done in MATLAB using a self-developed iterative and modular code. The processes were first simulated considering their part-load efficiency and then applied to load profiles for one year of operation.

The electrolyzers efficiency is modeled by determining a polarization curve with values for exchange current density and resistance given by [1]. The operating temperature and pressure are 80 °C and 30 bar. The power required for pumps is calculated by a pressure drop of 0.5 bar and electric controls are assumed to require 1.5 % of the maximum power input.

The compression of hydrogen is considered to be done by piston compressors with an isentropic efficiency of 80 %. Their part-load efficiency is assumed to be constant [2] and the storage pressure is considered to be constant 200 bar.

To compare different solid oxide fuel cells and combined systems two sets of characterizing parameters were chosen. One anode-supported (AS) operating at 700 °C [3] and one electrolyte-supported (ES) operating at 800 °C [4]. The turbo machinery is calculated with maps taken from the Gas Turbine Simulation Program (GSP) with the design pressure ratio chosen for highest efficiency. The part-load strategies are constant fuel-to-air ratio operating only the SOFC and constant rotational speed for the combined SOFC-GT systems. The heat loss over the insulation of the SOFC-stack is considered to be 5 % of the maximum power; the fuel utilization is 95 % because pure hydrogen is used. The remaining hydrogen is burned by catalytic burners after the stack. The maximum current density is set as 0.6 A/cm² for all cells. The exhaust gases are finally used for co-generation of heat with 60 °C supply and 40 °C return temperatures.

The load profile for hydrogen generation is a linear extrapolation based on a 100 % renewable energy scenario [5] of 2012’s solar and wind power supply and vertical grid load in Fig. 1.

![Electric load profiles for (a) hydrogen generation and (b) hydrogen use](https://example.com/fig1.png)

Fig. 1. Electric load profiles for (a) hydrogen generation and (b) hydrogen use [6]

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Germany. The loads are provided in 15 min intervals. The profiles are shown in Fig. 1 and more details can be viewed in. Since the SOFC-stack should not cool down, it is considered to operate at least at its minimum power and thus changing the depicted load profile.

The exergy model used is given in [6].

III. RESULTS AND DISCUSSION

In Fig. 2 the simulated electric exergy efficiencies of the PEM-electrolyser as well as the different SOFC-configurations are illustrated.

The PEM electrolyser's efficiency increases from full load to about 25 % load and then drops rapidly. The pure SOFC systems efficiency shows a trend of increasing efficiency in part-load due to lower polarizations at lower current densities. The AS SOFC-GT system on the other hand reach their highest efficiency at full load and then gradually decline. The ES SOFC-GT efficiency curve is determined by counter-trends in strongly increasing fuel cell and decreasing Brayton cycle efficiency. Overall the efficiency of the higher temperature systems is higher due to turbo machinery efficiency.

It can be seen that the electrolyser can be operated down to 3% of load while the fuel cell and fuel cell gas turbine combined systems are limited to around 43% to 55%, respectively.

Single process and complete process chain efficiencies are given in Table 1. When comparing full-load to load-profile operation, both PEMEL and SOFC systems gain an increase in efficiency while ES-SOFC-GT systems suffer from a decrease. Despite higher full-load efficiency of the SOFC-GT systems this leads to similar or even lower efficiencies compared to the SOFC units.

The reason for this is the low efficiency of the Brayton-cycle using the waste heat from the fuel cell stack. Simulations regarding an increase of temperature by burning additional hydrogen before the turbine inlet decreased the overall efficiency because this hydrogen was not used in the high efficiency fuel cell. In fact, it is shown that most of the power provided by the turbine was needed to drive the air compressor.

The complete chain exergy efficiency, when being able to use all co-generated heat, ranges from 29 % to 35 % with the ES SOFC-GT bringing the highest overall efficiency.

When using solid oxide fuel cells operating at intermediate temperatures, the considered Brayton cycle is inadvisable. Instead lower temperature processes such as a steam-based Rankine-cycle, organic Rankine-cycle or supercritical carbon dioxide Brayton-cycle might be better suited for this application and will be reviewed by the authors in a next step.

The proposed hydrogen-based system prospectively offers a higher efficiency than when synthesizing natural gas from CO₂ and hydrogen via the Sabatier reaction due to saving both methanation and (optional) reforming steps. Despite requiring a new hydrogen distribution system, methanation and (optional) reforming steps. Despite requiring a new hydrogen distribution system, methanation and (optional) reforming steps.

ACKNOWLEDGMENT

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REFERENCES


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![Electric exergy efficiency of PEMEL, SOFC and SOFC-GT systems over load](image)
INTERFACIAL BEHAVIOR OF ALKALIMETAL CARBONATE COEXISTING WITH LITHIUM SILICATE FOR CO2 STORAGE AND RELEASE

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For improvement of surface activity of Li4SiO4 which is utilized for one of CO2 storage materials, the effect of surface modification of silicate on CO2 storage phenomena was discussed. Total storage amount of CO2 into Li4SiO4 are constant with increase of a surface area of silicate, however, the storage temperature is rapidly decreased. Coexisting alkali-metal carbonates promote the absorption of CO2. The absorption amount of CO2 depends on the composition of carbonates.

Index Terms – LT-SOFC, CO2 absorption, lithium silicate molten carbonate, thermochemical properties

I. INTRODUCTION

Generally considering, the one of major factor of global warming is consumption of the fossil fuel which causes CO2 emission. Enormous effort for decease of energy consuming is proceeded, however it is important to minimize the CO2 emission using hydrogen energy resources and storage from the origin of CO2 emission. Recent decades, various kinds of CO2 capture devices are developed using CO2 chemisorption materials, such as LiZrO3, LiSiO4, LiAlO2, and so on. Among these materials, Li4SiO4 is expected as the high CO2 storage materials of which ratio reach to 36.7 wt% and less volume change up to ca. 46vol%. It is expected to be utilized to CO2 separation of exhaust gas from high-temperature fuel cells [1]. Numerous studies have been carried out for the CO2 storage properties of the lithium silicate not only Li2SiO3, Li4SiO4 but also lithium silicate composite coexisting with carbonate. Recently, various kinds of interfacial treatment for the silicate ware carried out and the relationship between surface activity and CO2 storage properties are discussed [2].

In this study, the thermophysical properties of Li4SiO4 which under coexistence with carbonate and ball-milling operation was measured. A dependence of lowering temperature of CO2 storage on treatment temperature and compositions.

II. EXPERIMENTAL METHODS

Li2SiO4 was prepared from stoichiometrically mixed Li2CO3 and SiO2 powder and calcined at 973 K for more than 3 hours. The weight of CO2 absorption into Li4SiO4 was calculated from gravimetry of obtained sample in CO2 gas flow. The thermal analysis of the sample was carried out using TG/DTA analyzer Rigaku Thermo plus EVO II. In order to confirm the effect of carbonate, the sample was mixed with excess amount of K2CO3 and Li2CO3. Excess amounts of these carbonate was 10-30 vol%. The effect of ball-milling was confirmed using planetary ball mill, Fritsch P-5 in Ar gas flow. Characterization of each sample was carried out using XRD, SEM, BET and thermal gravimetry.

Fig. 1. XRD pattern of Li4SiO4 synthesized at 973 K in air flow.
III. RESULTS AND DISCUSSION

Obtained Li$_4$SiO$_4$ sample was obtained stoichiometrically at 973 K. XRD pattern indicated the crystallite size was enough to be coagulated more than ca. 1 µm as shown in Fig.1. As Li$_4$SiO$_4$ is metastable phase in lower temperature, the reaction of CO$_2$ capture is indicated as follows:

\[
\text{Li}_4\text{SiO}_4 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{Li}_2\text{SiO}_3
\]  

(1)

Thermal treatment for Li$_4$SiO$_4$ sample shows that CO$_2$ capture began from ca. 873 K and deformation of the sample is observed over 1173 K under the opposite way of Eq(1). In Fig.2, thermal gravimetric curve for the CO$_2$ absorption for various composition of Li$_4$SiO$_4$ with/without alkali metal carbonate such as Na$_2$CO$_3$ and K$_2$CO$_3$. During heating process, weight of sample increased with the temperature due to reaction of Eq(1). Comparing to the result for pure Li$_4$SiO$_4$, an increase of the weight was observed in lower temperature. Especially, for the system Li$_4$SiO$_4$/Na$_2$CO$_3$ samples, an increase of weight was observed from around 400 K. It is suggested that the Na/K mixed carbonate promotes the reaction of CO$_2$ sorptions at the interface of the carbonate and silicate.

In case of using ball-milled Li$_4$SiO$_4$, surface activity was enhanced by the increase of surface area. Weight changes of ball-milled Li$_4$SiO$_4$ samples during heating process was shown in Fig.3. It is found that the weight of Li$_4$SiO$_4$ above 1173K was equal to original weight at room temperature, which means that CO$_2$ was completely desorped from the sample. However, the weight of ball-milled sample above 1173 K is less than of original ball-milled samples. It is suggested that the sample during ball-milling operation has already adsorbed in room temperature. These samples have a large surface area which is more than ca 20m$^2$/g, therefore ball-milled sample is partially reacted with CO$_2$. Then the Li$_4$SiO$_4$ has a high activity by the milling operation and depends on the surface areas.

IV. CONCLUSION

Thermal gravimetry of Li$_4$SiO$_4$ in CO$_2$ gas flow was measured for Li$_4$SiO$_4$/carbonate samples in order to improve the surface activity of Li$_4$SiO$_4$ which is utilized for one of CO$_2$ storage materials. The effect of surface modification of silicate on CO$_2$ storage phenomena was discussed. Total storage amount of CO$_2$ into Li$_4$SiO$_4$ are constant with increase of a surface area of silicate, however, the storage temperature is rapidly decreased. Coexisting alkali-metal carbonates promote the absorption of CO$_2$, and its absorption amount of CO$_2$ depends on the composition of carbonates.

REFERENCES


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In order to discuss the interaction between carbonate ion and solid oxide electrolyte at an interface in Sm doped CeO₂-carbonate LT-SOFC, high temperature Raman spectroscopy is measured. Using in-situ high temperature Raman spectroscopy, solid state diffusion of ions in carbonate mixture is found below eutectic point. Degree of diffusion depends on the Sm content in Sm doped CeO₂ kinds of solid oxide.

Index Terms – LT-SOFC, cerium oxide, carbonate, Raman spectroscopy

I. INTRODUCTION

Fuel cells operated at high temperature; such as MCFCs and SOFCs at about 923-1273 K, have high power and fuel efficiency. For example, solid phase fuel cell(SOFC)s with co-generation system achieved 90% of fuel efficiency. However component material and cell configuration that sustainable at high operating temperature under oxidation/reduction atmosphere are undefined, so comprehensive improvement that includes electrode and electrolyte is necessary. Ceria(CeO₂) based oxide is one of the candidates for electrolyte which has high O²⁻ conduction in SOFCs and for which numerous studies has been carried out. Later, in order to lowering the operation temperature, solid oxide and carbonate composite electrolyte such as CeO₂/M₂CO₃ has been studied in which CO₃²⁻ conduction is appended in carbonate phase. Furthermore, Samaria (Sm³⁺) or gadolinia (Gd³⁺) doped ceria (SDC or GDC) has been also used instead of CeO₂ for low temperature SOFCs[1]. These rare-earth doped ceria is strong Lewis acids and perform as the proton conductive materials. Therefore it is known that SDC/carbonate composite has a mixed ionic conductive electrolyte of which carriers are O²⁻, H⁺, CO₃²⁻. In case using heterohedral system such as solid oxide/carbonate composite system, it is important to consider the interfacial properties and behavior of ionic species at boundary surface. Zhu et. al. consider that there is an interaction at the interface of solid oxide particles and sodium carbonate phase, leading to the superior proton conduction[2].

CeO₂ is used also as a co-catalyst from oxygen storage ability, and numerous studies were carried out for surface adsorption which contributes to surface ionic conduction. In this study, the influence of solid surface conduction of SDC to ionic conduction and diffusion of carbonate below the eutectic temperature using various flow gases. We therefore investigate about interaction and each property of composite electrolyte and solid oxide surface by observing diffusion process of carbonate mixture using Raman spectroscopic method.

II. EXPERIMENTAL METHODS

CeO₂ and Sm doped CeO₂ samples(SDCs) were synthesized by co-precipitation method[3]. Obtained precursor was separated, dried, milled and calcined under air atmosphere. The amount of doping of Sm in CeO₂ is indicated as SDC10(10 mol%), SDC30(30 mol%), and SDC50(50 mol%). Na₂CO₃ and K₂CO₃ was dried at 473 K for 48 hours under CO₂ atmosphere, and mixed at Na:K = 41:59 and milled(apply the word NK to mixture of Na₂CO₃ and K₂CO₃). This carbonate mixture is mixed with CeO₂ or SDCs(CeO₂ or SDC-NK).

The crystalline nature of the solid oxides and composite materials was checked by XRD. The XRD analyses were carried out on a Rigaku SmartLab system. The radiation applied was CuKα(1.5418 Å) from Cu inclusion X-ray tube operating at 40kV/30mA. XPS spectra were acquired in a JEOL JPS-9010MC. Monochromated AlKα X-rays (hv = 1486.6 eV) were used as an exciting source for irradiating samples. XRF spectra were acquired in a Shimadzu XRF-1800 with Rh target operating at 40 kV/95 mA as an X-ray source for irradiating samples.

To investigate surface state and solid state diffusion in carbonate, Raman spectroscopy was employed. The Raman
spectroscopic analyses were performed on a HORIBA Jobin Yvon T64000 equipped with GLG 3100(Ar, 488 nm) and JUNO 532-100S(Nd/YVO4, 532 nm). In the high temperature measurement, high temperature unit manufactured by AABSPEC A-#2000 was used.

III. RESULTS AND DISCUSSION

According to XRD patterns of solid oxide samples, CeO2, SDC10, 20 and 30 has fluorite structure specific to pure CeO2. Patterns of fluorite structure CeO2 and pure Sm2O3 was observed in SDC50 which has two coexisting phases of CeO2-Sm2O3 solid solution and segregated pure Sm2O3 phase 20 position of d111 in CeO2, SDC10, 20, 30 and 50 shifted to lower diffraction angle and indicates that lattice constant increases in associate with dope amount increasing. It is found that the lattice constant increased in Sm contents by formation of solid solution.

Observation of surface state and defect by Raman spectroscopy shows that F2g band, which is assigned to Ce-O8 breathing mode[3], in samples CeO2 and SDC20 shifted to lower wavenumber in associate with dope amount increasing, but in SDC30 and SDC50, F2g band shifted to higher wavenumber. It indicates that surface property of SDC10, 20 and 50 are different from SDC30.

Deviation of Sm composition between surface and bulk is expected in calcination process. Quantitative analysis by XPS and XRF, deviation of Sm amount reached ca 20% in SDC30 as shown in Fig. 1. Change of surface structure associated with solid solution formation and segregation of Sm2O3 makes a profound difference on surface state. Interaction at the interface between solid oxide surface and carbonates may be influenced by Sm doping content.

Variations of Raman spectra with temperature of carbonate in NaKCO3 with Sm-doped ceria in initial heating process in Fig. 2. Whereas separated ν1(CO32-) bands assigned to sodium and potassium carbonates are observed at lower temperature, unifying of these bands was observed due to solid state diffusion of carbonates at temperature lower than eutectic point(983 K). Degree of diffusion is affected by Sm amount in coexisting oxide. In SDC30-NK, carbonate was difficult to diffuse well. It is suggested that cationic species diffused at the solid oxide-carbonate interface below melting point. XRD measurement of samples after Raman spectroscopy measurement, diffraction patterns of NaKCO3 produced in solid state diffusion and Na2O and K2O produced in decomposition of carbonates as shown in Fig. 3. It is suggested that conduction of carbonate species is promoted by solid state diffusion.

IV. CONCLUSION

Solid state diffusion at temperature lower than eutectic point of carbonate mixture is assisted by coexistence of solid oxides. Diffusion degree vary depending on the kind of solid oxides, it is suggested that solid state diffusion was affected according to Sm dope amount. It is suggested that surface state of solid oxides effect on strength of solid oxide-carbonates interaction.

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Fig. 1. Deviation of Sm composition at a surface of Sm doped ceria from bulk composition.

Fig. 2. Variations of Raman spectra with temperature of carbonate in NK with Sm-doped ceria in initial heating process and distance of Raman band position of ν1(CO32-) of sodium and potassium carbonates coexisting with Sm-doped ceria.

Fig. 3. Crystal structure of carbonates after Raman spectroscopy measurement.
In this article a zero-dimensional and stationary simulation model of a direct internal water gas shift (WGS) SOFC system fed by syngas for the electric and thermal powers production is formulated and implemented in Matlab environment.

The simulation model evaluates the thermal and electric powers produced by the SOFC system, when recirculated anode exhaust gas percentage is varied, and the amount of carbon that can be formed in the anode.

In this system the percentage increase of recirculated anode exhaust gas determines an increase of thermal power produced, because the system exhaust gas mass flow and temperature increase; but on the other hand it penalizes the electric power production of the system, because the fuel cell voltage is reduced.

The cathode inlet mass flow is varied so as to ensure fuel cells thermal equilibrium at the current density, owing to which a high fuel cell electrical efficiency is obtained.

Keyswoeds: syngas, SOFC system, simulation model.

Nomenclature

SYMBOLS

\( T, p, P, K, \chi \) temperature, pressure, power, equilibrium constant and mass fraction

\( V, J, \Delta V, \Delta N \) voltage, current density, cell voltage losses and Nernst voltage

\( F, G, V, \eta, S/C \) molar flow, mass flow, molar coefficients, efficiency and steam to carbon ratio

\( AGi, H, Fa, q, f \) molar Gibbs free energy variation, enthalpy, Faraday constant, ratio between CO and H\(_2\) molar flows electrochemically consumed, anodic recirculation factor

\( r, g, U, R \) rate equation, generic function, utilization factor, ideal gas constant

SUBSCRIPTS

\( i, w, j, k, h \) referred to \( i^t \) and \( w^t \) chemical compound, \( j^a \) anodic, \( k^c \) cathodic, and \( h^t \) carbon deposition reactions

\( e, cf, hf, mc, f \) referred to cell element, to cold fluid, to hot fluid, to carbon and to fuel

\( ohm, act, conc \) ohmic, activation and concentration voltage losses

\( in, out, tot, lost \) at the inlet, at the outlet, total, lost for chemical irreversibilities, joule effect and polarization phenomena

\( heating, th, h, rec, wgs \) for fuel cell feeding gases heating, thermal, electrochemically consumed, recirculation and referred to the water gas shift reaction

SUPERSCRIPTS

\( \theta \) standard condition

1 INTRODUCTION

High temperature fuel cells (Molten Carbonate Fuel Cells, MCFC and Solid Oxide Fuel Cell, SOFC) can be fed by alternative fuels such as syngas, i.e. the gas produced by coal or woody biomass gasification, which is mainly composed of carbon monoxide (CO), hydrogen (H\(_2\)) and carbon dioxide (CO\(_2\)).

Before entering in the fuel cell, anode syngas is mixed with steam to promote the conversion of CO into H\(_2\) by the water gas shift (WGS) chemical reaction directly in the anode. The hydrogen produced by the WGS chemical reaction together with that already contained in the syngas is consumed at the anode for electric energy production.

In particular only SOFC can consume part of the CO content in syngas to produce electric energy directly in the anode and therefore it require less steam for the conversion of the remaining CO part content in the syngas in \( H_2 \) by the WGS reaction.

A part of the anode exhaust gas, consisting mainly of steam and carbon dioxide, can be recirculated at the anode inlet. In this article a zero-dimensional stationary simulation model of a SOFC system fed by syngas for the production of electric and thermal energies has been formulated and implemented in Matlab language.

By this simulation model it is possible to vary some SOFC system characteristic parameters, including the anode exhaust gases recirculation factor. The simulation model can also estimate the carbon mass that can be formed on average in the fuel cell anode.

2 SIMULATION MODEL

In this article the SOFC system for the production of electric and thermal energies has been studied. It is composed of an SOFC, of a burner and of a heat exchanger. In the heat exchanger the anode feeding gas (syngas and steam) and the cathode feeding gas (air) are pre-heated at the expense of the burner exhaust gas thermal energy. In the burner anode exhaust gases are completely oxidized using the cathode exhaust gas as oxidant. In the SOFC system analyzed a part of the anode exhaust gas is recirculated to the anode inlet.

The main hypotheses of the mathematical model with their explanations or justifications are summarized in Table 1.
The main equations of the model are shown in Table 2.
If the cell element is in thermal equilibrium condition the thermal power required to heat its feeding gases from their cell inlet temperature to the fuel cell operative temperature, \( P_{\text{th,sofe}} \), is equal to the sum of thermal power lost for chemical irreversibilities, \( P_{\text{irr,chem}} \) and thermal power produced by WGS chemical reaction, \( P_{\text{wgs}} \) (equation (7)).

At the fuel cell operating temperature the molar flow of CO electrochemically consumed at the anode is calculated by equation (10).

### TABLE 1 MAIN MODEL HYPOTHESES

<table>
<thead>
<tr>
<th>Hypothesis</th>
<th>Explanations/Justifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>zero-dimensionality</td>
<td>each system component is characterized by set of parameters which does not depend on the position ((x, y, z)) in the component</td>
</tr>
<tr>
<td>stationary condition</td>
<td>each system component is characterized by set of parameters which does not depend on the time</td>
</tr>
<tr>
<td>uniform voltage in cell plane</td>
<td>the current collectors and gas distributors of the fuel cell are equipotential surfaces</td>
</tr>
<tr>
<td>carbon formation at the anode in chemical equilibrium condition</td>
<td>The chemical reactions are fast and the chemical equilibrium condition is not obtained, therefore the value of carbon mass calculated is maximum and precautionary</td>
</tr>
</tbody>
</table>

### TABLE 2 FUNDAMENTAL MODEL EQUATIONS

#### Local Kinetics

- **Voltage**
  \[
  \Delta V = \frac{\Delta V_{\text{an}}}{\xi} + \frac{\Delta V_{\text{cat}}}{\xi} + \frac{\Delta V_{\text{rec}}}{\xi} = \xi \left[ \Delta V \right]
  \]  
  (1)

- **Resistance**
  \[
  \Delta V_{\text{an}} + \Delta V_{\text{cat}} + \Delta V_{\text{rec}} = \Delta V_{\text{cell}} = \frac{\Delta V_{\text{cell}}}{\xi}
  \]  
  (2)

- **Cell voltage**
  \[
  V_{\text{cell}} = \frac{\Delta V_{\text{cell}}}{\xi}
  \]  
  (3)

#### Mass Balance

- **Anode**
  \[
  \Delta \xi = \sum \frac{\xi_i}{\xi}
  \]  
  (4)

- **Cathode**
  \[
  \Delta \xi = \eta_{\text{rec}} \xi
  \]  
  (5)

- **Burner, mixing points**
  \[
  \sum G_{\text{inj}} = \sum G_{\text{outj}}
  \]  
  (6)

#### Global Energy Balance

- **Cell element**
  \[
  \frac{P_{\text{th,cell}}}{T_{\text{cell}}} + \frac{P_{\text{wgs}}}{T_{\text{cell}}} - \sum_{\text{anodic reactions}} \eta_{\text{rec}} \xi = 0
  \]  
  (7)

- **Burner**
  \[
  \eta_{\text{rec}} \sum H_{\text{inj}}(\xi) = \sum_{\text{recolutions}} H_{\text{rec}}(\xi)
  \]  
  (8)

### 4 CONCLUSIONS AND RESULTS

By the calculation code it is possible to trace the trends of the electrical and thermal powers produced by SOFC system when the recirculation factor is varied, and they are shown in figure 1. The increase of the recirculation factor determines the reduction of the electrical power produced by the SOFC system, because it reduces the fuel cell voltage; on the other hand it determines an increase of the thermal power produced by the same SOFC system, because it increases the mass flow and temperature of the gas at the heat exchanger outlet.

The calculation code also calculates the parameter \( \chi_{\text{mc}} \), which represents the carbon mass that can be formed at the anode in chemical equilibrium condition for mass unit of syngas, which feeds the SOFC system.

In the operating conditions examined anode carbon formation was not recorded owing to the high value of the S/C ratio chosen.

#### FIGURE 1 TRENDS OF THE ELECTRICAL AND THERMAL POWERS PRODUCED, VARYING THE RECIRCULATION FACTOR

### REFERENCES


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HIGH PERFORMING SOFC STACKS FOR SOFC AND SOEC APPLICATIONS


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Abstract - In the past years SOFCpower-HTc has advanced an innovative stack design which has been optimized for high performance, particularly with respect to electrical efficiency at intermediate temperatures (650-750°C) in reformate conditions. Electrical efficiency as high as 70% under stem reforming at 750°C (S/C = 2 ) have been achieved. Stack offers also a good robustness, more than 50 full thermal cycles been demonstrated without any significant performance drop. In early 2013 the stack has been transferred to the pilot production and has been integrated in the EnGen-2500™ cogenerators to be installed in field tests.

Within the frame of a SOFCpower/KACST joint collaboration, the innovative SOFCpower’ stacks have been tested in both SOFC and SOEC conditions. The work summarized the electrochemical performances obtained by stack testing in SOFC and SOEC mode in both SOFCpower’s Labs in Mezzolombardo (IT) and Kacst’s Labs in Riyadh (KSA).

Index Terms – Steam-reforming, electrical efficiency, micro-CHP, high temperature electrolysis

I. INTRODUCTION

In the past years KACST developed a significant experience in fuel cell technologies, including collaboration with Saudi Aramco to establish SOFC lab, and Testing commercial SOFC stacks and with CGCRI, Kolkata, India to Establish SOFC Testing Facility at ERI. Finally a joint testing and demonstration program has been started with SOFCpower on planar SOFC stack technology.

SOFCpower-HTceramix is a European leader in development and manufacturing of SOFC-based stacks and (co)-generators based on its proprietary Gen-II anode supported cells. The company includes in its product portfolio 1 and 2.5 KW electric micro-CHP appliances designed for the residential market and is capable of providing also stack modules of different sizes for other applications, including High Temperature Electrolyzers, offgrid generators and biogas/syngas fuelled systems.

HTceramix SA – SOFCpower has developed a new stack concept aiming for higher performance and reliability while allowing a drastic reduction of production costs. The novelty of the stack design is the unique fuel distribution system allowing an excellent homogeneity of the fuel distribution inside and among elements, this being achieved at low manufacturing cost. Thanks to this, and even using standard materials, we can achieve very high electrical efficiencies. Standard Ni-YSZ anode-supported cells are used, on which a barrier layer and a LSCF composite cathode are deposited and sintered. Stack offers also a good robustness, more than 50 full thermal cycles been demonstrated without any significant performance drop. In early 2013 the stack has been transferred to the pilot production and has been integrated in the EnGen-2500™ cogenerators to be installed in field tests.

II. STACK PERFORMANCE

A typical performance map of this type of stack is shown in Fig. 1. Operated with a 60% H₂ = 40% N₂ mixture to simulate CPOX conditions, the stack is able to convert more than 90% of the fuel in a wide range of fuel flow rates. With a stack outlet temperature fixed at 800°C, the maximum electrical efficiency
achieved in such conditions is slightly above 60% (LHV) for a power density of 0.17 Wcm\(^{-2}\) and a fuel utilization of 94%. This is very close to the maximum achievable electrical efficiency for this fuel mixture and when operating in single pass fuel flow, i.e. at the point where the cell potential equals the fuel outlet’s Nernst potential (potential pinch).

At a nominal power density of 0.32 Wcm\(^{-2}\), the maximum achievable electrical efficiency is 55% using hydrogen as fuel (LHV).

At a nominal power density of 0.32 Wcm\(^{-2}\), the maximum achievable electrical efficiency is 55% using hydrogen as fuel (LHV).

Using steam-reformed natural gas as fuel, correspondingly high efficiencies can be achieved, as shown in Fig. 2 and Table 1. In this test, 50% of the methane was reformed externally before entering the stack. At the maximum fuel utilization of 95% and a current density of 0.31 Acm\(^{-2}\), a peak efficiency of 71% (LHV) was recorded. At a fuel-utilization of 85%, efficiencies were in a range of 61% to 65% for current densities of respectively 0.5 and 0.31 Acm\(^{-2}\) and a stack temperature of 750°C.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Power Density (Wcm(^{-2}))</th>
<th>FU</th>
<th>Max. efficiency</th>
<th>(T_{\text{air, outlet}}) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2 + \text{N}_2)</td>
<td>0.32</td>
<td>92%</td>
<td>55%</td>
<td>800°C</td>
</tr>
<tr>
<td>(\text{H}_2 + \text{N}_2)</td>
<td>0.17</td>
<td>94%</td>
<td>60%</td>
<td>800°C</td>
</tr>
<tr>
<td>SMR</td>
<td>0.25</td>
<td>95%</td>
<td>71%</td>
<td>750°C</td>
</tr>
<tr>
<td>SMR</td>
<td>0.37</td>
<td>85%</td>
<td>61%</td>
<td>750°C</td>
</tr>
<tr>
<td>SMR</td>
<td>0.27</td>
<td>85%</td>
<td>65%</td>
<td>750°C</td>
</tr>
</tbody>
</table>

Table 1. Overview of the stack performance under various operating conditions

Thanks to the good reversibility of the anode supported cells used in this work, the same stack concept has been tested under Solid Oxide Electrolysis (SOE) mode and SOFC/SOE cycles.

SOFC/SOE cycles were performed on a 6 repeating elements stack based on standard ASC. The test was performed at 700°C, under a 50vol% H\(_2\)/H\(_2\) atmosphere and by ranging the electrical load between 0.21 and -0.21 A/cm\(^2\). The current was applied by 0.21 mA cm\(^{-2}\) min\(^{-1}\) ramps, followed by a 10 min plateau at the maximum load. The calculated steam conversion is 24% at -0.21A/cm\(^2\). The results, given in Fig. 3, shows a very good stability of the voltage after 50 cycles.

Fig. 3. SOFC/SOE cycles performed at \(I = \pm 0.21\) Acm\(^{-2}\), at 700°C and 50vol\%H\(_2\)/H\(_2\)\(_2\).

These results demonstrate that, even using low-cost manufacturing processes, the new stack design is capable to reach excellent performances on both SOFC- and SOE-mode and on cyclic SOFC/SOE operation. This new stack concept is suitable for operation in natural-gas fuelled CHP systems offering electrical efficiencies of at least 50% net AC.

III. CONCLUSION

These results demonstrate that, even using low-cost manufacturing processes, the new stack design is capable to reach excellent performances on both SOFC- and SOE-mode and on cyclic SOFC/SOE operation. This new stack concept is suitable for operation in natural-gas fuelled CHP systems offering electrical efficiencies of at least 50% net AC.

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EXPERIMENTAL PROCEDURES FOR ACCELERATED AGING TESTS USING MCFC BUTTON CELLS
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Abstract - The aim of this work is to study whether the effects of electrolyte evaporation in long term operation of MCFCs can be accelerated at button cell level due to the increased rate of evaporation in the open-chamber configuration. This study is being carried out with several trials: the first trial aims to generate a benchmark of performance at button cell level, i.e. with accelerated electrolyte evaporation, at reference operating conditions, carrying out regular polarization curves and EIS until the performance degrades below a predefined level. The second trial aims to compensate the evaporation of electrolyte from the button cell by periodically adding carbonate and maintain a constant performance for the length of time that the first button cell (without carbonate addition) achieved. Once the isolated effect of electrolyte evaporation has been thus quantified, successive trials can be set up to superimpose other degradation and evaluate their interaction with the mechanism of electrolyte evaporation.

Index Terms - Accelerated test, electrolyte evaporation, electrolyte refilling.

I. INTRODUCTION
In order to introduce molten carbonate fuel cells (MCFCs) in commercial applications, the target lifetime of a MCFC has been set at 40,000 hours. One of the most promising application of MCFC seems to be the carbon capture, thanks to internal electrochemical reactions of the cell that allows to concentrate CO2 from cathode side (fed with exhaust gas of a power plant) to anode side. This particular application added more degradation phenomena (SO2 poisoning, present at the cathode inlet) and the interaction with other known degradation mechanisms (electrolyte evaporation) has to be studied to well understand how much the simultaneous presence of different mechanisms can influence the performance decay. To achieve this goal it will be crucial to understand how to perform tests in shorter times accelerating degradation phenomena. Button cells are particularly indicated to study a testing procedure for the acceleration of degradation phenomena because of their flexibility (shorter startup) and their (spatially) uniform operating conditions. This work will focus to establish the experimental procedures to separate the different contributes of degradation mechanisms and how to accelerate them.

II. RESULTS AND DISCUSSION
Accelerated testing it’s a big challenge for fuel cell, generally and for MCFC particularly, will be of crucial relevance to study how it is possible to carry out experiments and results in a faster way. The aim of this work it’s to define a procedure to separate the effects of electrolyte evaporation from other degradation phenomena such a way it will be possible to isolate the contribution of degradation due to the evaporation of electrolyte and superimpose other degradation phenomena (SO2 poisoning), distinguishing the different contribution to the performance decay it will be easier to accelerate one or another.

A. Background
Use of MCFC as CO2 concentrator it’s the final goal of this work but for a good operation 3% of CO2 it’s the lower limit. To simulate a real case (exhaust gas from a power plant at cathode side) several tests were carried out to determine which composition was more appropriated to use.

Fig.1: I-V curves at different CO2 concentration
The figure 1 shows the I-V curves performed with several concentrations of CO2 at cathode side, the concentrations are
representative of different exhaust gas of different power plants.

<table>
<thead>
<tr>
<th>MCFC gas mixtures used for accelerated testing trials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (%)</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>Cathode Standard Oxidant gas</td>
</tr>
<tr>
<td>Cathode CCS 6% CO₂</td>
</tr>
<tr>
<td>Anode gas</td>
</tr>
</tbody>
</table>

Fig.2: Gas composition

Gas composition used for experimental activities is a tradeoff between experimental apparatus and real operating conditions of an MCFC. CO₂ concentration of 6% seemed to be a good compromise.

B. Trials

The first trial aims to generate a benchmark of performance at button cell level, i.e. with accelerated electrolyte evaporation, at reference operating conditions, carrying out regular polarization curves and EIS until the performance degrades below a predefined level. Once that the first trial it’s finished it will be possible to evaluate the amount of electrolyte loss. The second trial aims to compensate the evaporation of electrolyte from the button cell by periodically adding carbonate and maintain a constant performance for the length of time that the first button cell (without carbonate addition) achieved.

Fig.4: superimposed effects

ACKNOWLEDGMENTS


Once the isolated effect of electrolyte evaporation has been thus quantified, successive trials can be set up to superimpose other degradation effects (due to contaminant poisoning, temperature, increased electric load etc.) and evaluate their interaction with the mechanism of electrolyte evaporation, such a way it will be easier to find a way to accelerate each degradation mechanism separately.
RESEARCH AND DEVELOPMENT OF HIGH TEMPERATURE ELECTROLYSIS AT ÚJV ŘEŽ, A. S.

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²Institute of Chemical Technology, Technická 5, 160 00, Prague 6, (Czech Republic)

Abstract - As many international research institutes, the Department of Hydrogen Technology, ÚJV Řež, a. s. works on application of solid oxide electrolysis cell for hydrogen production. In the past three years, the research team focused on preliminary investigation, feasibility study, equipment development and fundamental research. Currently, lab-scale equipment for the studying of high temperature electrolysis process has been designed, constructed and tested. The research group made rapid progress in the developing of own planar electrolyte-supported single cell based on yttrium-stabilized zirconia. The anode and cathode materials were applied by screen-printing method in cooperation with Institute of Chemical Technology in Prague. In addition, a sealing method based on combination of mica-paper layers with a high-temperature sealing paste was tested.

Index Terms – high temperature electrolysis, hydrogen production, SOEC

I. INTRODUCTION

It is predicted that hydrogen as an energy carrier would play a significant role in the future. Hydrogen technologies have a great potential to be an important part of energy transport and storage sector due to its possibility to be directly converted to electricity. As a promising hydrogen production method, high temperature electrolysis (HTE) using solid oxide electrolysis cells (SOEC) has recently received an increasing interest. This technology provides a large-volume and high-purity hydrogen production method, especially when it is coupled with a Gen IV nuclear reactor VHTR (very high temperature reactor) [1].

II. HIGH TEMPERATURE ELECTROLYSIS

The main advantage of high temperature electrolysis is a higher efficiency in hydrogen production in comparison with low temperature electrolysis. To achieve high overall hydrogen production efficiency inlet steam temperature needs to be 800 °C or above [2]. An electrolyzer is used for splitting of water into hydrogen and oxygen. Its function is based on reverse principle of Solid Oxide Fuel Cell (SOFC).

The test equipment of HTE used at ÚJV Řež is shown in figure 1. The reactants are introduced to the electrolyzer in form of a gaseous mixture from nitrogen, hydrogen and water vapor. The composition of the incoming mixture is controlled by two mass flow controller (MFC) for nitrogen and hydrogen, and by one liquid flow meter (LFM) for water. Water is vaporized in a controlled evaporator and mixer (CEM). The gas is heated to the operating temperature of 800 – 900 °C before entering the electrolyzer. After the electrochemical conversion the composition of the product gas is analyzed by determination of the water dew point (Tdp).

Fig. 1. Scheme of HTE experimental set-up at ÚJV Řež

A. Solid oxide electrolysis cell components

The SOEC basically consists of three main layers. There is...
an ion-conducting gastight electrolyte in the middle. Today the most common material used for electrolyte is an yttria-stabilized zirconia (YSZ, typically with 8 mol% of Y₂O₃). Second and third layer represent electrodes deposited on one and the other side. A cathode basically consists of a cermet of nickel oxide (NiO) and YSZ material to provide a porous structure. An anode is applied on the other side of electrolyte. There have been tested many different anode materials, the one of the most common is an LSM – lanthanum-strontium-manganite. This standard design has been chosen for the cell testing at ÚJV Řež.

The tested SOEC has been based on a planar electrolyte prepared by CoorsTek Advanced Material Company. The electrolyte has been made by pressing and sharpening to thickness of 250 µm. The layers of both electrodes have been made from commercially available powders (NexTech Materials) and applied by screen-printing method. An active area of the tested electrolysis cell corresponded to 10 cm². As a main sealing components a mica paper frames of different thicknesses have been used. Interconnects with flow fields for gas (water vapor, nitrogen) distribution have been prepared from Crofer 22 APU. All components materials, method for their fabrication, thicknesses and suppliers are presented in table I. Cell testing scheme and its photo are shown in figure 2.

### TABLE I

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
<th>Supplier</th>
<th>Method</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>Yttria-stabilized zirconia (8YSZ)</td>
<td>CoorsTek Advanced Materials</td>
<td>Pressing</td>
<td>0.25 mm</td>
</tr>
<tr>
<td>Anode</td>
<td>Lanthanum-Strontium-Manganite (LSM)</td>
<td>NexTech Materials</td>
<td>Screen-printing</td>
<td>0.05 mm</td>
</tr>
<tr>
<td>Cathode</td>
<td>NiO/8YSZ cermet</td>
<td>NexTech Materials</td>
<td>Screen-printing</td>
<td>0.05 mm</td>
</tr>
<tr>
<td>Interconnects</td>
<td>Crofer 22 APU</td>
<td>UnionOcel</td>
<td></td>
<td>1.00 mm</td>
</tr>
<tr>
<td>Sealing</td>
<td>Mica paper</td>
<td>fuelcellmaterials.com</td>
<td>Screen-printing</td>
<td>0.25 mm, 0.50 mm</td>
</tr>
</tbody>
</table>

**Fig. 2. Scheme (left) and realization of SOEC testing (right)**

**B. I-V characteristic**

The electrolysis cell described above has been tested under conditions of 800 °C. I-V curve from testing is shown on the figure 3. Obtained current densities are relatively low (0.05 A.cm⁻² at 1.5 V) when compared with state of the art [1, 2]. There are two main reasons: Firstly a higher initial area specific resistance (ASR) values are typical for electrolyte-supported cells due to the bulk resistance of electrolyte (250 µm compared to ~10 µm for electrode-supported SOEC). Secondly the low current densities are given by an insufficient ionic conductivity of electrolyte, probably caused by excessively sintered YSZ grains due to manufacturing method.

**III. CONCLUSION**

Experimental equipment for high temperature electrolysis has been developed and constructed at ÚJV Řež, a, s., Czech Republic. This equipment allows testing of solid oxide electrolysis cells and short stacks. First experiments have been conducted with a single SOEC (10 cm²) completely prepared by ÚJV Řež in cooperation with Institute of Chemical Technology Prague. The obtained I-V curve shows a potential for improvement of SOEC performance by means of layer preparation and deposition. Plans for the near future are production, testing and evaluation of anode-supported SOECs as well as the possibility of HTE coupling with high-temperature nuclear reactors.

**ACKNOWLEDGMENT**

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**REFERENCES**


EXPERIMENTAL AND THEORETICAL ANALYSIS OF BIOGAS REFORMING FOR SOFC APPLICATIONS

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Abstract – An investigation on biogas reforming reaction have been carried out. The inlet gas mixture consisted of CH₄/CO₂ (60/40 vol.%) as a model biogas composition was taken into account. Experiments were carried out, varying reforming process (dry, steam and autothermal reforming). Subsequently, optimal operational windows were identified in order to supply a solid oxide fuel cell (SOFC) system.

Index Terms – Biogas, Coke, Refomer, SOFC

I. INTRODUCTION

In this last years the hydrogen production from biogas has attracted particular attention. The biogas stream composition depend on the raw material, anyway, the most important components are methane (approximately 60%) and carbon dioxide (40%) [1]. The potential use of biogas in fuel cells could represent a way to increase its conversion efficiency and reduce NOx emissions to the atmosphere. In particular, high temperature fuel cells, i.e., solid oxide fuel cells (SOFC) offer the peculiarity of being able to tolerate the presence of impurities in the fuel, more than other fuel cell technologies [2]. However, in order to operate FCs supplied by biogas, a reformer section have to be designed in order to convert the biogas into a hydrogen rich gas mixture. However, this last process is affected by some problems that remain to be solved, one of these is related to the carbonaceous deposition. Considering the impressive efforts addressed towards the development of SOFCs, a wide investigation has been carried out to evaluate the potential use of biogas as a fuel for these systems. In particular, the conversion of a simulated biogas (CH₄/CO₂=60/40%) and the effects of steam and oxygen as gasifier agent have been explored with respect to CH₄ conversion and carbon formation rate. In this way, the process performance under thermodynamic and kinetic conditions were analyzed with respect to major operational parameters: oxygen/carbon and steam/carbon ratios.

II. BIOGAS REFORMING TESTS

Catalytic biogas reforming process is, generally, affected by the risk of carbon formation, therefore, performances of dry (DR), steam (SR) and autothermal reforming (ATR) of a simulated biogas stream (CH₄/CO₂=60/40%) were investigated at 1073K and 150,000 h⁻¹ of GHSV (see Table I) in order to evaluate the activity and stability of a suitable catalyst (G56-A, SUD-CHEMIE) [3].

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>OPERATIVE CONDITIONS USED IN CATALYTIC REFORMING TESTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H₂O)/(CH₄)</td>
<td>(O₂)/CH₄</td>
</tr>
<tr>
<td>DR</td>
<td>1.2</td>
</tr>
<tr>
<td>SR-1</td>
<td>2.5</td>
</tr>
<tr>
<td>ATR-1</td>
<td>1.2</td>
</tr>
<tr>
<td>ATR-2</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Results reported in Fig. 1 depict that when steam was added, into feed gas composition, until to reach 1.2 molar ratio of steam/carbon (SR-1), CH₄ conversion increased in comparison to DR run test. However, adding more steam (SR-2) a conversion rate very close to SR-1 (63%) was detected, moreover an evident catalytic deactivation was observed. This behavior suggest that the presence of steam in the inlet gas composition increases appreciably the biogas reforming process. Nevertheless, an excessive increase of S/C ratio (SR-2) did not improve the methane conversion.

According to literature data, this result confirms that, at high temperature (>1023K) and GHSV rate, CH₄ conversion remains practically constant and independent from S/C [4].

Anyway, SR-2 experiments showed, also, an evident catalytic deactivation trend, that appeared contrary to thermodynamic calculation. In this way, TEM analysis highlighted that the Ni catalyst used in SR-2, has been effected by sintering (increasing of particle diameter from 20nm to 46nm).
Catalytic performance carried out in ATR conditions showed that CH₄ conversion increased with O₂/C ratio, moreover higher CH₄ conversion values were depicted than SR operative conditions. Finally, the carbon formation rate detected on used sample catalysts showed that the carbon formation could be eliminated in presence of steam and/or oxygen in the inlet gas composition (Fig. 2).

On the basis of the results obtained, two experimental tests (SR-1 and ATR-2) were performed at low GHSV (15,000 h⁻¹), in order to obtain the molar fractions product by reforming processes selected under thermodynamic conditions. Results presented in Table II where CH₄ conversion was about 98% for all tests and no carbon formation was detected on samples used catalyst (after 40 h).

### III. SOFC SYSTEM CONFIGURATION

The influence induced by syn-gas production process on a SOFC has been evaluated on the basis of a mathematical model. In particular, in order to find out the best syn-gas composition for SOFC, it was decided to compare the polarization curve for a SOFC monocollex fed with different syn-gas. The trend of voltage losses at different current densities has been obtained taking into account experimental data on a single cell by 100 cm² obtained from experimental tests already carried out.

To calculate polarization curves has been assumed that: i) ohmic losses are not influenced by inlet gas compositions; ii) the influence of the inlet syn-gas composition on activation losses is negligible, whereas the differences in inflows composition is not likely to induce a significant error; iii) diffusional losses, dependent by gas compositions.

Fig. 3 shows polarization curves of the SOFC fed with different reform gas, as previously described. It is evident that the autothermal reforming of biogas is the most efficient syn-gas production process to be integrated with SOFC. In fact, the overall effects of reactants concentration, due to biogas ATR process, produce an overall positive effect on cell voltage.

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ACKNOWLEDGMENT

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THEORETICAL STUDY OF THE ORR MECHANISM ON IRON, COBALT AND MANGANESE MACROCYCLE ACTIVE SITES

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Abstract - The best performing non-precious PEM fuel cell catalysts so far have been manufactured by incorporation of iron and cobalt to carbon in the presence of nitrogen. First principles calculations have been performed to investigate the oxygen reduction reaction (ORR) on active sites within transition metal macrocycle structures containing iron, cobalt or manganese. The effect of the transition metal nature, as well as the macrocycle type, has been investigated. It has been found that the efficiency of the active site is dependent on the transition metal, but is independent on the type of macrocycle. Models of the active sites have been proposed and the detailed potential energy profiles of the ORR overall process including all intermediate steps have been obtained. In the macrocycle-based active sites, iron central atom demonstrates the highest ORR activity, cobalt gives a slower reaction rate, and manganese may favour hydrogen peroxide formation.

Index Terms – active sites, oxygen reduction reaction mechanism, transition metal macrocycle.

I. INTRODUCTION

The problem in the development of non precious PEM fuel cells catalysts is to identify the structure of their active sites and determine the mechanisms of the oxygen reduction reaction (ORR) on them. The most promising experimental performance among non precious catalysts has been demonstrated by carbon based materials that contain iron and cobalt in the presence of nitrogen. In this paper, first principles calculations have been used to study the ORR mechanisms on iron (Fe), cobalt (Co) and manganese (Mn) macrocycle-based active sites.

This first principles study involves the following elements. (i) Investigation of the effect of macrocycle structure and calculation of the binding energies of molecular oxygen on the four macrocycles with Fe, Co or Mn atoms in the centre; (ii) Investigation of the effect of the transition metal atoms in the centre of a selected macrocyclic structure on the ORR. The ORR potential energy profiles have been constructed including all intermediate steps of the reaction. (iii) Proposing modified models of the active sites based on a transition metal macrocycle structure and obtaining the refined ORR potential energy profiles.

II. COMPUTATIONAL DETAILS

All calculations have been performed with Gaussian09. Molecular oxygen chemisorption on different macrocycles has been calculated using HF/3-21G model chemistry in vacuum. The ORR mechanism investigations have been performed using the B3LYP/6-31G density functional theory (DFT) method, and accounting for the solvent effect of water.

III. RESULTS AND DISCUSSION

A. Effect of macrocycle structure

Based on experimental and theoretical studies of non precious catalysts, four types of macrocycles have been identified and employed in the calculations: phthalocyanine, porphyrine, corrin and tetraaza-annulene. Relative energy levels of molecular oxygen chemisorption on the four types of Fe, Co or Mn macrocycles have been obtained and arranged in diagrams illustrating the optimized product structures. It has been found that the energy of molecular oxygen chemisorption on the Fe, Co or Mn macrocycles do not correlate with the types of macrocycles but rather depends on metal-oxygen and metal nitrogen interatomic distances, i.e. the metals’ oxidation state. Thus, the strength of molecular oxygen chemisorption is insensitive to the local geometry of a macrocycle-based active site, and the efficiency of such an active site is independent on the type of macrocycle.

B. Effect of transition metal

Since it has been concluded that the vicinal macrocycle structure does not influence the efficiency of the active sites,
the structure of tetraaza-annulene has been chosen to investigate the effect of transition metals: Fe, Co and Mn. High exothermic values of the calculated molecular oxygen chemisorption energies indicate that the metal centre in the macrocycle is blocked at one side by a functional group, e.g. OH. The ORR thermodynamics has been modeled on the other side of the OH-blocked macrocycle with either Fe, Co or Mn in the centre, as illustrated in Figure 1.

![Fig. 1. OH-blocked Fe macrocycle.](image)

Two and four electron pathways of the ORR have been modeled, and Table I provides the calculated energies of the ORR elementary steps on the Fe, Co and Mn macrocycles.

<table>
<thead>
<tr>
<th>Elementary ORR step</th>
<th>Energy, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactants</td>
<td>0</td>
</tr>
<tr>
<td>Molecular oxygen chemisorption</td>
<td>-0.64</td>
</tr>
<tr>
<td>First H addition</td>
<td>-2.53</td>
</tr>
<tr>
<td>Second H addition (4 electron pathway)</td>
<td>-4.90</td>
</tr>
<tr>
<td>Second H addition (2 electron pathway)</td>
<td>-2.59</td>
</tr>
<tr>
<td>H₂O₂ desorption</td>
<td>-0.18</td>
</tr>
<tr>
<td>Third H addition</td>
<td>-3.14</td>
</tr>
<tr>
<td>Fourth H addition</td>
<td>-2.80</td>
</tr>
<tr>
<td>2H₂O desorption</td>
<td>-0.15</td>
</tr>
</tbody>
</table>

### C. ORR mechanisms on the Fe, Co and Mn N-coordinated model clusters

In order to evaluate kinetic aspects of the ORR on Fe, Co and Mn macrocycle active sites, activation barriers of the elementary reactions have been determined using the technique of a “relaxed” potential energy surface (PES) scan. The size of the macrocycles has been reduced to smaller metal-nitrogen coordinated systems with all the C-N and C-C bonds set constant and equal to those in the large macrocycle shown in Figure 1. The smaller model systems are henceforth referred to as M-4N clusters, where M = Fe, Co or Mn.

Modeling the ORR on Fe-4N using the PES scan calculations resulted in obtaining two four electron pathways and referred to as the H₂O₂ and HO-HO mechanisms, each proceeding via 5 intermediate structures, as illustrated in Figure 2. Notably, a two electron pathway leading to hydrogen peroxide formation has not been found. The dashed lines in Figure 2 denote that PES scan calculations for those steps did not identify an activation barrier. Non-zero activation barriers have been obtained only on the step of third H addition.

Considering the non-activated potential energy profile, it is suggested that the Fe-4N active site might be very effective in catalyzing the ORR in the four electron pathway.

![Fig. 2. ORR mechanisms on the Fe-4N cluster.](image)

Similarly, the ORR mechanisms have been obtained on the Co-4N and Mn-4N clusters. For the Co-4N cluster, few ORR steps of the four electron pathway have been found to have non-zero activation barriers, unlike for the Fe-4N cluster. Active sites modeled by Mn-4N clusters have been found to be potentially ORR active via both two and four electron mechanisms.

### IV. CONCLUSION

The ORR has been studied on the active sites constructed based on Fe, Co and Mn macrocycles. The energies of molecular oxygen binding on the macrocycles do not correlate with the types of macrocycles but depend on the degree of metals’ oxidation state. Therefore, the efficiency of the active sites is independent of the type of macrocycle but is determined largely by the transition metal. The metal centre in a macrocycle should be blocked by a functional group, e.g. OH group, at one side, and the ORR can occur at the other free side of the macrocycle. The ORR energy diagrams on these clusters show that the Mn-containing active centre binds molecular oxygen stronger than Fe and Co active centres and thus is likely to remain blocked with a second OH group. Potential energy profiles obtained on the smaller model systems confirmed that transition metal nature is the factor influencing the ORR kinetics. Fe atom in the centre of active sites accounts for the highest activity. The ORR kinetics on Co centre should be slower than that on Fe. The Mn active centre allows for relatively easy hydrogen peroxide formation.

**ACKNOWLEDGMENT**

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FORMIC ACID AS A SUITABLE MATERIAL FOR H₂ AND CO₂ CATALYTIC STORAGE AND RELEASE

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Abstract - Herein, we present the catalytic hydrogen (H₂) release from the renewable fuel formic acid (FA, HCO₂H) under ambient conditions. Also, reversible hydrogen storage as FA or formates is provided by highly stable catalysts even at room temperature. The way to continuous FA dehydrogenation is exemplified by the set-up of a pressure stable reaction system. This was used for stability and performance tests as well as subsequent catalyst optimization to yield a suitable hydrogen gas mixture for its direct use in fuel cells (FC). The ruthenium catalyst was stable for 45 days performing H₂ generation with a turnover number (TON) of one million at room temperature. Hydrogen flows of 47 L/h could be achieved in the 100 W electrical power range. Finally, looking for cheap and abundant metals, an iron-based catalyst system has been developed with high activity and stability comparable to those of noble-metal based catalysts.

Keyword - Catalytic Dehydrogenation, Formic Acid, Hydrogen Storage, Ruthenium

I. INTRODUCTION

Formic Acid (FA, HCO₂H) is a promising hydrogen storage material which allows catalytic hydrogen release already at room temperature. Also, FA can be formed by hydrogenation of CO₂ thus linking favourably H₂ generation with the valorization of CO₂ to a renewable fuel. Apart from using FA in a direct methanol fuel cell (DMFC), the released gas mixture (H₂ + CO₂) from FA could be used directly in a LT-PEM fuel cell if the CO content is low (< 10 ppm). The idea is the realization of a CO₂-neutral storage cycle, composed of hydrogenation of CO₂ with renewable hydrogen, e.g. from water, to form FA and H₂ release from FA for conversion to electrical energy in fuel cells (Fig. 1). Therefore, catalysts need to be selective, active and stable. So far, the dehydrogenation of FA has been mainly advanced by homogeneous noble-metal catalysts, such as ruthenium, which is the most active one to date.

II. CATALYTIC H₂ GENERATION AND GAS ANALYSIS

In our catalytic tests, we applied mainly ruthenium (Ru) catalysts. The released gas during catalysis from FA/formates was analyzed via gas-chromatography and quantified with gas burettes or gas flowmeters.

III. ON THE WAY TO REVERSIBLE HYDROGEN STORAGE

A. Using Bicarbonates

A single catalyst is capable of catalyzing formate dehydrogenation to bicarbonate and the back reaction with full conversion even at room temperature: [RuCl₂(benzene)]₂ / 3 equiv. bis-(diphenylphosphino)methane (dppm) in a DMF/H₂O mixture (Fig. 2, left).
B. Using CO₂

With a defined catalyst [RuH₂(dppm)₂], 8 hydrogenation/dehydrogenation cycles could be run in the presence of amine with only slight deactivation of the catalyst (Fig. 2, right). The catalyst performed 800,000 turnovers.⁰

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IV. CONTINUOUS HYDROGEN GENERATION FROM FORMIC ACID

With respect to small-scale applications, it is necessary to provide constant H₂ flows with sufficient quality for the H₂/O₂ PEM fuel cells. In a first generation set-up, commercial FA was fed (0.74 mL/h) to a glass reactor containing 10 µmol [RuCl₂(benzene)]₂ / dppe in amine. It was possible to generate H₂ (0.45 L/h) over 11 days with high catalyst performance of 260,000 (TON) at room temperature (CO < 10 ppm).⁵

Then, 20 µmol of the same catalyst were applied at 80 °C and higher FA dosation (82.6 mL/h) which gave 800,000 turnovers and 47 L H₂/h (~ 130 W) (CO < 10 ppm).

In a third generation, glass components, such as reactor (Fig. 3), cooler and tubes were substituted by stainless steel to allow higher hydrogen flows and a pressure stable system.

By using [RuCl₂(benzene)]₂ and 1,2-bis(diphenylphosphino)-ethane (dppe) the active catalyst was formed in situ and H₂ generation was achieved by FA dosation. At room temperature, this catalyst was stable for more 45 days reaching an outstanding turnover number > 1,000,000. To reach higher H₂ flows, the reaction conditions were optimized and 47 L H₂ per hour were generated at 60 °C corresponding to an electrical power of 70 W. Finally, the FA reactor was connected to a low temperature PEM FC set-up including heat exchange where more than 50 W electrical power have been produced.⁶ The CO₂ did need to be separated from H₂ before feeding the gas into the fuel cell. During the lecture the development and set-up will be shown in more detail.

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VI. CONCLUSION

During the lecture we will present active and stable ruthenium catalysts for clean H₂ generation from formic acid and reversible H₂ storage in FA and formates. H₂ generation from formic acid could be scaled up with the established ruthenium catalyst resulting in impressive H₂ rates. Besides, the quality of the released gas mixture (CO < 10 ppm) allows for continuous operation of a fuel cell. Apart from ruthenium, also iron catalysts were shown to be very active for H₂ generation from formic acid under base-free conditions.

ACKNOWLEDGMENT

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REFERENCES

INTEGRATION OF MCFCS AND MEMBRANES FOR CARBON CAPTURE IN NATURAL GAS POWER PLANTS

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Abstract - MCFCs and gas separation membranes were integrated for CO₂ segregation applied to a NGCC (Natural Gas Combined Cycle) plant.

Using distributed parameter models for the fuel cells and for the membranes in a global plant simulation, it was possible to take into account both the fuel cell operational constraints and the specific limitations of the membrane technology. In particular, a new kinetic model experimentally validated was used for the MCFC simulation in order to correctly take account of CO₂ concentration effects on performance.

Moreover, a key finding was that large carbon dioxide recoveries are only possible if the maximum temperature limit on the MCFC cell plane is tackled, so that, in comparison with authors' previous works, also a proper cathode recirculation has been added.

Results showed that NGCC-fuel cells-membranes system outperforms conventional capture technologies especially in terms of a reduced impact on the electrical conversion efficiency.

Index Terms - Molten Carbonate Fuel Cells, Carbon Capture, Membranes, Natural Gas Combined Cycle, Simulation.

I. INTRODUCTION

Although currently the price of emitting carbon dioxide is at an all-time-low, there are hints from the EU commission towards a revised approach for the third phase (2013-2020) of the EU Emissions Trading System. Even if natural gas is a clean and relatively abundant fossil fuel, to remain competitive on the market, combined cycle power plants will need practical and sustainable capture solutions.

One promising option for NGCC (Natural Gas Combined Cycle) is to employ MCFCs for CO₂ concentration and GSM (gas separation membranes) for CO₂ segregation.

This paper analyses distributed parameter models for fuel cells and membranes in a global plant simulation, so as to propose an optimized NGCC-MCFC-GSM process configuration that takes into account both fuel cell operational constraints and the specific limitations of membrane technology.

II. REFERENCE PLANT

A reference, state-of-the-art, NGCC plant with a 800 MW electrical output was taken as the base case [1]. The process model is based on simplified box units for the open cycle (OC) and the steam cycle (SC). Integration of the base NGCC power plant with a CO₂ concentration/separation MCFC-GSM unit is obtained by interposing latter unit between the OC and the SC to treat the high-temperature OC exhaust, as shown in Figure 1.

Fig. 1. NGCC-MCFC-GSM integrated solution

By this way the OC exhaust is sent to the MCFC-GSM unit to reduce its CO₂ content (about 4%) before being expelled as flue gas (with about 2% of CO₂), while the concentrated CO₂ stream (quite pure) is sent to transportation and then to storage. The actual fuel for the MCFC is provided by an other amount of natural gas which is fed into the MCFC-GSM unit and converted here into hydrogen in a reformer.

Details of the MCFC-GSM unit are shown in Fig. 2.

Thanks to the electrochemical reactions, the CO₂ coming from the OC and fed to MCFC cathode is transferred to the MCFC anode, where it is concentrated up to about 35%. Then, after a condensation step, which allows the achieving of a CO₂ concentration of about 60%, the gas is fed to the GSM, where CO₂ is finally separated.

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A cathode recycle is added to optimize temperature management, which resulted a critical aspect in a previous authors’ work [2], where plant model details are discussed too.

Another feature of the present approach is the new semi-empirical model of the MCFC electrochemical kinetics. It was developed for laboratory and industrial simulation [3] and now used in the present fuel cell model. The rigorous theoretical approach which it is based on takes account of polarizations due to chemical as well as physical phenomena, but the number of parameters to be identified in the kinetic formulation was reduced to the minimum, in order to obtain an effective, accurate, but at the same time simplified instrument.

The resulting kinetics formulation is:

\[ V = E - R_{tot} J = E - (R_{ohm} + R_{cat} + R_{an}) J \]  \hspace{1cm} (1)

where

\[ R_{ohm} = P_1 \cdot e^{P_{2/T}} \]  \hspace{1cm} (2)

\[ R_{cat} = P_3 \cdot T \cdot e^{P_{6/T}} pCO_2^{-1} + P_2 \cdot T \cdot e^{P_{5/T}} pO_2^{-0.5} pCO_2 \]  \hspace{1cm} (3)

\[ R_{an} = P_4 \cdot T \cdot e^{P_{7/T}} pH_2^{-0.5} \]  \hspace{1cm} (4)

Parameter identification was performed thanks to experimental tests carried out in the range of interest of low CO₂ concentrations at the Fuel Cell Center laboratories of Korea Institute of Science and Technology (KIST) using 100 cm² single cell facilities [3]. I-V curves, EIS and gas analysis were carried out to support the investigation.

In particular, such a formulation allowed the evaluation of CO₂ concentration effects on MCFC performance, that is of great importance in this application aimed to carbon capture.

IV. SIMULATION TOOL

The modeling tool used to perform the process simulations was LIBPF version 1.0.1015 [4]. To make it possible to perform a trial-and-error design procedure to find the optimum operating parameters, we adopted the intermediate fidelity modeling approach for the MCFC and GMS units. This solution played a key role in accelerating the process of understanding the complex interactions between the subsystems, and obtaining an optimized configuration compliant with all constraints.

On a typical workstation, the calculation time for the intermediate-fidelity model is in the range of minutes for the first execution, and about 2 seconds for subsequent evaluations.

V. CONCLUSION

An innovative configuration based on NGCC-MCFC-GSM integration was been preliminary studied [2] putting in evidence a great margin for improvement by increasing fuel and CO₂ utilization factors. In that case, the limits due to diffusion effects for high conversion factors and the maximum hot-spot temperature in fuel cells resulted the main process limitations.

In the present work, thanks to the use of a proper MCFC kinetics model and the introduction of a cooled cathode recycle, these limits have been tackled.

The results confirmed the proposed configuration as a very interesting solution able to couple carbon capture to an additional energy generation.

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ANALYSIS OF THE OPERATING STRATEGY OF A SOFC BASED UNIT FOR THERMAL AND ELECTRIC RESIDENTIAL LOADS

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Abstract – In order to bring High Temperature Fuel Cells (HT-FCs) on the market, on-site experiments are crucial to understand HT-FCs based units performance and their actual applicability to residential power generation. The authors present here the results of recent experimental and numerical analysis conducted on a micro-cogenenerative Solid Oxide Fuel Cells (SOFCs) based unit. A new measurement system has been designed by the authors on the basis of an a-priori uncertainty analysis, and additional meters have been installed in order to perform an a-posteriori uncertainty analysis. Effective application of HT-FCs to residential use has been studied using the validated numerical model developed by the authors in order to follow electric and thermal loads, and technical and economic analysis have been carried out.

Index Terms – solid oxide fuel cell, energy balance, electricity cost, measurement system.

I. INTRODUCTION

In the last few years, the authors conducted both numerical and on-field experimental activities on a 5 kW micro-cogenenerative SOFC based unit, also developing an a-priori uncertainty analysis on the basis of the on-board instruments metrological features declared by the manufacturer [1, 2]. In order to accurately reproduce everyday residential electric energy needs, a variable electric load has been connected to the unit, while fan coils have been installed in order to reproduce thermal loads in the cogenerative loop.

Besides experimental work, the authors developed a 0D numerical model able to reproduce the behavior of the micro-cogenenerative module under investigation. The model allowed to investigate thermal management related issues, highlighting the conditions in which the micro co-generative unit is able to efficiently operate avoiding undesired shut-downs.

In this paper, the authors numerically reproduce the actual behavior of the micro-cogenenerative unit for residential use. The effective application of this device to actual residential needs is assessed, following electric and thermal loads. Moreover, the authors present here the new measurement system, with higher metrological performance, that has been installed on the basis of the a-priori uncertainty analysis, in order to perform an a-posteriori uncertainty analysis.

II. SOFC COGENERATION UNIT

The cogenerative unit under investigation is fed by natural gas, which is converted in a mixture of hydrogen (H2) and carbon monoxide (CO) in a catalytic partial oxidation reformer. A sketch of the main components of the system, together with the main information about the on-board measuring system, is presented in Fig. 1. The system is capable to produce a maximum of 5 kW of electric power and is also equipped with a heat recovery section for the production of hot water for residential needs. Detailed information about the system are available elsewhere [1, 2] and are not presented here for the sake of brevity.

III. THE NUMERICAL MODEL

The mathematical model developed by the authors to analyze the operating conditions of the SOFC-based micro-cogenenerative unit is based on the mass, energy and entropy balance equations applied to five control volumes used for simulating the SOFC module (Fig. 1): the partial oxidation section, the stacks, the cathodic air pre-heater, the off gas burner and the heat recovery section. The equations have been solved under the following assumptions: one-dimensional flow, steady-state conditions, and ideal gas behavior. The numerical
The uncertainty analysis carried out by the authors in a recent work [2] highlighted the need to have more accurate measurements of the volumetric flow rate of fuel and air. Therefore, meters with better metrological performance, and properly calibrated, have been employed to perform an a-posteriori uncertainty analysis.

The new measurement system includes a digital board which controls a group of relays that have been inserted between the module and the electric load to remotely control the power-up and shutdown of electrical loads. Two current and two voltage transducers have been inserted in the electrical circuit, in order to measure the actual electrical power absorbed by the lamps. The transducers have been installed upstream and downstream of the inverter, therefore it is possible to calculate the electric efficiency of the inverter. In the cogenerative loop, four Pt100 resistance thermometers have been installed. An electromagnetic flow meter has been installed on the return pipe, to provide current signal of 4-20mA, acquired by the data acquisition card, after transformation into voltage by means of resistors.

V. MODELING UNIT’S OPERATION UNDER RESIDENTIAL LOADS

In order to study the effective use of the SOFC based micro-cogenerative unit under investigation to residential applications, two constant load operations have been considered in this work: 1 kW and 2 kW. Monthly and daily energy (both electric and thermal) needs have been obtained from [3]. In the following analysis it has been assumed that electricity costs are regulated in two rates: F1, during the day, that corresponds to the most expensive rate; F23, the cheapest one, applied during night time. The adopted criterion was to fit as near as possible electric needs during the day (F1 rate), when electricity costs are higher, and keep the module operating at its minimum power (power required for on-board auxiliary equipment operation) during the night. As a consequence, the unit has been supposed to operate from 8.00 to 19.00 during winter and from 8.00 to 18.00 during summer.

Table 1 shows the energy balance, over a year, for the unit operating at 1 kW and 2 kW, respectively. From Table 1 it can be easily observed that operating at 1 kW of output power, the energy produced by the unit better fits typical energy needs of domestic users during the F1 rate.

As regards the thermal energy produced, the only advantageous option from the economic point of view would consist of keep the module operating at its minimum power during the night (F23 rate period). In particular, in order to satisfy typical residential thermal energy needs for domestic hot water, it has been supposed the SOFC based unit connected to a 300 l tank, containing water heated from 10–15°C up to 65°C. In such conditions, the SOFC based unit is able to satisfy thermal energy needs during the daily operation (F1 rate period) and a money saving of about € 700 could be achieved.

VI. CONCLUSION

The 0D mathematical model has been used to assess the performance of the unit in typical residential applications. In particular, the most advantageous condition consists of operation at a constant electric power of 1kWe during the day, switching off the unit during the night.

A new measurement system has been designed for the unit on the basis of the uncertainty analysis carried out by the authors, and additional meters characterized by better metrological performance have been installed in order to perform an a-posteriori uncertainty analysis.

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ANIONIC EXCHANGE MEMBRANES FOR FUEL CELL APPLICATIONS


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Abstract - The preparation and characterization of polymeric anionic membranes for alkaline fuel cells were investigated. Starting from chloromethylated aromatic polymer (PSU), we introduced anionic exchange groups by reaction with different kinds of amines. The characterization was done studying various chemical and physical parameters of the membrane using various techniques like NMR and impedance spectroscopy, TGA and water uptake measurements. Good results are obtained in terms of stability and ionic conductivity; the amines utilized and the degree of chloromethylation of the polymer strongly influence the final properties.

Index Terms – anionic, conductivity, ionomers, PSU

I. INTRODUCTION

The need for reduction of pollution and the continuous increase of petrol cost have reinforced the impact of fuel cells (FCs) for the conversion of fuels into energy.

We focus our attention on polymer electrolyte membrane fuel cells, because they exhibit excellent characteristics of weight, volume and current density for automotive application and cogeneration systems [1].

Taking advantage of our previous studies and knowledge about proton exchange membranes [2,3,4,5], our recent investigations are focused on the development of anionic exchange membranes (AEMs) for FCs, which have several advantages: i) faster fuel cell reaction kinetics, ii) less expensive metal electrodes, iii) less corrosion problems, iv) the possibility to use various fuels, v) less fuel crossover. However, AEMs generally present lower ionic conductivity, low stability and risk of carbonation [6].

II. EXPERIMENTAL PART

A. Polymer synthesis and membrane preparation

The synthesis is based on aromatic polymers, such as PSU and PEEK [7], which can have tailored structures with desired properties by use of various monomers or by post-functionalization. They can be synthesized by relatively inexpensive procedures, can be easily cast as membranes, are relatively free from environmental pollution problems, can be recycled, are stable in oxidative and reductive media, and present a low gas permeability.

We synthesized anionic aromatic polymers (in particular PSU) by the reaction of a chloromethylated precursor with different degree of substitution with various amines (fig. 1), such as trimethylamine and cyclic amines. The amines were chosen to explore the stability in alkaline medium of the anion exchange membrane.

![Fig. 1. Amination reaction](image)

Membranes were obtained by casting in DMSO or other solvents (fig.2).
In order to further stabilize the membranes we cross-linked the amminated polymers via sulfone bridges by simple thermal treatments.

Fig. 2. Example of PSU-trimethylammonium hydroxide membrane after casting

B. Characterization

The membranes were characterized by different techniques (NMR, water uptake, titration, thermogravimetry TGA). Fig. 3 shows a typical $^1$H NMR spectrum of chloromethylated PSU. The degree of chloromethylation (1.2) is determined from the area of the peak around 4.5 ppm.

Fig. 3. $^1$H NMR spectrum of chloromethylated PSU in DMSO-d$_6$

As shown by TGA (fig. 4), the main chain decomposition is observed above 400°C; peaks at lower temperature are due to solvent evaporation and decomposition of ammonium groups. We demonstrated that the hydration in liquid water strongly depends on the amine utilized and on the degree of chloromethylation of the polymer. We also studied the anionic conductivity by impedance spectroscopy using a Swagelok cell both in 2M KOH and in water. We reach in KOH a conductivity of $5.8 \times 10^{-2}$ S/cm in the case of trimethylamine (degree of amination = 0.85); the conductivity after 24 h immersion in water is $1.2 \times 10^{-2}$ S/cm, almost stable after 240 h of immersion.

III. CONCLUSION

Perspectives of this work: 1) find the optimal degree of amination for the best compromise between high conductivity and low swelling, 2) use precursors with the highest stability in alkaline medium, 3) improve the casting conditions in terms of handling and operation procedure.

Fig. 4. TGA of the PSU-trimethylammonium-hydroxide derivative

ACKNOWLEDGMENT

The financial support by the Franco Italian University (UFI/UIF), Vinci 2013 program, is gratefully acknowledged.

COMMENT OF THE REFEREE

The work is interesting but it should include some electrical characterizations of fuel cell membrane. It is needed to arrange the manuscript following the guidelines for Authors.

REFERENCES


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LATTICE-BOLTZMANN-BASED MODEL FOR THE CHANNEL-POROUS INTERFACE OF PEMFC

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Abstract - Two-phase flow management is a major issue in the optimization of Polymer Electrolyte Membrane Fuel Cells (PEMFCs). The purpose of the present study is to identify the most significant single-phase and two-phase flow mechanisms in porous media and porous interfaces such as the gas channel (GC) – gas diffusion layer (GDL) interface with the Lattic-Boltzmann algorithm. In particular, a Lattice Boltzmann Shan-Chen two-phase method with mid-range interactions and with a special pseudopotential inhibition treatment is firstly validated in a single-phase representative domain within the theoretical framework of Spatially Averaged Navier-Stokes (SANS) equations. Secondly, it is used to perform two-phase numerical simulations with varying porous medium hydrophobicity. Pressure drag and skin friction have been found to play a pivotal role in the gas phase momentum transfer across porous medium. Moreover laminar separation zones have been noticed at the open-porous interface.

Index Terms – Lattice-Boltzmann, multi-phase, simulation channel-porous interface.

I. INTRODUCTION

The Lattice Boltzmann Method (LBM) is a promising alternative to direct numerical simulations of fluid flows allowing easy implementation and algorithm parallelization, especially in presence of complex geometries and multi-phase flows. Several attempts have been made in order to model the complex two-phase flows mechanisms either in the gas diffusion layer (GDL) or in the gas channel (GC) of fuel cells [1,2], but only few studies have considered both of them together [3], including the GC-GDL interface. This paper presents a LBM capable of representing the hydrodynamic forces at the channel-porous interface of a fuel cell. Results are discussed in the light of their relevance for application in PEMFC optimization.

II. NUMERICAL MODEL

In order to correctly simulate two-phase flows with a liquid-to-gas viscosity ratio of the order of 100, in the framework of minimizing spurious currents and preventing artificial condensation, the two-dimensional Lattice Boltzmann Mid-Range Shan-Chen method proposed by Sbragaglia el al. [4] has been numerically implemented.

The Lattice Boltzmann Shan-Chen method represents intermolecular interactions in two-phase flows by means of a density-dependent pseudopotential \( \psi(\rho) \). The intermolecular attraction/repulsion force depends exponentially on the spatial density distribution. Consequently, weak variations of the density, which is a dependent variable in LBM, can strongly affect the local momentum balance even in single-phase fluid zones. Even though this intermolecular force can be physically consistent in single-phase zones of dipolar fluids, it is here considered negligible in single-phase zones far from the gas-liquid interface in order to represent incompressible two-phase flows. A new special inhibition treatment is herein proposed following the idea of De Maio et al. [5]: one can add the pseudopotential surplus \( \Delta \) only if the mean value of the pseudopotential function of the surrounding fluid sites \( \bar{\psi} \) exceeds some threshold value. This yields:

\[
\psi(\rho) = \psi(\rho_g) + \Delta \cdot H{\bar{\psi} - i \cdot \psi(\rho_l)}
\]

where \( \rho_g \) and \( \rho_l \) are the gas and liquid density, \( \Delta = \psi(\rho) - \psi(\rho_g) \), \( H \) is the heaviside step function and \( i \) is a free parameter which gives the threshold value \( T = i \cdot \psi(\rho_l) \).

III. RESULTS

In order to validate the numerical method against Spatially Averaged Navier-Stokes (SANS) [6] equations, a single-phase uniform pressure-driven flows in the domain shown in Figure 1 has been considered, that represents a simplified GC-GDL interface. This paper presents a LBM capable of representing the hydrodynamic forces at the channel-porous interface of a fuel cell. Results are discussed in the light of their relevance for application in PEMFC optimization.
incompressible. Pressure boundary conditions are imposed at inlet and outlet as to provide the Reynolds number value in the channel $Re_{GC}=14$.

**IV. Conclusion**

The Lattice Boltzmann pseudopotential model can affect momentum balance due to compressibility effects which are inhibited in the proposed model here. This model has been successfully validated against the analytic solution of incompressible Spatially Averaged Navier-Stokes equations.

The shear stress partitioning at the GC-GDL interface shows that in the gas channel the fluid viscous stress determines the momentum transfer, while in the gas diffusion layer the presence of pressure drag and skin friction acting on the porous medium reduces the fluid viscous stress and reactant diffusion. Moreover laminar separation zones appear at the GC-GDL interface, which leads to a major limitation of reactant diffusion and can increase fuel cell mass transport loss.

Results of two-phase simulations confirm that gas phase shear stress partitioning changes only weakly due to presence of liquid phase in two-phase uniform flows with density and viscosity ratios of the order of 100.

Simulations with more realistic GDL geometries are going to be performed in the future to substantiate this result.

**V. References**


Ceria-based Electrolytes with Enhanced Ionic Conductivity for Intermediate Solid Oxide Fuel Cells (SOFCs)

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Abstract - The electrolyte ionic conductivity plays an important role in the performance of SOFCs. To explore electrolytes with improved conductivity, ceria-based electrolytes including Gd0.2Ce0.8O1.9 (GDC) and Sm0.2Ce0.8O1.9 (SDC) are synthesized and characterized. Samples sintered at 1400–1500°C possess relative densities as high as 97.7% suggesting that this temperature range leads to improved densification of electrolyte. This is also confirmed by the micrograph images of the electrolyte. Moreover, NiO-GDC/GDC/Ba0.5Sr0.5Co0.8Fe0.2O3-δ (BSCF) and NiO-SDC/SDC/BSCF cells are fabricated and polarization curves are obtained. The thickness of the SDC and GDC electrolytes are identical and about 8 µm. Based on polarization results, with humidified hydrogen as fuel and air as oxidant, maximum power densities of 0.368 W.cm⁻², 0.619 W.cm⁻² and 0.790 W.cm⁻² are recorded at 500°C, 550°C, and 600°C, respectively, for the NiO-GDC/GDC/BSCF cell and NiO-SDC/SDC/BSCF cell generates MPDs of 0.398 W.cm⁻², 0.810 W.cm⁻² and 1.1 W.cm⁻² at 500°C, 550°C, and 600°C, respectively.

Index Terms - Ceria-based electrolyte, Ionic conductivities, Solid oxide fuel cells.

I. INTRODUCTION

Solid oxide fuel cell is an attractive power generation option which produces high electrical efficiency, but low emissions of gases (CO₂, NOx and SOx). Decreasing the electrolyte thickness is one approach to reduce the cell ohmic loss, thus directly improving the cell’s performance. Exploiting the thin-film membrane necessitates the support of a substrate to compensate the poor mechanical strength of the thin-film electrolyte. SOFCs with cathode or anode-supported structures have been widely investigated, and some great electrochemical performances have been reported [1, 2]. Alternatively, to reduce the ohmic resistance of lower temperature SOFCs, some electrolyte materials with higher ionic conductivity have been developed [3, 4].

Low temperature single cell fabricated with a 20-µm-thick SDC electrolyte film with fully humidified hydrogen as the fuel, and air as the oxidant has presented a great performance. Maximum power densities of 1.01 W.cm⁻² and 0.402 W.cm⁻² were obtained at 600°C and 500°C, respectively. Liu et al. found out that the maximum power densities of a single cell operating at low temperatures may be improved by further decrease in the thickness of a doped ceria Gd₁₀₋₁Ce₀·₉O₁·₉₅ (GDC) electrolyte to almost 10µm [5].

II. EXPERIMENTAL WORK

The single-electrolyte samples are prepared by die-pressing of the powder, followed by sintering at 1200°C, 1300°C, 1400°C and 1500°C for 4h in air environment.

The full cell is composed of NiO-SDC/GDC as the anode, SDC/GDC as the electrolyte, BSCF as the cathode material and hydrogen as the fuel gas. Before sintering the button cells are about 24 mm in diameter and 1.1 mm in thickness and after co-sintering, the are 18mm and 0.8mm, respectively.

Impedance measurement and electrochemical performance of the cell are done to evaluate the cell performance. Surface of the electrolytes and cross section of the cells are inspected using field emission scanning electron microscopy (FESEM).

III. RESULTS AND DISCUSSION

A. Studying the cell microstructure

Sintering temperature of the electrolytes plays an important role in the whole process. The electrolyte must be almost fully dense, without any open pores. From the microstructure point of view, both SDC and GDC electrolytes, sintered at 1500°C, are highly dense, but the grain size of SDC, is slightly smaller than the one in GDC, sintered at 1500°C. The normal trend is that the smaller the grain size is, the lower the conductivity will be. Fig. 1 presents Arrhenius plots of GDC and SDC conductivities determined by impedance spectra. As can be seen with increasing temperature, the conductivity increases and SDC is showing higher conductivity than GDC.
NiO-GDC/GDC/BSCF and NiO-SDC/SDC/BSCF cells are fabricated successfully. Fig. 2 shows the FESEM image of the cross sections of cells with GDC (a) and SDC (b) electrolytes after testing. It clearly presents the porous microstructure of both cathode and anode. Both GDC and SDC electrolytes exhibit good interfacial contacts with the anode and the cathode.

B. Electrochemical study

The impedance characteristics of NiO-GDC/GDC/BSCF and NiO-SDC/SDC/BSCF single cells at 500°C, 550°C and 600°C under open-circuit condition are shown in Fig. 3(a) and 3(b), respectively. Each impedance spectra includes two overlapping arcs, which present the electrodes polarization resistances indicating two rate-limiting processes for the electrode reaction. The low frequency arc increases significantly with the decrease of operating temperature and is dominant. In contrast, the arc related to higher frequencies increases relatively slower than the dominant arc. $R_p$, $R_p$ and $R_{total}$ are the ohmic resistance, the electrode polarization resistance and the total cell resistance, respectively.

Fig. 4 presents the polarization and power density against current density for the two cells with SDC and GDC electrolytes with identical thickness operating at 600°C. It clearly shows that the cell with SDC electrolyte presents a better performance compared to the cell with GDC electrolyte.

IV. CONCLUSION

GDC and SDC electrolytes are synthesized and characterized. Samples sintered at 1400-1500°C present relative densities as high as 97.7% suggesting that this temperature range leads to improved densification of electrolyte as reflected by the high open circuit voltages. This is also confirmed by the micrograph images of the electrolyte structures revealing that electrolytes prepared at higher temperature produce structures with very few pores. The Arrhenius plots of GDC and SDC conductivities exhibit that SDC electrolyte presents higher conductivity compared to GDC, especially those sintered at 1400-1500°C.

NiO-GDC/GDC/BSCF and NiO-SDC/SDC/BSCF cells are fabricated and polarization curves are obtained. Based on polarization results, MPDs of 0.368 W.cm$^{-2}$, 0.619 W.cm$^{-2}$ and, 0.790 W.cm$^{-2}$ are achieved at 500°C, 550°C, and 600°C, respectively, for the NiO-GDC/GDC/BSCF cell. With humidified hydrogen as fuel and air as oxidant, the NiO-SDC/SDC/BSCF cell generates MPDs of 0.398 W.cm$^{-2}$, 0.810 W.cm$^{-2}$ and, 1.1 W.cm$^{-2}$, respectively, which represents a well-performed SOFC.

Furthermore, it is realized that the limiting current density increases with increase in the hydrogen flow rate. It demonstrates that the observed diffusion polarization is due to hydrogen diffusion limitations at the anode.

REFERENCES

An investigation into the Hydrogen separation, purification and transport behavior of a ceramic \( \alpha \)-alumina membrane and its comparison with a \( \gamma \)-alumina membrane modified with AIOOH sol

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Abstract- The main purpose of this work is to investigate the hydrogen permeation behavior of a commercial ceramic alumina membrane and compare same with that of a \( \gamma \)-alumina membrane graded with an AIOOH sol using the dip coating method. The permeance of hydrogen and 5 other single gases (He, \( N_2 \), \( CH_4 \), \( CO_2 \) and Ar) were investigated at high temperatures. Mixed gas permeation tests for a \( H_2 \) gas mixture were also carried out. Results show that the permeance of \( H_2 \) increased with increasing temperature for the graded \( \gamma \)-\( Al_2O_3 \) membrane while it decreased for the \( \alpha \)-\( Al_2O_3 \) support. For the single gas tests, the \( \alpha \)-\( Al_2O_3 \) support show higher permeance of up to 9.45 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1} \) compared to 1.03 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1} for the \( \gamma \)-\( Al_2O_3 \) but the graded substrate was permeable to only \( H_2 \) at fifth coating. The mixed gas tests for a gas mixture (\( H_2 \)= 50%, \( CO \)= 28%, \( CO_2 \)=10% \( CH_4 \)=8%, \( N_2 \)=4%) show lower \( H_2 \) permeance which was attributed to the inhibition effect of \( CO_2 \) in the gas mixture. The \( H_2/N_2 \) permselectivity for both membranes was lower than the theoretical Knudsen value of 3.73 which suggests a viscous flow transport mechanism.

Index Terms: Hydrogen, Alumina membranes, Dip Coating, Gas permeance.

Introduction: Membrane technology for hydrogen separation and production processes is becoming an important and enabling technology in the current global decarbonisation efforts aimed at combating climate change and ensuring energy security. It is still ‘work in progress’ before \( H_2 \) is fully adopted as the global energy carrier to replace fossil fuels. During this transition period from fossil fuels to \( H_2 \), research into several \( H_2 \) separation and purification processes is gaining increased attention. One of these processes is membrane technology which offers several advantages in hydrogen processes including energy efficiency, cost effectiveness and infinite selectivity to hydrogen for dense palladium membranes when defect free. Alumina membranes are thermally and chemically stable and can withstand harsh operating conditions.

Experimental: The experiment was carried out for a mesoporous \( \alpha \)-alumina support with a 30 nm pore size and i.d= 7mm, o.d= 10 mm, effective length= 0.34 m. Another 30 nm \( \alpha \)-alumina support was graded with AIOOH sol and converted to \( \gamma \)-alumina by 5 sequential dippings using the dip coating method. The objective was to investigate the hydrogen permeation and selectivity at high temperature including the gas transport mechanisms. The tubes were dried at 65° C for 2 hours in an oven to remove any water vapor or moisture and sealed at both ends. The modification of the \( \alpha \)-\( Al_2O_3 \) support was carried out using a multilayer deposition process by a dipping-drying-calcining method. After each dipping, the support was dried for 10 hours at 65° C and calcined at 873 K for 24 hours. Permeation tests were carried out in a membrane reactor module at 298, 323, 373, 473 and 573K.

Fig.1. \( H_2 \) permeance as a function of average pressure at different temperature for the \( \gamma \)-\( Al_2O_3 \) membrane at first coating.
Results and Discussion: In Fig.1 the H₂ permeance increased with temperature but decreased with the number of coatings as more layers of the Boehmite sol were deposited. This decrease in permeance is in conformity with the principle that the higher the membrane thickness, the higher the resistance to permeation and therefore the lower the permeance. The γ-Al₂O₃ substrate was only permeable to H₂ at fifth coating. In Fig. 2 the decrease in H₂ permeance with increasing temperature for the α-Al₂O₃ support indicates low mobility of the gas molecules in the pores and also suggests that surface adsorption was inversely proportional to temperature hence high temperature negates surface diffusion of hydrogen in the α-alumina support while low temperature enhances it. In Fig 3, the maximum H₂/N₂ permselectivity of 3.07 was measured for the γ-alumina at 573 K while in Fig. 4, it was 2.9 for the α-alumina support at 298 K and both are lower than the Knudsen value of 3.73 which suggests the existence of viscous flow mechanism. The slightly higher H₂/N₂ permselectivity of the γ-alumina substrate at 3.07 indicates less dominance of viscous flow and more closeness to Knudsen diffusion.

The SEM image in Fig. 5 shows the α-Al₂O₃ structure increasingly open and flowery with more open pores layerwise going top, intermediate and inner.

Conclusion: A commercial Al₂O₃ support was graded with Boehmite sol using the dip coating method and its hydrogen permeation behaviour and H₂/N₂ permselectivity investigated. The results for the graded γ-Al₂O₃ substrate were compared with those of a macroporous α-Al₂O₃ support. The results show that H₂ permeance increases with temperature for the γ-Al₂O₃ membrane while it decreases for the α-Al₂O₃ substrate. The measured H₂/N₂ separation ratios indicate a viscous flow mechanism.

Acknowledgement: Sincere thanks to PTDF, Nigeria for sponsoring this work.

References:
1. X. Li, B, Liang, Journal of the Taiwan Institute of Chemical Engineers, 43(2012) 339-346.
Abstract – The study summarized in this paper proposes a new tool for PEMFC non-intrusive diagnosis based on voltage singularity measurement and classification. The method takes advantage of the non-linearities associated with discontinuities introduced in the dynamic response data resulting from various failure modes. Continuous wavelets and multifractal formalism, named WTMM (Wavelet Transform Modulus Maxima), are used together to quantify the singularity strength of the signal. The singularities signature of poor PEMFC operating conditions (faux) is first revealed through multifractal spectra. Then, these ones are classified using SVM (Support Vector Machine). The good classification rates obtained demonstrate that the multifractal spectrum based on WTMM is effective to extract the incipient fault features during PEMFC operation. The proposed method leads to a promising non-intrusive and low cost diagnostic tool to achieve on-line characterizations of dynamical PEMFC behaviors.

Index Terms – Classification, Diagnosis, PEMFC, Singularity.

I. INTRODUCTION

One of the main issues to be treated in Fuel Cell (FC) development remains the detection and identification of disturbances occurring during stack operations. Various internal and external factors are known to affect the useful life of PEMFCs. When any FC operational parameter (e.g. gas pressures or stoichiometry rates) is deflected from its nominal value, the stack performance can be strongly impacted. Stack and / or cell voltage changes can reveal some damage phenomena and failure modes such as electrode flooding, membrane drying, gas leakage, loss of electroactive surface area. In this context, the proposal of new diagnostic tools aims to provide potential solutions for improving stack durability, reliability, efficiency and for optimizing system development. Indeed, numerous publications have already proposed signal processing based methods as diagnostic FC tools based on Fourier transform [1], wavelets [2].

Many natural and artificial phenomena such as turbulence, diffusion limited aggregates, and electrical discharges exhibit multifractality. Since these phenomena are highly nonlinear and non-stationary, regular analyses such as Fourier decomposition cannot characterize them effectively. To encounter this limit, multifractal analysis can be introduced. It consists in computing the singularity strengths of a signal.

Our study is launched in order to create a tool for FC dysfunction diagnostics, which requires minimum of instrumentation. In fact, our method proposes to use the information contained in the singularities of the voltage signal which reflects the state of the FC in a dimensionally reduced representation. That consists in quantifying the irregularities (or singularities) degree of the voltage according to the introduced operating faults. To this purpose, continuous wavelets and multifractal formalism are first used to compute the singularity spectrum of the voltage signal; then, this spectrum is classified using SVM (Support Vector Machine). More details about the method and the results are given in section II and III, respectively.

II. MATERIALS AND METHODS

A. Experimental process

The experimented FC is an 8 cell PEMFC stack manufactured by CEA LITEN in France. It has been designed for automotive applications. It is made of metallic gas distributor plates. Its size is 220 mm x 160 mm x 186 mm and the electrode active surface is 220 cm². The nominal current is 110 A; the nominal current density is thus equal to 0.5 A.cm⁻².

The PEMFC stack was operated under a variety of conditions using the ‘in-house’ self-developed 1 kW test bench of the FC test platform in Belfort - France. More descriptions of the test bench are given in details in [3].

It is well known that FCs are complex systems: many different properties and processes influence their operation.
Therefore, the localization of an error in operation proves to be difficult. To avoid this difficulty, we propose a simple experimental procedure that makes the faults isolation easy. Indeed, we introduce some faults by varying parameters such as cathode stoichiometry rate (FSC), anode stoichiometry rate (FSA) and gas pressures (P) from their nominal values (Ref). The singularity spectrum is then computed on the new stack voltage obtained. More details on the operating conditions are summarized in Table I.

<table>
<thead>
<tr>
<th>Parameter values</th>
<th>Nominal conditions (Ref)</th>
<th>Cathode flow fault (FSC fault)</th>
<th>Anode flow fault (FSA fault)</th>
<th>Gas pressure fault (P fault)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSC</td>
<td>2</td>
<td>1.5</td>
<td>2</td>
<td>1.3</td>
</tr>
<tr>
<td>FSA</td>
<td>1.5</td>
<td>1.5</td>
<td>1.3</td>
<td>2</td>
</tr>
<tr>
<td>P (bars)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

### B. Singularity spectrum calculation

We propose here some information on the computing of a singularity spectrum from the FC voltage signal. This one is associated with the Hölder exponent $h$ (parameter used to quantify the singularity degree of a temporal point) and the Hausdorff dimension $D(h)$ (dimension of set of points, named ‘Hölder’ that exhibit the same value of $h$). The Hölder exponents of the voltage signal are estimated from the local maxima points of its wavelet coefficients $W_q$ at a position $u$ and a scale $s$ via the partition function for different statistical moments of $q$ order [4]:

$$Z_q(s) = \sum_{1 \leq |l|} \left( \sup_{(u,s') \in S} W_q(X(u,s'))^q \right)^\tau$$

$I$ is a maxima line obtained after linking different wavelet transform maxima points detected at different scales for position $u$. And, $L(s)$ is the set of maxima lines that exists at scale $s$.

Then, the scaling function is computed with a linear regression in the (log-log) space of $Z(q, s)$:

$$\tau(q) = \lim_{s \to 0} \left( \inf \frac{\log(Z(q,s))}{\log s} \right)$$

The Hölder exponent $h$ is computed as follow:

$$h = \frac{d \tau(q)}{dq}$$

The singularity spectrum is estimated using the Legendre transform: $D(h) = \inf_{q \in \mathbb{R}} \left( qh - \tau(q) + c \right)$ where $c$ is a constant.

### III. RESULTS AND DISCUSSION

In this work, we adopt the multifractal analysis of voltage signal in order to extract and identify the singularity signature of the defaults related with the imposed poor operating conditions. Some examples of stack voltage recorded in the four different operating conditions and their multifractal spectra are plotted in Fig. 1. As we can see at first sight, each operating condition gives its own stamp on the morphology of the stack voltage. The singularity signature of each fault is revealed by the distinguished singularity spectra. Therefore, the singularity parameters can be used as discriminant parameters to develop a PEMFC non-intrusive diagnostic tool.

To implement this diagnostic tool, we apply the supervised classification method named SVM to recognize the singularity spectrum and therefore the fault. Indeed, 6 spectra faults are considered for the learning step and 4 others for the test with 4 classes. The global good classification rate is about 73.3%. The classification rates for each class are given in Table II (confusion matrix). As it is shown, the cathode and anode flow faults are successfully identified (classification rate of 100%). However, the pressure fault and the nominal conditions (Ref) are identified at 50%.

#### IV. CONCLUSION

The relevant information describing the regularity of the stack voltage is used to develop a new diagnostic tool for PEMFC without additional instrumentation. The results of singularity spectra show that each fault imposes its own singularity signature on the produced voltage. The classification rate results encourage us to further develop this study by considering other faults.

### REFERENCES


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ELECTRICITY GENERATION POTENTIAL FROM SWINE MANURE IN SOUTHERN BRAZIL VIA SOFC

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Abstract - Brazil is a major producer of pork, with a herd of approximately 39 million pigs. The majority of this herd is concentrated in the southern region of the country. A high electrical efficiency CHP plant, based on high temperature SOFCs technology, is proposed as the best way for harvesting the energy content of biogas (from swine manure) already being produced in many farms. The proposed plant is based on thermodynamic and transport phenomena simulation using FactSage and Matlab software. One can verify that, for a gaseous mixture with a typical composition of 60% CH₄ and 40% CO₂, it is possible to reach net electrical and thermal efficiencies of 48.8 and 33.0% (LHV), respectively. This makes the projected SOFC-CHP plant a very attractive route for biogas utilization.

Index Terms – swine manure, biogas, SOFC

I. NOMENCLATURE
SOFC, Solid Oxide Fuel Cell
CHP, Combined Heat and Power
LHV, Lower Heating Value
BoP, Balance of Plant

II. INTRODUCTION
Brazil is a major producer of pork, with a herd of circa 39 million pigs. The majority of this herd is concentrated in the southern region of the country (18,643,470 million heads), with the State of Santa Catarina (SC) taking first place (7,817,536 million), followed by Rio Grande do Sul (RS) (5,729,710 million) and Paraná (PR) (5,096,224 million).

The swine concentration in a relatively small geographic area can impact the environmental resources, particularly soil and water. So, in order not to limit this economic activity, the anaerobic biodigester technology has been introduced as a means capable of producing a residue with lower environmental threat than raw manure, with the benefit of recovering part of the energy contained in the waste as biogas.

This work aims to propose a high electrical efficiency plant for biogas utilization based on high temperature SOFC technology, as a better alternative for harvesting this energy instead of biogas burning. Additionally, the electrical energy generation potential via SOFC from biogas produced with swine manure in Southern Brazil is analyzed.

III. METHOD OF SIMULATION
The simulation of the SOFC-CHP system with anode exhaust gas recycling is based on an iterative approach that considers the composition of the anode exhaust gas as a variable, and the SOFC system model is solved until the accuracy of 10⁻⁶ is satisfied. The gas reformer and afterburner are modeled as Gibbs reactors, and the planar SOFC is modeled according to the steady-state 1D model described by Kang et al. [1]. The electrochemical model and the heat balance applied to each control volume are described by Saebea et al. [2]. The model employed in the present study was coded and solved using MATLAB and FactSage software and databases.

IV. RESULTS AND DISCUSSION
A. Validation of the prepared computer code at the cell level
The performances of commercially available electrolyte supported cells (ESC2) and (ESC10) produced by H.C. Starck Company were simulated, considering the same experimental conditions described in the manufacturer’s manual, in order to validate the developed computer code at the cell level. From Fig. 1, one can see that theoretical and experimental results are in excellent agreement, which suggests that the steady-state 1D and electrochemical models considered in this research can describe satisfactorily the performance of ESC cells. ESC10 was chosen for modeling the CHP plant due to its superior performance compared to ESC2. In the plant simulation, the
single cell operating voltage should not be taken directly from Fig.1, since the fuel cell is running on a gaseous mixture composed of CH₄, CO, CO₂, H₂ and H₂O. Note, however, that the values do not differ significantly, e.g. at 600mA/cm², 0.78V (Fig.1) and 0.71V (Table I).

B. Biogas-fuelled SOFC-CHP plant project

A SOFC-CHP power plant running on biogas with a generic composition of 60% CH₄ and 40% CO₂ was projected. The plant configuration for 1kW el net AC delivered can be seen in Fig. 2. In this plant, labels showing temperature, pressure and major species mole fraction are also indicated. Biogas is contaminated by H₂S, which poisons Ni catalyst. Thus, a desulfurization unit is required. Cleanup subsystems, however, were not modeled. Multiple technologies could be used, and many of them do not affect the mass and energy balance of the system significantly [3]. Results show that a biogas volume of 8.3 m³/day is required per 1kW el net AC delivered. This value is consistent with the value of 8.8 m³/day determined by Farhad et al. [4]. BoP was carried out for different system sizes (1kW, 5kW and 1MW), as indicated in Table I. The net electrical efficiency and the CHP efficiency are equal for all system sizes. Therefore, for a given daily production of biogas, n, in m³, the net AC power is calculated by n/8.3, where 8.3 m³/day stands for 1kW el net AC. The number of pigs can be determined by using the data shown in Table II [5].

TABLE I
SOFC SYSTEM PERFORMANCE FOR SMALL AND A LARGE SCALE BIOGAS SOURCE

<table>
<thead>
<tr>
<th>NET AC/POWER CHP plant</th>
<th>1kW</th>
<th>5kW</th>
<th>1000kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogas m³/day</td>
<td>8.3</td>
<td>41.5</td>
<td>8300</td>
</tr>
<tr>
<td>Number of pigs</td>
<td>206</td>
<td>1030</td>
<td>205853</td>
</tr>
<tr>
<td>Area of single cell (cm²)</td>
<td>100</td>
<td>100</td>
<td>552</td>
</tr>
<tr>
<td>Number of cells</td>
<td>28</td>
<td>140</td>
<td>5071</td>
</tr>
<tr>
<td>Single cell voltage (V)</td>
<td>0.71</td>
<td>0.71</td>
<td>0.71</td>
</tr>
<tr>
<td>Stack Voltage (V)</td>
<td>18.9</td>
<td>94.5</td>
<td>3422</td>
</tr>
<tr>
<td>(A m⁻²)</td>
<td>6002.6</td>
<td>6002.2</td>
<td>6002.4</td>
</tr>
<tr>
<td>Fuel utilization (%)</td>
<td>65.8</td>
<td>65.7</td>
<td>65.8</td>
</tr>
<tr>
<td>Eexe (K)</td>
<td>1123</td>
<td>1123</td>
<td>1123</td>
</tr>
<tr>
<td>Compressor Consumption (W)</td>
<td>39</td>
<td>194.7</td>
<td>39025</td>
</tr>
<tr>
<td>Net AC electrical efficiency (%)</td>
<td>48.8</td>
<td>48.8</td>
<td>48.8</td>
</tr>
<tr>
<td>CHP efficiency (%)</td>
<td>81.8</td>
<td>81.8</td>
<td>81.8</td>
</tr>
</tbody>
</table>

TABLE II
DATA USED FOR THE DETERMINATION OF BIOGAS PRODUCTION PER PIG

<table>
<thead>
<tr>
<th>Average manure per pig</th>
<th>Total solids (TS)</th>
<th>Volatile solids (VS)</th>
<th>Biogas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>3.2</td>
<td>40</td>
<td>50</td>
</tr>
</tbody>
</table>

Considering only the most promising arrangements of factors (high number of pigs and producers at a short distance) and the SOFC-CHP plant data resulting from this work, the electricity generation capacity within the three States combined can be estimated as being above 11.7 MW, supporting the modern distributed generation (DG) concept.

V. CONCLUSION

The proposed SOFC-CHP plant offers net electrical and thermal efficiencies of 48.8 and 33.0% (LHV), respectively.

ACKNOWLEDGMENT

The authors would like to thank FAPERGS and CAPES for their financial support (Postdoctoral fellowship — DOCFIX).

REFERENCES

SYSTEM LEVEL MODELING APPROACH FOR PERFORMANCE PREDICTION OF HIGH TEMPERATURE FUEL CELLS

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Abstract - In this paper numerical models of high temperature fuel cells (MCFC and SOFC) are presented. These models, that are based on a thermochemical and electrochemical approach and employ semi-empirical equations, have been validated by using experimental data both measured in test stations and available from technical literature.

Numerical results show that the models allow to characterize the behavior of the high temperature fuel cells with a good approximation so, due to the simplicity of the simulation procedure, they can be useful tools for performance prediction and analysis of more complex systems in which the fuel cells are one of the component.

I. INTRODUCTION

High-Temperature Fuel Cells (HTFC, e.g. SOFC and MCFC) have more fuel flexibility than Low-Temperature Fuel Cells (LTFC, e.g. PEMFC) because the carbon monoxide does not poison the anode electrocatalyst, whereas it works as a fuel (if the anode gas is humidified the Boudouard reaction is also avoided).

As a result, various fuels can be processed to produce a reformate, including fossil fuels (natural gas, oil and coal) and renewable fuels (i.e. biomass and waste) for direct use in high temperature fuel cells.

In this paper numerical models of high temperature fuel cells (MCFC and SOFC) are presented. These models, that are based on a thermochemical and electrochemical approach and employ semi-empirical equations, have been validated by using experimental data available from technical literature.

II. MODELING METHODOLOGY

Fuel cells modeling can be dealt with a different level of detail and rigor (from zero dimensional approach to three dimensions) and their usefulness depends on the application field. In particular the modeling issues can be view at cell level to improve understanding of complex physical and chemical phenomena or at fuel cell system level to investigate the impact of their operating conditions on the overall system.

In order to evaluate the HTFC performance, in terms of electric and thermal power generated, the one-dimensional model, developed by using the AspenPlus™ code, considers the thermochemical (i.e. reforming and shifting reactions) and electrochemical (i.e. electro-oxidation of hydrogen) reactions which take place in the anode and cathode sides.

The fuel cell designs considered are planar and tubular configurations with co-flow arrangement.

The basic assumptions are i) steady state, ii) isothermal conditions, iii) ideal gas mixtures, iv) equilibrium in the gas reactions, iv) negligible pressure drop.

As shown in Figure 1, the unit cell is discretized in N-elements along the flow direction and each J-element consists of anode, cathode and electrolyte.

Figure 1. Schematic of the planar (a) and tubular (b) cells

The model flowsheet of the J element is depicted in Figure 2. It comprises a cathode block (CAT,J), in which the oxygen (SOFC) or the oxygen and carbon dioxide (MCFC) react producing the negatively charged ions (O⁻ or CO₃⁻, CAT,ION stream) and an anode block (AN,J) in which the electro-oxidation reaction occurs. These blocks have been modeled as stoichiometric reactors.

Because during the cell operation the anodic gas composition varies along the channel, a further reactor (SHIFT,J), has to be placed down to the AN,J block to evaluate the actual anode gas composition. It has been modelled as a Gibbs reactor.
In order to estimate the thermal fluxes generated in each J element during cell operation, the energy block (QBAL,J) has been used in the model.

The developed model allows to solve the mass balances by an iterative procedure: assigned the fuel utilization factor (U F), the air utilization factor (U Air) and the number of elements, the model calculates the chemical composition of each stream and its enthalpy variation, for a given cell operating temperature.

The numerical results are the anodic and cathodic activation overpotentials, the ohmic overpotential, and the concentration overpotential due to mass transfer limitations (the WGSR is very fast (the nichel-based catalyst that covers the anode speeds up this reaction), so that it is possible to assume that the whole CO is converted into hydrogen (the electricity is entirely produced from the electrochemical oxidation of hydrogen).

In order to estimate the performance of a SOFC, the terms of the eq.1 have been calculated by using the following equations.

\[ E_{\text{Nernst}} = E^0 + \frac{RT}{2F} \ln \left( \frac{p_{H_2} \cdot p_{O_2}^{0.5}}{p_{H_2O}} \right) \]  

\[ \eta_{\text{act}} = \eta_{\text{act,an}} - \eta_{\text{act,cat}} - \eta_{\text{ohmic}} - \eta_{\text{conc,cat}} \]  

\[ \eta_{\text{ohm}} = \frac{RT}{nF} \cdot \ln \left( \frac{i}{i_{\text{ohm}}} \right) \]  

\[ \eta_{\text{conc,cat}} = \frac{RT}{2F} \cdot \ln \left( 1 - \frac{I_{\text{cell}}}{I_{L,\text{cat}}} \right) \]

The terms and the coefficients of these equations are explained and detailed in [1].

### III. SOFC MODELING

The SOFC is fed by syngas and air into the anode and cathode side respectively.

The electrochemical oxidation of CO has been neglected because the WGSR is very fast (the nichel-based catalyst that covers the anode speeds up this reaction), so that it is possible to assume that the whole CO is converted into hydrogen (the electricity is entirely produced from the electrochemical oxidation of hydrogen).

In order to estimate the performance of a SOFC, the terms of the eq.1 have been calculated by using the following equations.

\[ E_{\text{Nernst}} = E^0 + \frac{RT}{2F} \ln \left( \frac{p_{H_2} \cdot p_{O_2}^{0.5}}{p_{H_2O}} \right) \]  

\[ \eta_{\text{act}} = \eta_{\text{act,an}} - \eta_{\text{act,cat}} - \eta_{\text{ohmic}} - \eta_{\text{conc,cat}} \]  

\[ \eta_{\text{ohm}} = \frac{RT}{nF} \cdot \ln \left( \frac{i}{i_{\text{ohm}}} \right) \]  

\[ \eta_{\text{conc,cat}} = \frac{RT}{2F} \cdot \ln \left( 1 - \frac{I_{\text{cell}}}{I_{L,\text{cat}}} \right) \]

The terms and the coefficients of these equations are explained and detailed in [1].

### III. MCFC MODELING

The MCFC is fed by syngas in the anode side and a mixture of air and carbon dioxide (recycled from the cathode and anode exhaust gasses) into the cathode side.

In order to estimate the performance of a MCFC, the terms of the eq.1 have been calculated by using the following equations.

\[ E_{\text{Nernst}} = -242000 + 45.8T - \frac{RT}{2F} \ln \left( \frac{p_{H_2} \cdot p_{O_2}^{0.5} \cdot p_{CO_2}}{p_{H_2O}} \right) \]  

\[ \eta_{\text{act}} = j \cdot (C_e \exp(\frac{\Delta H_{f,e}}{RT}) \cdot \frac{p_{H_2} \cdot p_{O_2}^{0.5}}{p_{H_2O} \cdot p_{CO_2}}) \]  

\[ \eta_{\text{ohm}} = j \cdot (C_i \exp(\frac{\Delta H_{f,i}}{RT}) \cdot \frac{p_{H_2} \cdot p_{O_2}^{0.5}}{p_{H_2O} \cdot p_{CO_2}}) \]

The terms and the coefficients of these equations are explained and detailed in [2].

### IV. CONCLUSIONS

The models have been validated by using experimental data available from scientific literature as reported in [1,2] and a good approximation has been found (the error on cell voltage is 2.8% and xx% for SOFC and MCFC respectively). Therefore, due to the simplicity of the modelling approach proposed, the developed models can be useful tools for performance prediction and analysis of more complex systems.

### REFERENCES


SOL-GEL SYNTHESIS OF GADOLINIUM DOPED CERIA (Gd–CeO₂) FOR INTERMEDIATE TEMPERATURE SOFC ELECTROLYTE

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Abstract - In this work gadolinium doped ceria (Gd–CeO₂) powder have been synthesized by a novel simple and low cost sol gel method. The synthesized and calcined (at 600°C) powders were characterized by X-Ray Diffraction analysis (XRD) and Transmission Electron Microscopy (TEM). Nanocrystalline powders of pure cubic ceria have been obtained.

Index Terms – Gd doped ceria, Nano structured powders, Sol gel synthesis, Solid Oxide Fuel Cell (SOFC).

I. INTRODUCTION

Currently yttria-stabilized zirconia (YSZ), fluorite structure materials, such as zirconia-based and ceria-based oxide, and perovskite LaGaO₃ based materials are widely used as electrolytes for SOFCs. YSZ has been used at temperature higher than 900°C. This temperature need high costs and decrease the durability, for electrode sintering and interfacial reactions. One of the technological challenges in SOFC technology is getting compatible materials with long term durability. An excellent choice, for improving durability of components and for lowering cost can be realized by reducing the operating temperature and by using different materials as solid electrolytes.

Doped cerium oxides (DCO) are the most extensively studied ceria based electrolytes, with the maximum ionic conductivity occurring at 10–20 mol% dopants. Compared to YSZ, DCO has a high conductivity and lower activation energy below 800°C. However, DCO suffers from the partial reduction of Ce⁴⁺ to Ce³⁺ in reducing atmosphere and at high temperature (>600°C), which leads to undesirable structural change, as well as electronic conductivity which reduces performance due to electronic leakage currents between the anode and cathode. Therefore, the operation of SOFCs with a DCO electrolyte is considered most effective in the 500–600°C temperature range.

Ceria doping is needed to increase the oxygen vacancy concentration and to reduce the intrinsic electronic conductivity.

Currently, the common synthesis routes to prepare doped ceria powders include solid-state reactions [1, 2], co-precipitation reactions [2–5] and other methods which are expensive in term of cost and time for reaction. Sol gel methodology can be an alternative and remarkably versatile approach for fabricating materials and components.

In this paper we report the synthesis of Gd-CeO₂ crystalline powders by a simple and low cost sol gel process adapted from [6]. The structural properties and morphology of the powders were studied by XRD, and TEM analysis.

II. EXPERIMENTAL

A. Synthesis of GDC powder

Gd doped ceria of composition Ce0.9 Gd0.1 O1.95 was synthesized, by sol gel route. At variance with classical sol gel methods, citrate was added to serve as a complexing polyfunctional hydroxy agent. In this work, commercial Ce(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99+% purity) and Gd nitrate hexahydrate (Gd(NO₃)₃·6H₂O, >99.9 % purity) were used as precursors. Ce nitrate and Gd nitrate were mixed in the required stoichiometric ratio and added to
distilled water until fully dissolved at room temperature, the appropriate quantities of metal nitrate salts were calculated and weighed accurately. Afterwards, citric acid monohydrate (C_6H_8O_7·H_2O >99.0 % purity) was added to this mixture so as to maintain the total metal to citric acid molar ratio of 1:1, to serve as a complexing polyfunctional agent. Final mixture was dissolved in a minimum amount of water. After stirred and heated at 80°C for 2 hours, the clear solution turned into a viscous gel. The yellow paste was then dried at 110°C for 1 hour and calcined at 600°C for 5 hours.

**B. Characterization**

The hardened dry gels were finely ground and successively characterized by X-Ray Diffraction Analysis (XRD) and Transmission Electron Microscopy (TEM).

XRD analysis was performed using a Philips diffractometer model PW1710 (CuKα radiation, 5°–80° 2θ range, step width 0.02° 2θ and 1s data collection per step with a scan rate of 1°/min).

TEM analysis was performed by a FEI Tecnai G2 Spirit Twin.

### III. RESULTS AND DISCUSSION

**A. XRD Analysis**

XRD analysis performed on the 110°C dried gel (not reported) shows that this sample is completely amorphous.

Calcination at 600°C results in the crystallization of a pure cubic ceria phase, as shown in figure 1.

![Figure 1. XRD pattern of Gd0.1 Ce0.9 sample calcined at 600°C](image)

The average crystallite size, D, of calcined powders, as determined by using the Debye–Scherrer method, is 18.7 nm.

**B. TEM Analysis**

Figure 2 shows a TEM image of the 600°C calcined sample.

![Figure 2. TEM image of Gd0.1 Ce0.9 sample calcined at 600°C](image)

Many nanocrystallites of less than 10 nm diameter are clearly evident.

### IV. CONCLUSIONS AND FUTURE DEVELOPMENT

The simple and low cost sol-gel method adopted allows to obtain pure nanocrystalline Gd-doped ceria. Produced powders need to be sintered and the obtained compacts have to be tested for electrical properties in order to assess the reliability for SOFC electrolyte.

### REFERENCES


SYNTHESIS OF Nb2O5-P2O5-SiO2 MATERIALS FOR PROTON EXCHANGE MEMBRANES FUEL CELL (PEMFC) APPLICATIONS

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Abstract - In this work an innovative sol-gel process to prepare an inorganic material based on the system Nb-P-Si is proposed for proton exchange membrane fuel cell applications. Nb2O5-P2O5-SiO2 gels were synthesized using NbCl5, POCl3 and TEOS as precursors of niobium, phosphorus and silicon, respectively. The synthesis procedure tuned in this work allowed to obtain transparent chemical gels with a high surface area for each studied composition. Materials were characterized for structural and textural properties by X-ray diffraction, thermogravimetry/differential thermal analysis, Fourier transformed-infrared spectroscopy and N2 adsorption.

Index Terms – Sol-gel synthesis, Nb2O5-P2O5-SiO2 system, PEMFC.

I. INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) have been looked as potential energy conversion devices alternative to conventional energy conversion systems such as combustion engines. Traditional membrane materials, like Nafion, were the most promising for use in fuel cells, due to inexpensive operating conditions at temperatures in the range 60–80°C with high efficiency, up to 60%. However, in this temperature range they are affected by some drawbacks, including poor carbon monoxide tolerance and thermal degradation. These drawbacks can be overcome by increasing the operating temperature range up to 120–130°C. Because the most widely use commercial Nafion membrane is not suitable for operating at high temperature due to degradation, sol-gel process can be a valid and economic alternative to prepare an inorganic material for fuel cells membranes [1-4].

The sol-gel process is a versatile wet chemical process to make different materials. This synthesis technique involves the transition of a system from a colloidal liquid, named sol, into a solid gel phase [3, 5]. In this research Nb2O5-P2O5-SiO2 gels were synthesized via an innovative sol-gel synthesis procedure using NbCl5, POCl3 and TEOS as precursors of niobium, phosphorus and silicon, respectively. Particularly, a wide compositional range was explored, with Nb2O5 and P2O5 content ranging from 2.5 to 10 mol%.

II. EXPERIMENTAL

Nb-P-Si mixed-oxide composites, whose nominal composition can be expressed by the formula (Nb2O5)x-(P2O5)y-(SiO2)1-x with x = 0.025, 0.050, 0.075 and 0.10, were prepared by sol-gel using niobium chloride, NbCl5 (99%, Gelest), phosphoryl chloride, POCl3 (99%, Aldrich Chemical) and tetraethoxysilane, Si(OC2H5)4 (99%, Gelest), as starting materials.

The hardened dry gels were finely ground to allow the thermal and structural characterization. Thermogravimetric/differential thermal (TG/DTA), X-ray diffraction (XRD), Fourier transformed infrared (FT-IR) spectroscopy and N2 adsorption-desorption isotherms analyses were carried out.

III. RESULTS AND DISCUSSION

Figure 1 shows the TG/DTA curves of the dried gels recorded in air at 10K min⁻¹. Weight losses were less than 25% for all samples. The highest value is attributed to the sample containing the highest phosphorus content.

FTIR spectra of dried gels and heat-treated samples are shown in Figure 2. Spectra report partially hydrolyzed TEOS molecules and the characteristic peaks of Si-O-Si
bending vibrations, P-O-P and Si-O-Si symmetric stretching, stretching of Si-OH bonds and Nb-O-Nb stretching [5].

$N_2$ adsorption-desorption isotherms for a typical sample (2.5NbP) show a mesoporous material with a high surface area (about 800 cm$^2$/gr), as showed in the Figure 3. The chemical stability significantly increases with the addition of NbO$_2$, while P$_2$O$_5$ increases proton conduction, because of strong hydrogen bonding characteristics of P-OH bond compared with Si-OH.

IV. CONCLUSIONS

In this work the preparation of an inorganic material by means of a sol-gel process for the production of fuel cells membranes has been proposed and developed. A novel ternary system based on Si-Nb-P has been studied. The presence of NbO$_2$ increases chemical stability through the polymerization of POH bond in the P$_2$O$_5$-SiO$_2$ system. Proton conduction can be increased by the presence of P$_2$O$_5$. This factor is important in these materials for practical application in fuel cell electrolytes.

REFERENCES


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SIMULATION OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF A SOLID OXIDE FUEL CELL ANODES

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Abstract—The electrochemical impedance technique is the analysis of current response of a fuel cell to a small sinusoidal perturbation in voltage. The variation in frequency response makes it possible to separate processes and mechanisms in the electrochemical phenomena that is occurring at electrode surfaces. The purpose of the current study is to present modeling and simulation of the impedance of solid oxide fuel cell (SOFC) anodes. SOFCs are energy conversion devices that produce electricity and heat directly from fuel by electrochemical reaction. For evaluating the performance of SOFCs, efforts are devoted to developing numerical analysis tools capable of investigating the transport and electrochemical phenomena within the passages of fuel cells. Electrochemical impedance spectroscopy (EIS) is a non-destructive method, which is an effective approach for performance optimization, failure mode diagnosis, revealing dynamic properties, and for obtaining information on individual losses in SOFCs.

Keywords—Solid oxide fuel cell (SOFC), transient simulation, electrochemical impedance spectroscopy (EIS), Impedance analysis

I. INTRODUCTION

Fuel cells appear as future energy conversion systems. Tremendous effort has been put into fuel cell researches over the last several decades. Fuel cells have higher efficiency compared to conventional combustion engines due to the fact that their efficiency avoid the limitations of Carnot cycle, in addition the fuel cell itself has no moving parts making it quiet and reliable. Furthermore they have lower pollutant emissions, lower equipment maintenance, and higher power density. Fuel cells generate electrical power by continuously converting chemical energy of a fuel into electrical energy through an electrochemical reaction [1].

The purpose of the current study is to numerically investigate the electrochemical impedance of a SOFC anode. As known the performance of SOFC is strongly influenced by gas phase transport of reactants and products. These phenomena affected the electrochemical impedance spectra and resulted in a capacitive semicircle in Nyquest plot. The present study investigates the performance of SOFC anode by analyzing these features.

II. MODEL DESCRIPTION

The one-dimensional schematic of the planar SOFC anode is depicted by Figure 1. The cell size is given in [20]. As shown by the Fig.1 hydrogen as the fuel passed through anode channel. For simplification the polarization losses from electrolyte and cathode are neglected. In addition concentration polarization of the species within the porous anode is ignored and the transport processes of porous anode are included in the global electrode kinetic behavior. Furthermore gases are assumed to behave as ideal gases. In EIS measurements the individual behavior of each electrode is investigated using symmetrical single cells operated with identical hydrogen or oxygen supply in both compartments. In this type typically there is only diffusive transport along electrode channel, and there is no convection. Therefore the observed impedance feature is due to anodic gas-phase concentration variations only.
III. RESULTS AND DISCUSSION

The electrochemical impedance is calculated in the time domain using the transient numerical simulation technique. Fig. 2 depicts the Simulated impedance spectra for $\eta_{\text{steady}}=0\,\text{V}$ and $\eta_{\text{excitation}}=1\,\text{mV}$.

Figure 2: Simulated impedance (a) Nyquist plot (b) Bode plot

For verification purpose model parameters are chosen in order to reflect the results by Bessler[16]. The channel cross section is $1\times1\,\text{mm}^2$, the width of the channel rib is 1 mm, the channel length is 1 cm, the temperature is set to 1123 K, hydrogen inflow concentration is 99%, and exchange current density is 0.483 A/cm$^2$. In the present study, impedance is calculated for a frequency range of $10^{-1} < f < 10^6$. Here capacitive behavior in the form of an RC-type semicircle in the Nyquist diagram is shown and its characteristic frequency is 23 Hz and gas diffusion resistance ($R_{\text{gas}}$) is about $0.25\,\text{ohm cm}^{-1}$. The difference between the low-frequency and the high-frequency real part is the gas diffusion resistance. As depicted in fig.2 the obtained results show good agreement with the published simulation results (ref. 16, fig.16). This arc is due to gas phase diffusion in the cell. In experimental anode characterization, this features are often referred to as gas conversion, gas diffusion or gas concentration impedance [11,12,14-16]. A parametric simulation study by changing parameters, such as supplied gas phase compositions, temperature, and the cell dimensions, can be carried out. Here the effect of temperature and cell cross sectional area on electrochemical impedance spectra is investigated.

4.1 Effect of Temperature

The influence of temperature on the gas diffusion impedance is shown in Fig. 3. This fig. shows that with decreasing the temperature the cell performance gets better and the resistance decreases.

4.2 Effect of channel cross section

The influence of the channel cross-sectional area on the gas diffusion impedance is shown in Fig.4. Decreasing the cross-sectional area strongly increases $R_{\text{gas}}$ and this parameter has a strong influence on the gas concentration impedance. This is expected as diffusive transport between the inside of the channel and the surrounding gas chamber decreases.

CONCLUSIONS

In this paper simulation and analyzing the electrochemical impedance spectra of a SOFC anode is considered. The obtained conclusions are as follows:

- Channel diffusion causes a capacitive behavior in the form of an RC-type semicircle in the Nyquist diagram.
- The effect of temperature on the gas diffusion impedance is investigated. The diffusion resistance decreases by decreasing the temperature and the cell performance gets better.
- The effect of cross sectional area on the gas diffusion impedance is considered. The diffusion resistance decreases by increasing the cross sectional area.

REFERENCES

NICKEL SINTERING IN A SOFC ANODE

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Abstract – The sintering behavior of a Ni/YSZ electrode has been modeled and compared to two long time measurements (2000 h/3000 h). Firstly, a model for the two-body sintering process has been developed, which bases on the assumption, that the shrinkage of a particle is directly proportional to the mass flux, which is determined by the surface bending. Secondly, the model has been extended to the nickel network in a porous media. Thirdly, the influence of the steam content and flux rate has been taken into account. The modeled grain size growth has been compared to a measurement of an electrode under low flux rates and low steam content in order to lessen the effects of the third step in the model. Since the results were in good agreement with the experiment, a similar measurement with high flux rates and high steam content were simulated. The modeled curve was acceptable, but did not have the same accurateness, as in the former case.

Index Terms – Analytical Modeling, Degradation, Sintering, SOFC Anode.

I. INTRODUCTION

The Solid Oxide Fuel Cell (SOFC) is a high-efficient and low-emission electricity generator, which can be fed with both hydrogen and fossil fuels. Due to its high operating temperature, it is envisaged for decentralized and stationary applications. Therefore, it has to run stable for at least 40,000 h, which means, that the degradation rate has to be minimized. In a SOFC many different degradation processes have already been identified and in several cases their basic mechanisms are understood. Nevertheless, a lifetime prediction model has still not been developed.

Analytical modeling of the anode degradation, especially on the effects, which base on the sintering of nickel particles, is the aim of this work. The agglomeration of nickel particles leads to the increase in the resistivity [1] and the change of the active catalytic area for the oxidation reaction of the fuel [2]. Moreover, the effects of the operating parameters like the humidity and the flow rate are investigated in order to determine the long-term behavior of a SOFC anode.

II. THE MODEL

A. Two-body Sintering Process

The sintering process can often be described by a shrinkage relation expressed as

\[
\frac{\Delta \rho}{\rho_0} \sim r^2 t,
\]

where \( r \) denotes the grain size radius of a particle and \( t \) the time since the beginning of the sintering process [3]. The parameters \( q \) and \( s \) depend on the underlying mechanism (grain boundary, volume, or surface diffusion). Obviously, the formula tends either to diverge as \( t \) goes to infinity or to lead to infinitely large grain size. Therefore, a formula for the shrinkage evolution was developed, without specifying the diffusion process in detail. It is only assumed, that the grain growth is proportional to a particle flux, which just depends on the surface bending. The resulting formula described as

\[
x = \frac{\Delta \rho}{\tau} = \frac{1}{\sqrt{2}} \sqrt{1 - \frac{\tau}{\sqrt{1 + \tau}}} \quad \text{with} \quad \tau = \frac{D r^2}{RT \rho_0 r_0^2}
\]

has a well-defined behavior for every \( t \). The effective diffusion coefficient is given by \( D \), the surface energy by \( \gamma \), \( RT \) is the thermic energy factor, \( \rho_0 \) describes the density on the surface and \( r_0 \) is the grain size radius at \( t = 0 \).

B. Contact Probability and Volume Growth

The sintering process can just occur, when a particle has one neighbor at least. The iterative formula is written as

\[
r_{i+1} = (1 - w_{1,i}) \cdot r_i^3 + g(\tau) \cdot w_{1,i} \cdot r_i^3
\]

and describes a particle with grain size radius \( r_i \), which has no neighbor with the probability \( 1 - w_{1,i} \) and at least one with the probability \( w_{1,i} \). The growth factor \( g(\tau) \) takes into account the effect of the sintering process via the shrinkage formula (2). An evolution of the difference equation (3) leads to a coupled system of differential equations. Decoupled, the system offers a solution for the probability.
\[ w_1 \sim \frac{V_0}{V} \exp \left( -\frac{\sqrt{3}}{2} \frac{4}{3} eV^2 - 1 \right) \]  
(4)

and finally for the resulting time-dependent averaged volume of a sintered particle

\[ V(t) = V_0 + \frac{1}{k} \ln(1 + kDt), \]  
(5)

with the starting volume \( V_0 \) and constant of integration \( c \). The parameter

\[ k = \left( g(x(t)) - 1 \right) \cdot w_1 \cdot V \quad \text{with} \]

\[ \frac{dk}{dt} = 0 = \frac{\partial k}{\partial t} + \frac{\partial V}{\partial t} \]  
(6)

involves all relevant information of the process.

C. Influence of the Humidity and Steam Content

Due to the adsorption of hydrogen and water, the nickel flux on the surface is hindered and will change the nickel sintering process. The adsorbed particles (or their reaction products) can also be desorbed, so the relative change of a species takes the form

\[ \frac{\Delta n(t)}{\sigma_0} \sim (1 - \exp(-k_{\text{ads},i}t)) \exp(-k_{\text{des},i}t) \]  
(7)

With the adsorption and desorption rates \( k_i \) and the surface densities \( \sigma_i \), where the index 0 stands for the nickel density in the case of no adsorption. The effective diffusion coefficient is defined as

\[ D_e(t) = D_0 \left( 1 - \frac{\sigma_{\text{Ni}}}{\sigma_0}(t) - \frac{\sigma_{\text{H2}}}{\sigma_0}(t) \right). \]  
(8)

Further effort has to be put into the determination of the rates \( k_i \).

III. COMPARISON WITH EXPERIMENTAL RESULTS

Jiang measured the composition and grain-size distribution for 2000 h under 1000 °C in a reducing atmosphere (10 % \( \text{H}_2 + 90 \% \text{N}_2 \)) [4]. The porosity was 24 %, whereas one sample had a nickel content of 53 % and the other sample had 38 % (see Fig.1). The nickel particles had an averaged diameter of 1.54 μm at the beginning of the measurement.

The humidity in the fuel was about 3 %. This allowed testing the model approximately without the effects of nickel surface coverage that means the diffusion constant was taken as time independent. Measurements performed within the SOFC-Life project in Yekaterinburg, Russia, show the impact of different flux rates and steam contents (see Fig. 2) [5]. The initial particle diameter was about 1.5 μm, the nickel content was 51 %, and the porosity 31 %. The measurement was performed at 700 °C and 800 °C with low humidity of 3 % and a flux rate of 1.05 \( \text{lh}^{-1} \) and with a high steam content of 80 % at a rate of 5 \( \text{lh}^{-1} \).

IV. CONCLUSION

A model for the sintering process in a porous SOFC anode was developed and compared to experimental results. One measurement was performed under low steam content and low flux rates, whereas the second one was under high conditions. While the influence of the parameter like the porosity and nickel content seem to be well included, the effects of the humidity and temperature on the sintering mechanism are not fully understood. This combination drives speculations, if the missing part is kind of a Boltzmann factor, because this would connect the adsorption/desorption rates with the temperature. Further effort has to be put to this extension of the model.

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CHANGING THE RULES WITH FUEL CELL POWER PLANTS
(250 KW TO >2.8 MW) IN DAILY OPERATION (>1.8 TWH BY TODAY)

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Abstract – With the total production of more than 1.8 TWh electrical power by today and an annual production of about 70 MW of new fuel cell power plants FuelCell Energy / Solutions are changing the game: largest commercial fuel cells of the world (2.8 MW), largest installation (58.8 MW) and lowest price per kW.

Index Terms – Fuel Cell, Power Plant, CHP, Megawatt

I. INTRODUCTION

FuelCell Energy Solutions GmbH, a Germany based joint venture of FuelCell Energy, Inc., and Fraunhofer IKTS, manufactures, sells and provides full service for the Direct Fuel Cell (DFC®) power plants for whole Europe. Their goal is to provide ultra-clean, decentralized power solutions for different market segments based on renewable biogas or natural gas with a power price below grid prices.

II. CHALLENGES OF MARKET DEPLOYMENT

A. Lessons learned: Quick transition from successful demo projects to "normal" sales, production, construction and service?

FuelCell Energy conducted the first commercial MCFC project in 2003. Since then a cost reduction of 60% to below 3,000 €/kW is achieved. There is a technical and a commercial part of the challenge to come from a showcase project to commercialization. Focus of the technical part was reliability and availability, lifetime (stack and BOP), maximization of the output and the optimization of the supply chain. The commercialization is focused on business cases with benefits for the customer, the financer and the producer as well. Therefore the operation model changes the usual rules of the fuel cell business with a strong orientation of the operational cost through long term full service agreements with guaranteed power output, operation and monitoring of the plant and included cost for planned and unplanned maintenance as well as stack replacement etc.

B. Regions and Segments: What are the challenges of Business Development in the individual markets?

Successful deployment of the regional markets is driven by EU and local policy (energy, environment, legal, taxes etc.), the cost of energy and also the general economic situation. There are also special key drivers and value prepositions of the single market segments which support the business development. FuelCell Energy Solutions is addressing the following key market segments:

### Natural gas
1. Utilities and service providers
2. Education & Healthcare
3. Gas network operator
4. Manufacturing and Industry
5. Retail & Hospitality
6. Government & Public, building
7. Oil production and refining

### Renewable biogas
1. Sewerage companies
2. Food Industry & Breweries
3. Agriculture
4. Landfill operator

Fig. 1: Market segments
There is a global trend to larger installations using DFC®-power plants for grid support.

Fig. 2: Multi MW Fuel Cell Park - 60MW

C. Value driver: Why customers buy a fuel cell (and why not)?

Every customer has usually a unique mix of value drivers for his motivation to buy a fuel cell: reduction of power cost, increasing of power quality, grid independence, image and environmental impact etc. FuelCell Energy Solutions provides the individual solution and also argumentation for their whole buying center to assure a successful project from a technical and business prospective as well.

III. CONCLUSION

The Fuel cell industry is facing a challenging time since there has to be a commercial breakthrough now after years of overestimation and under delivery. Key is the value for the customer and not only the proudness about the technical solution. Fuel cell developer have to understand the customer and market focus and have to accomplish the transition from a R&D company to business developer and market maker.
A DEFINED CO-CULTURE OF GEOBACTER SULFURREDUCENS AND ESCHERICHIA COLI IN A MEMBRANE-LESS MICROBIAL FUEL CELL

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Abstract - Wastewater-fed microbial fuel cells (MFCs) are a promising technology to treat low-organic carbon wastewater and recover part of the chemical energy in wastewater as electrical power. Defined co-culture MFCs provide a detailed understanding of the interactions between electrochemically active and fermentative microorganisms such interactions. We characterize the extracellular metabolites in laboratory-scale membrane-less MFCs inoculated with Geobacter sulfurreducens and Escherichia coli co-culture and compare them with pure culture MFCs. G. sulfurreducens MFCs have a power output of 128 mW m \(^{-2}\), compared to 63 mW m \(^{-2}\) from the co-culture MFCs. Succinate production in co-culture MFCs decreases current production by G. sulfurreducens and its removal is responsible for the increased current density in the late co-culture MFCs. Co-culture MFCs provide clear insights into metabolic interactions among bacteria.

Index Terms - Co-culture MFC, Escherichia coli, Geobacter sulfurreducens.

I. INTRODUCTION

Microbial fuel cells (MFCs) are bioelectrochemical systems that convert chemical energy into electrical energy through electrochemically active bacteria (EAB) [1]. EABs can transfer electrons extracellularly to the electrode, either by direct or mediated mechanisms [1, 2]. MFCs enable energy recovery from wastewater and might improve sludge quality in full-scale wastewater treatment plants, for both conventional [3] and high strength wastewater [4].

MFCs are composed of two chambers: anode and cathode compartments, where anaerobic and aerobic conditions, respectively, are maintained. EABs that grow on anodes are anaerobes like Geobacter, or facultative anaerobes like Shewanella. Most MFCs implement abiotic oxygen reduction at the cathode to increase power output [5].

Wastewater-fed MFCs produce a few W.m \(^{-2}\) when equipped with high-surface carbon electrodes [6]. Additionally, mixed communities are also capable of consuming a wide range of substrates, thus making them versatile for energy recovery from various wastewaters. However, little is known about the interactions between EAB and fermentative organisms. A thorough understanding of the metabolic interactions between EABs and fermentative microorganisms will help to steer the overall microbial community to increase power output and coulombic efficiency.

Co-culture MFC using EAB and model fermentative bacteria enables the study of metabolic interactions in a simplified setup. [7]. Previous studies have shown that G. sulfurreducens MFC has the highest power density, while the power production by E. coli alone has been very low.

Here, we compare the metabolism and power output of a pure culture air-cathode MFC system containing only an electron to a co-culture containing an electron (G. sulfurreducens) and a facultative anaerobic organism (E. coli).

II. MATERIAL AND METHODS

The MFC were equipped with carbon fiber anode and platinized carbon paper cathode. No membrane was used. Electrode separation was approximately 5 mm and the anode volume was 0.4 L. G. sulfurreducens was grown at 30 °C in anaerobic tubes and bottles in NBAF medium containing 20 mM acetate as electron donor and 40 mM fumarate as electron. E. coli strain C was initially plated from freezer stocks onto LB plates and incubated overnight at 37 °C. Colonies were then transferred to 10 mL aerobic tubes of LB medium, containing 100 mM D-glucose as electron donor, and then incubated at 37 °C for 12 h. Subsequent generations were grown at 30 °C in anaerobic NB medium sparged with N2/CO2 (80:20, v/v). The MFC medium was NB medium with an additional 10 mM NaCl to increase conductivity. For co-culture MFCs the medium initially contained 10 mM acetate as the substrate for G. sulfurreducens, and was supplemented with additional acetate as necessary. 100 mM D-glucose was added to the MFCs immediately prior to E. coli addition. In E. coli MFCs, 100 mM D-glucose was added at the beginning of the experiments. G. sulfurreducens batch MFCs were allowed to reach a steady current, at which point a power curve and operating curve was determined for the cell. E. coli strain C was then inoculated and
the MFC was allowed to reach a steady current, at which point power curves were taken again. The power curve was taken a third time after glucose was completely consumed. Samples of the anode supernatant were taken regularly to measure the carbon source (glucose) and the main extracellular metabolites using HPLC analysis. MFCs were inoculated with mid-log phase culture of either *G. sulfurreducens* in co-culture cells, and subsequently with *E. coli* once current had reached a steady level, or solely with of *E. coli* in pure culture MFCs. *G. sulfurreducens* cells were sparged continuously with N2/ CO2, until 12 hours after *E. coli* addition. *E. coli* MFCs were sparged with the same gas only for the first 12 hours. External resistance was 240 Ω. Power and operating curves were constructed by varying external resistance between 10 kΩ and 10 Ω. The current and power were normalized to the projected anode surface area. HPLC analysis was done according to standard procedures.

III. RESULTS

The *G. sulfurreducens* MFC showed a typical growth curve. 20 mM acetate additions were made when current production began to decline due to acetate depletion. Residual fumarate from the inoculum was rapidly reduced to succinate. At this time, *G. sulfurreducens* began to grow on the anode and to produce current. Succinate was completely depleted by 65 h. The coulombic efficiency based on acetate mass balance was less than 10%. The pH of the *G. sulfurreducens* MFC remain about 7-7.5 throughout the experiment.

*E. coli* was inoculated when a sustained current was observed. Acetate and lactate began to accumulate in the cells as glucose was depleted. Succinate accumulated at a much lower rate until it peaked. The ethanol concentration remained very low. Succinate, lactate and acetate concentrations all began to decrease as they began to be consumed after the complete consumption of glucose at approximately 315 h, and succinate was completely removed from the system after 550 h. There was a subsequent decline in current until 600 h after *E. coli* addition (1087 h after *G. sulfurreducens* addition) at which time the current increased again. Acetate and lactate concentrations continued to decrease during this resurgence in current production. The polarization curve at 759 h (1246 h after *G. sulfurreducens* addition) gives a coulombic efficiency for *E. coli* inoculation was 1.97%. Upon addition of *E. coli* to the MFCs, the pH gradually dropped to pH 6.8 due to the production of organic acids in fermentation (first 300 h), and then reverted back to pH 7.5 after these acids were consumed.

The *E. coli* MFC produced the maximum power when *E. coli* was consuming glucose. Following glucose depletion, lactate and succinate were consumed, while a lag was observed before acetate consumption began. The *E. coli* MFCs showed a rapid drop in pH, which was neutralized through base addition.

Glucose was completely removed in bottle culture of *E. coli* after 160 hours, and then the metabolite concentrations remained nearly constant. Lactate, acetate and succinate were the main fermentation products. The acetate concentration stabilized after approximately 50 hours, significantly before glucose was completely consumed. Ethanol reached approximately 2 mM, much lower than the other metabolites.

The internal resistance increased following *E. coli* addition. The *G. sulfurreducens* MFCs reached a peak power of 128 mW m⁻², compared to 63 mW m⁻² for the early co-culture and 56 mW m⁻² for the late co-culture. The limiting current density was 404 mA m⁻² for the *G. sulfurreducens* culture, 184 mA m⁻² for the early co-culture, and 282 mA m⁻² for the late co-culture.

IV. CONCLUSIONS

Compared to pure culture MFCs, mixed culture MFCs had the following advantages: a) they do not require anode sparging with anaerobic gas; b) they do not require pH control; and c) they can oxidize complex artificial wastewater, using glucose as primary carbon source. The coulombic efficiency of the co-culture MFCs was about 2% on the total COD; in the co-culture MFC, this value increased to 19% on *E. coli* fermentation products accessible to *G. sulfurreducens* (acetate). Succinate production by *E. coli* inhibits power production, supporting the utility of co-culture microorganisms that minimize succinate production when grown in MFCs.

REFERENCES


ENHANCED BIFUNCTIONAL ACTIVITY OF LaNiO₃-BASED GAS DIFFUSION ELECTRODES FOR REGENERATIVE FUEL CELLS

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Abstract – Perovskites are of great interest when searching replacements for precious metals as catalyst for bifunctional oxygen electrodes involving the oxygen evolution (OER) and oxygen reduction reaction (ORR) as is the case of regenerative fuel cells. In this work a full electrochemical study on the electrochemical properties of gas diffusion electrodes (GDEs) using LaNiO₃-based catalysts, conducted in alkaline media, led to a study of cyclability and durability. The incorporation of GDEs in a low power electrolyzer/fuel cell prototype was also attempted. The stability of the electrodes was assessed by potential cycling and at constant current density with good results.

Keywords – Bifunctional oxygen catalyst; perovskite-type oxides; gas diffusion electrodes; regenerative fuel cells.

I. INTRODUCTION

RFCs are promising energy storage systems for uninterrupted power supplies, which can provide very high energy storage at minimal weight, by combining an electrolyzer and a fuel cell. Although an appealing technology, their development is still at an early stage. Perovskite-type oxides, with the general formula ABO₃, are potential catalysts for next generation of regenerative fuel cells. Nickel containing perovskite type oxides has been recognised as one of the most promising oxygen electrodes [1]. In this work, a full electrochemical study on the electrochemical properties of gas diffusion electrodes using LaNiO₃ based catalyst was carried out. The stability of the electrodes was assessed by potential cycling and at constant current density with good results. Results obtained after incorporation of the compounds in GDE and in low power electrolyzer/fuel cell prototypes are presented.

II. EXPERIMENTAL

Perovskite-type oxide LaNiO₃ was prepared by a self-combustion method using citric acid, as previously reported [1]. Structural characterisation was performed by X-ray diffraction (XRD) using a Philips PW 1730 diffractometer, operating with Cu Kα radiation. Electrodes were prepared on carbon paper substracts, consisting of a diffusion, a catalyst and a Nafion® layer. The GDLs were prepared from carbon black Vulcan XC-72 R, with a loading of 2.5 mg cm⁻². To fabricate the catalyst layer, an ink was prepared by suspending the material in isopropanol, and stirring in an ultrasonic bath for 10 min to thoroughly wet and disperse it. A 5% Nafion® dispersion solution (Electrochem, Inc) was then added to the mixture. The catalyst inks were dispersed onto the GDL with a brush, and dried at 50 °C until a catalyst loading of 5±0.5 mg cm⁻² was achieved. Finally, a Nafion layer was painted and dried at 50 °C until a loading of 0.7 mg cm⁻² was reached. The morphology of the oxide electrodes was observed using a Phillips scanning electron microscope, Model XL 30 FEG, coupled to an energy dispersive spectrometer, EDS.

A conventional three-electrode glass cell was used for the electrochemical studies using a PARC model 173 potentiostat. The measurements were carried out at room temperature, using Ag / AgCl / KCl (sat) as the reference electrode to which all potential are referred. A Pt rod was used as counter electrode. A 1M KOH solution was prepared using Millipore Milli-Q ultrapure water. Prior to each electrochemical measurement, the solution was purged with high-purity N₂.

Stability at constant current density (0.4 and 6 mA cm⁻²), during cycles between the OER and ORR with simultaneous potential monitoring, was assessed.

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of acrylic resin were machined to accommodate the polymeric electrolyte membrane, GDEs land the current collectors. Current collectors were connected to an electronic load for the running of the polarization / power curves.

III. RESULTS AND DISCUSSION

The electrodes based on LaNiO$_3$ perovskite type oxide were primarily developed as oxygen evolution (OER) electrocatalysts for water electrolysis in alkaline medium. The formation of the desired oxides was confirmed by XRD. SEM morphology analysis of the powders revealed a globular morphology and uniform size nano-particulated aggregates [2]. A full electrochemical study was conducted in order to kinetically characterize electrodes prepared on carbon paper as a base for GDE in alkaline media. Results indicated that, due to the enhancement of the catalytic activity for both the ORR and OER, the LaNiO$_3$ composite with Pt/Ru nanoparticles (LaNiO$_3$-Pt/Ru/C) and La$_{0.8}$Sr$_{0.2}$FeO$_3$ are the catalysts of choice for incorporation in a PEM E/FC [2].

Fig.1a) shows the polarization curves in both fuel cell and electrolyzer mode indicating enhanced catalytic activity for LaNiO$_3$-Pt/Ru/C as compared with plane LaNiO$_3$. In the inset results are presented of the cycling between OER and ORR potential at constant current evidencing stability only for ORR. This is consistent with electrode stability studies performed by applying the potential cycling program stated in section 2, using cyclic voltammetry and electrochemical impedance spectroscopy to check on stability after cycling, with complementary SEM/EDS analysis of fresh and degraded electrodes. Evident degradation after 200 cycles will be documented. A SEM/EDS study was instrumental in detecting voids between the backing and the catalyst layers (CL) which promoted the partial detachment of the latter. Detected loss of fluoride from the Nafton® ionomer network within the CL appears in backing layers together with the presence of potassium from the electrolytic solution. This is compatible with the increased resistance found after cycling, indicated by the EIS. Usually, the carbon support is chosen for the catalysts because of its high conductivity, rather than enhancement of activity. Since the anode of the water electrolyzer is operated at potentials higher than 0.9 V, carbon corrodes [2]. This corrosion can create a loss of electrical contact necessary for the transport of electrons, thus decreasing the performance.

A more stable catalyst also studied in this work is La$_{0.8}$Sr$_{0.2}$FeO$_3$. Meaningful current densities for OER and ORR could be measured for potentials around 0.52 and -0.23 mV respectively, see fig 1b), with a $\Delta E$ values better than those obtained for noble metal catalysts such as Pt (1.16 V) and Ir (0.92 V) [3].

IV. CONCLUSION

Developed catalyst made effective bifunctional oxygen GDEs when used in alkaline medium. The given potentials for the on-set of OER and ORR are separated by only 0.75 mV after 140 cycles for La$_{0.8}$Sr$_{0.2}$FeO$_3$.

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ELECTROCATALITIC ACTIVITY OF PLATINUM DEPOSITED ON CARBON FUNCTIONALIZED WITH SULPHONIC GROUPS

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Abstract – Results are presented for Pt deposited on 4-aminobenzenesulphonic acid-functionalized carbon, Pt/C_ABSA. Vulcan XC-72R was functionalized in order to influence catalyst dispersion and decrease the resistance of three phase boundary, by introducing sulphonic groups and lessening the amount of Nafion® added to the catalyst layers.

Electrochemical characterization of the supported catalyst was done in a 0.5 M H₂SO₄ solution with added methanol or chloride demonstrating well defined features and stable voltammograms after cycling, with apparent higher currents when compared with commercial catalyst. The structure sensitive adsorption of anions on platinum is confirmed by either the blocking effect of chloride ions or methanol, evident in both anodic and cathodic features of the voltammograms. Optimal performance was found for a Nafion® concentration of 15-20 wt%.

Keywords – Pt electrocatalysts, chemically modified carbon, sulphonic groups, methanol oxidation, Pt dissolution, chloride.

I. INTRODUCTION

Carbon blacks surface chemistry modifications, with a view to increase the number of anchoring sites, loading and dispersion of metal catalyst, have received a great deal of attention [1-3].

In this work, the strategy used for carbon functionalization consisted, first, on the introduction of oxygenated groups at the surface by chemical oxidation and then their reaction with aminoaromatic sulphonic groups. The objective of this kind of functionalization is to improve the dispersion of catalyst nanoparticles and the resistance of the three phase boundary layer by diminishing the amount of nafion ionomers in the catalyst layer, key to transport properties, and also to modify the acid/base properties of the support. Better catalyst utilization is envisaged. Preliminary results obtained with Pt deposited on 4-aminobenzene-sulphonic acid-functionalized carbon are reported.

II. EXPERIMENTAL

The chemicals were of analytical reagent grade, used without further purification. FTIR spectra were recorded on a Perkin-Elmer Spectrum BX v5.3.1 spectrometer.

Vulcan-COCI and 4-aminobenzenesulphonic acid-functionalized carbon, C_ABSA, were prepared following published procedures [2]. The synthesis of catalyst, Pt/C_ABSA, was performed by a formate ion reduction method previously described [3]. The preliminary physical characterization of the catalysts was performed by SEM and EDX analysis using a JEOL8500F Field Emission Gun, EDX (SSD type) instrument.

The voltammetric experiments were carried out with a PAR wave form generator, model 273, controlled by a PC (software “Corrware”) using a Greene cell with a three electrode configuration. The auxiliary electrode was a platinum rod and the reference electrode was a commercial Ag/AgCl electrode, connected to the electrochemical cell by a salt bridge. All the potentials in this work are quoted to this reference electrode. The working electrode was prepared by depositing 10 µL of a catalyst ink on a glassy carbon rod base surface with 7 mm diameter. The ink was prepared by mixing the catalyst, isopropanol and Nafion® solution (5 %, Aldrich) and finally the mixture was sonicated by 30 min. After deposition, the ink was dried at 50 ºC for 2 h. The specimens were also weighted before and after the deposition, and also during the drying operation, in order to estimate the catalyst load. The catalyst loadings were 1.0 and 1.3 mgcm⁻², for the study of effect of the chloride and methanol, respectively. The electrochemical active surface area (ESA) of the catalyst was estimated from voltammograms carried out within the potential range from -0.2 to 1 V, run at a scan rate of 50 mVs⁻¹ in 0.5 M H₂SO₄ solution. Before running the experiments the solution was purged with N₂ for 30 min, in order to remove any oxygen present. During the experiments the gas purging was maintained above the solution. The methanol oxidation reactivity was studied by exposure of the catalyst ink, at the open circuit potential, to a solution of 0.5 M H₂SO₄ + 1 M CH₃OH after N₂ purging for 30 min. Oxidation and voltammetric features recovery were assessed in a 0.5 M H₂SO₄ solution, at a sweep rate of 50 mVs⁻¹. Chloride contaminations were undertaken introducing NaCl in a concentration of 0.005 M. The effect of Nafion® was studied covering concentrations from 2 to 25 wt%. All measurements were carried out at 25°C.
III. RESULTS AND DISCUSSION

The electrocatalytic activity of the functionalized catalyst Pt/C_ABSA is reported in three different fronts: capacity for methanol adsorption and oxidation; the effect of chloride as catalyst layer contaminant and the effect of Nafion® concentration on electrode performance.

III.1 Methanol adsorption

The adsorption of methanol at the open circuit on Pt/C_ABSA was examined after exposure to a N₂-purged acidified 1 M CH₃OH solution. Exposures up to 45 minutes were followed by cyclic voltammetry characterisation in a methanol free 0.5 M H₂SO₄ solution, at a sweep rate of 50 mVs⁻¹.

Typical results are presented in figure 1, for a 30 min. exposure. Oxidation of the adsorbed methanol is evident in the first sweep (peak at ~+0.620 V). Also evident is the site selectivity in the hydrogen region of the voltammograms consistent with single crystal Pt studies for CO oxidation [3]. It is observed that after the second sweep the voltammogram shows complete recovering of the features obtained after acid activation (before methanol exposure). The catalyst provides the needed adsorbed oxygen containing species required to complete the oxidation of methanol suggesting that Pt adsorbed oxygen species in the potential range in question, play a role in the reaction with surface-bonded intermediates, producing results comparable to those obtained with Pt-Ru catalyst.

III.2 Chloride contamination

The chloride structure sensitive adsorption in the Hupd region is demonstrated. The activity of the supported Pt can be correlated with the blocking effect of chloride ions on specific crystal planes, namely (100) facets. The capacitive region is shown to be extended due to the suppression of the formation of Pt oxide followed by a quasi-linear current increase, adjudicated to platinum dissolution. The effect of chloride is found to be partially reversible.

The CV profile is recovered, even though with less electrochemical surface area. After 30 cycles in the presence of chloride the ESCA has reduced in 31.60 %. Initial ESCA value was estimated in 41.75 m²g⁻¹Pt. Furthermore, the loss associated to the chloride effect appears to be smaller with Pt/C_ABSA when comparing with the commercial catalyst.

III.3 Effect of Nafion® content

The effect of Nafion® on the performance of the catalyst was examined using different Nafion® loading varying from 2 up to 25 wt%. A maximum charge in the hydrogen region is found for 15-20 wt %. The effect is illustrated in figure 2. The estimated optimal Nafion® content for Pt/C_ABSA catalyst is far lower that of 30–35 wt% found for conventional Pt/C catalysts such as E-TEK.

IV. CONCLUSION

- Pt/C_ABSA catalyst demonstrated good capacity for methanol oxidation including adsorbate adsorption formation and removal.
- CV profiles are recovered after chloride contamination, even though with a reduction in ESCA due to Platinum dissolution.
- Preliminary results indicate that a maximum of 15-20 wt% Nafion® in the catalyst layer produces the best catalyst performance.

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PT “HOLLOW” NANOPARTICLES: TOWARD THE PROMISING DESIGN OF ACTIVE AND STABLE ORR ELECTROCATALYSTS


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Abstract - Bimetallic Pt₃Co/C electrocatalysts are now classically used at the cathode because of their enhanced oxygen reduction reaction (ORR) activity. However, these materials are neither compositionally nor structurally stable, as evidenced by scanning transmission electron microscopy (STEM) coupled with electron energy loss spectroscopy (EELS). The dissolution of Co from the mother electrocatalyst induces a decrease of the cathode performance due to depreciated intrinsic specific activity and contamination of the ionomer/proton-exchange membrane by Co²⁺ ions. Learning from these findings, an innovative route towards more active and stable ORR electrocatalysts is proposed. Pt “hollow” nanoparticles synthesized in-house feature 2-3 fold improvement of the ORR activity over “bulk” Pt/C nanoparticles, and are structurally stable over time.

Index Terms – atomic-scale spectroscopic imaging, electrocatalyst degradation mechanisms, oxygen reduction reaction, Pt “hollow” nanoparticles.

I. INTRODUCTION

The sluggish oxygen reduction reaction (ORR), cathodic reaction in a proton-exchange membrane fuel cell (PEMFC) is the reaction limiting their performance. From a kinetic point of view, Pt remains the best electrocatalyst and its activity can be increased by a factor 2-4 upon alloying with a 3d-transition metal (Cr, Co, Ni) [1]. However, the stability of Pt-based materials remains challenging.

In this study, we firstly combined conventional and advanced electron and X-ray based techniques to provide new insights into the structural changes of Pt₃Co/C nanocrystallites in real PEMFC conditions. The second part of this study is dedicated to the synthesis of Pt “hollow” nanoparticles. This particular nanostructure, still yet understudied in the literature, combines several advantages with respect to the three decisive issues for practical applications (activity, stability and cost).

II. RESULTS AND DISCUSSION

A. Durability of Pt₃Co/C ORR electrocatalysts

The long-term stability of Pt₃Co/C electrocatalysts was investigated following long-term (3422 h) operation at constant current density. Similar to pure Pt/C nanoparticles, Pt₃Co/C lose their catalytic activity, mostly as a result of the loss of electrochemically active surface area (ECSA). In addition, Pt₃Co/C electrocatalysts present the disadvantage to be compositionally unstable. Previous work from our own [2] and other groups evidenced that Co atoms can diffuse from the bulk to the surface of the particle where they are instantaneously leached out. Figure 1 shows representative high-angle annular dark-field (HAADF) images of the fresh and of the 3422 h-aged Pt₃Co/C. Scanning transmission electron microscopy (STEM) coupled with electron energy loss spectroscopy (EELS) indicate the formation of three different Pt-Co nanostructures over time: (i) Pt-Co/C core-shell particles characterized by an alloyed (but depleted, compared to the fresh material) core surrounded by a 3-5 monolayer thick Pt-rich shell, (ii) Pt-Co/C “hollow” particles and (iii) pure Pt/C “hollow” particles, from which Co dissolution has been completed [2]. The dissolution of Co atoms causes
contamination of the ionomer/proton-exchange membrane, and mass-transport issues, as shown by experiments with a self-designed “dry cell” able to operate in well-controlled conditions (relative humidity, temperature) [3].

Figure 1: Representative HAADF images of fresh/aged nanoparticles acquired simultaneously with electron energy loss spectra acquired in spectrum imaging mode.

**B. Toward an active and stable ORR electrocatalyst via in-house synthesis of Pt “hollow” particles**

The Pt “hollow” nanoparticles that form on the long-term in PEMFC conditions are attractive materials to fulfil the cost, performance and durability requirements of proton-exchange membrane fuel cell (PEMFC) for practical deployment. Indeed, such nanomaterials (a) possess increased surface-area-to-volume ratio (better utilization of Pt atoms vs. “bulk” materials), (b) feature enhanced ORR specific activity (per cm² of Pt) and enhanced durability (see Figure 2) and (c) do not release non-noble metals in the ionomer/membrane therefore avoiding contamination issues.

![Normalized ECSA determined from COad stripping coulometry.](image)

To shed light on the stability of these nanostructures, an accelerated stress test (AST) composed of 5000 potential cycles between 0.60 and 1.05 V vs. RHE was performed. Such AST simulates the variable potential range experienced by a cathode material during operation (E = 0.60 V vs. RHE) and open circuit potential conditions (E = 1.05 V vs. RHE start-up/shutdown). The identical location transmission electron microscopy (IL-TEM) measurements demonstrate no change in structure, therefore opening a new route to highly active and durable PEMFC electrocatalysts with minimal Pt mass.

**Figure 3: IL-TEM images of Pt “hollow”/C particles before and after 5000 potential cycles between 0.60 and 1.05 V vs. RHE – 0.050 V s⁻¹ - 0.1 M H₂SO₄ – T = 298 K.**

**III. CONCLUSIONS**

At the light of these results, bimetallic ORR Pt₃Co/C electrocatalysts are not a viable solution for PEMFC application due to their failing stability. In contrast, in-house synthesized Pt-Hollow have great potential to replace Pt-based catalyst by fulfilling activity, stability and cost requirements.

**ACKNOWLEDGMENTS**

This work was funded by Oseo-AII in the framework of the H2E project.

**REFERENCES**

EVALUATING METHANE AND ACETATE PRODUCTION IN MICROBIAL ELECTROLYSIS CELLS: REACTOR PERFORMANCE AND MICROBIAL DIVERSITY

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Abstract - The work investigated the potential of microbial electrolysis cells (MECs) for methane and acetate production from synthetic wastewater. In a single-chamber MEC operating with acetate as the electron and carbon source, methane and hydrogen were the main reduction products. Acetate consumption as Chemical Oxygen Demand (COD) was 0.26 Kg-COD m⁻³ d⁻¹, compared to only 0.04 Kg-COD m⁻³ d⁻¹ in the open circuit control which did not produce considerable biogas amounts. In a two-chamber reactor provided with a cation exchange membrane, acetate could be retrieved from the cathode with an efficiency of up to 85% and rates of 2.5 mM d⁻¹. Phylogenetic analysis revealed that the initial microbial population was enriched with substantially different bacterial species on the two electrodes of each MEC. Distinct tasks were carried out by these different microbes, as also supported by the cyclic voltammograms.

Index Terms – biocathodes, carbon dioxide reduction, microbial diversity, microbial electrolysis cells

I. INTRODUCTION

Municipal wastewater treatment can account for around 3% of the total energy spent in many developed countries[1]. However, wastewater itself contains a chemical energy of around 4 times the energy currently spent for wastewater treatment[2],[3] and could be used as a free organic feedstock of anodic processes in bioelectrochemical systems[4]. In a sustainable biorefinery concept, anodic wastewater treatment could be merged with microbial electrocatalysis, where microbes serve as “catalysts” by accepting electrons from a conductive surface to synthesize fuels and organic molecules from carbon dioxide[4] (Fig.1).

II. MATERIALS AND METHODS

Both single-chamber and membrane-separated MECs (585 mL total working volume) were used in this study. All electrodes were made of graphite felt (180 cm²) and were placed within a 3 cm distance from each other. In two-chamber reactors a cation exchange membrane (196 cm² CEM; CMI-7000) was used to separate the anode from the cathode. A two-channel potentiostat (MLab 200) was used for chronoamperometry (anode operated between 0 to -300 mV vs. Ag/AgCl) and cyclic voltammetry (CV; 1 mV sec⁻¹) experiments. Mesophilic anaerobic sludge was taken from the local wastewater treatment plant.
plant (Gryaab AB, Gothenburg, Sweden) and was used to seed the MEC reactors. A minimal medium supplemented with acetate was used. Acetate was periodically added such that acetate concentration was kept between 200-1,000 mg L\(^{-1}\). Reactors operated at ambient temperature, around 20\(^\circ\)C. The characterization of bacterial populations was performed by extraction of the total DNA and sequencing of the 16S ribosomal RNA genes.

### III. RESULTS

#### A. Reactor performance

In the membraneless reactor, acetate consumption (as Chemical Oxygen Demand; COD) was 0.26 Kg-COD m\(^{-3}\) d\(^{-1}\) on average for all anode potentials (85% Coulombic efficiency; CE), compared to only 0.04 Kg-COD m\(^{-3}\)d\(^{-1}\) in the open circuit control. Up to 85% of the produced biogas was methane, which was the main end-product of the cathode; while no biogas could be retrieved from the open circuit control. In a two-chamber provided with a CEM, acetate was produced in the cathode at rates up to 2.5 mM d\(^{-1}\), capturing up to 85% of the electrons released from the anode. However, the presence of the CEM caused a serious pH imbalance. When a 35 cm\(^2\) opening was made to the CEM to stabilize the pH, acetate continued to be produced from the cathode. CE was up to 150% in this instance and less methane and hydrogen were produced, compared to the membraneless reactor.

#### B. Microbial diversity

Microbial populations differed significantly on the two electrodes of the same reactor. In the single-chamber reactor, bacteria populations on the anode consisted mainly of Proteobacteria (Fig. 2; no membrane), 94% of which were *Geobacter sp.*, a \(\delta\)-Proteobacterium. *Geobacter sp.* were absent from the cathode, where the majority (75%) of the bacteria belonged to the \(\beta\)-Proteobacteria class.

In the reactor which started with the anode and cathode separated from each other (Fig. 2; sliced membrane), *Geobacter sp.* were again the only \(\delta\)-Proteobacteria present on the anode and represented 94% of the total Proteobacteria. Bacteria on the cathode were mainly Proteobacteria (76%), 97% of which were \(\gamma\)-Proteobacteria and mainly *Pseudomonas sp.* (83% of the total \(\gamma\)-Proteobacteria). *Geobacter sp.* were absent from the cathode but *Acetobacterium sp.* were present, explaining the observed acetate production.

### IV. CONCLUSION

MECs can be integrated into the biorefinery processes where fuels and commodities are produced from the energy present in wastewater. Herein we demonstrate that mixed microbial populations offer important adaptation flexibility in MECs, and depending on the electrodes’ microenvironments they can carry out very diverse tasks as biocatalysts.

ACKNOWLEDGMENT

We would like to thank Göteborg Energi AB for funding this project and Gryaab AB for providing the microbial inoculum.

### REFERENCES


Fig. 2: CVs and phylogenetic analysis of the bacterial populations present on the anode and cathode of a single-chamber reactor (a and b) and a reactor where the membrane was sliced after pH imbalances were observed (c and d). CVs are compared with those of a reactor operated as an open circuit control.
ANODIC AND CATHODIC MICRIBIAL COMMUNITIES IN SINGLE CHAMBER MICROBIAL FUEL CELLS

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Abstract – Microbial fuel cells (MFCs) are a new technology for energy production from biomass. Nowadays little information is present in literature about the structure of the microbial communities operating in MFCs, particularly in biocathodes. The aim of this work was the characterization of the microbial communities operating in a membraneless Single Chamber Microbial Fuel Cells, to gain more insight into the extracellular electron transfer (EET) mechanisms. Taxonomic characterization of the microbial community was carried out by DGGE fingerprinting and by Next-Generation Sequencing (NGS) of 16S rRNA gene. DGGE analyses showed that the anodic microbial populations differed in relation to the material and the geometry of the anode. Moreover the sequence of the most intense bands on the cathodic biofilms revealed the interesting presence of purple non-sulphur bacteria (PNS). NGS revealed that microorganisms belonging to Geovibrio genus dominated the anodic community. This population has never been detected in MFCs so far.

Index Terms - DGGE fingerprint, Extracellular electron transfer mechanisms, Microbial fuel cells, Next-Generation Sequencing

I. INTRODUCTION

Microbial fuel cells (MFCs) are attracting considerable attention as innovative systems for energy production from renewable residual biomass and biomass-derived wastes. Potential applications include niche devices such as sediment-powered remote data collection. In an MFC, a microbial biofilm oxidises organic matter and transfers electrons from reduced compounds to an anode as the electron acceptor. The electrons then pass through a circuit and combine with a terminal electron acceptor and protons at the cathode where the reduction process can be mediated by microorganisms (biocathode). The wide range of processes that allow microbes to transfer electrons to/from the electrodes are called extracellular electron transfers (EET). Bacteria may either produce extracellular mediators (shuttles) or directly transfer electrons by membrane cytochromes [1]. Recent studies proposed the possibility to use biocathodes to make the MFCs technology more scalable. The EET involving cathodic communities may be similar to mechanisms described for the anodic biofilms [2], however the global process needs to be more extensively studied. Details about the electrochemical performance and bacteria operating in membraneless single chamber MFCs fed with raw wastewater from a municipal plant were reported in other works [3], the attention is here focalized on the microbial communities operating bio-anodes and biocathodes in a MFC operated with digestate from a biogas plant in comparison with others operated with raw wastewater from a municipal plant.

II. MATERIALS AND METHODS

A. MFCs operation

Experiments were carried out with a set of single chamber MFCs. Cathodes were prepared using carbon cloth (30 wt% PTFE) and carbon paper covered with a Micro Porous Layer with or without platinum. Untreated carbon cloth of 5 cm² was normally used as the anode. A few MFCs operated with larger anodes of 100 cm², carbon brush and stainless steel commercial mesh [3]. The cells were inoculated with raw wastewater and sludge form a biogas plant. Anodic and cathode biofilm samples were collected after one month and after three months for the fingerprint analysis. The anodic biofilm of one MFC with a carbon cloth anode and sludge from a biogas plant as inoculum was in depth described by 16S rRNA gene Next-Generation Sequencing (NGS).

B. Communities characterization

For the Denaturing Gradient Gel Electrophoresis (DGGE)
the V3-V5 hypervariable regions of the 16S rRNA gene were amplified by using 357F with a 40-bp GC-clamp and 907R primers. Band relative intensity allowed calculation of the abundance-based Jaccard index as a measure of the pairwise distances between the microbial communities. Selected bands were sequenced and the Ribosomal Database Project (RDP) classifier was used for the taxonomic assignment.

For the NGS the hypervariable V6 region of the 16S rRNA was amplified by using 783F and 1027R primers [4]. The sequencing was performed by an Illumina HiSeq1000 sequencer with 2x100 paired end sequences. A quality filter (cut-off Q=30 was applied) and the reads were combined. 10000 random sequences were classified using the RDP classifier with 50% of confidence.

III. RESULTS

DGGE analyses were carried out of MFC inoculated with raw wastewater and showed that after one month of operation, the anodic microbial population fingerprints differed in relation to the material and the geometry of the anode (Fig.1). Interestingly, the anodic communities after three months did not differ significantly from those found in the cathodes. Moreover the sequence of the most intense bands after three months revealed the interesting presence of purple non-sulphur bacteria (PNS), i.e. anoxicigenic photosynthetic bacteria on the cathodic biofilms.

NGS sequencing was carried out on MFCs inoculated with sludge from a biogas plant as inoculum and revealed that the most abundant order in the anodic biofilm is **Deferribacterales** (29.8% of the sequences) (Fig. 2). Most of the sequences belong to **Geovibrio** genus, which are iron-reducing microorganisms [5]. This population represents an isolated clade of iron-reducing bacteria compared to the microorganism belonging to **Proteobacteria** phylum and has never been detected in MFCs so far. Furthermore 5.2% of the sequences of the anodic community belong to the **Rhodospirillales** order, mainly in the **Rhodospirillaceae** family confirming the presence of PNS.

IV. CONCLUSION

DGGE fingerprinting analyses and NGS sequencing were successfully applied for studying microbial community in single chamber MFCs. The former technique is used for comparison of microbial communities developed under different conditions, while the latter is nowadays the method of choice for deeply analyzing the microbial community compositions. The results confirmed the needs of in-depth characterization of the microbial community for a better understanding of EET processes in MFCs. While the role of iron-reducing bacteria is already well established in anodic EET processes, the understanding of the role PNS is still to be clarified.

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IRON CHELATES AS LOW-COST AND EFFECTIVE ELECTROCATALYSTS FOR OXYGEN REDUCTION REACTION IN MICROBIAL FUEL CELLS


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Abstract - Iron-chelated electrocatalysts for the oxygen reduction reaction (ORR) in a microbial fuel cell (MFC) were prepared from sodium ferric ethylenediamine-N,N’-bis(2-hydroxyphenylacetic acid) (FeE) and sodium ferric diethylene triamine pentaacetic acid (FeD) supported on carbon Vulcan XC-72R and multi-walled carbon nanotubes (CNTs). The catalytic activity of the prepared catalysts towards ORR was studied by cyclic voltammetry, showing the higher electrochemical activity of FeE in comparison with FeD and the superior performance of catalysts supported on CNT rather than on carbon Vulcan. FeE/CNT was used as cathodic catalyst in an MFC using domestic wastewater as fuel.

Index Terms - Iron-based catalyst; Iron chelates; Oxygen reduction reaction; Microbial fuel cell.

I. INTRODUCTION

Among the numerous systems under investigation to develop sustainable energy production devices, microbial fuel cells (MFCs) have the added value to contribute to wastewater treatment while producing energy. These bio-electrochemical systems in fact, convert the chemical energy stored in the biodegradable organic matters present in wastewater into electrical energy through the catalytic action of microorganisms. [1-2]. The power density of MFC is mainly governed by the cathode side [3], where oxygen is the most popular cathodic electron acceptor due to its charge-free nature and high redox potential characteristic. The use of precious platinum as catalyst for the oxygen reduction reaction (ORR) significantly contributes to device cost, thus representing an important obstacle to the commercial development of MFCs. The cathodic materials account for 47% of MFCs total cost which would be largely reduced replacing platinum with less expensive species. Several non-platinum materials, i.e. cobalt, manganese, titanium, lead, copper, were investigated for platinum substitution. Among these metals, iron is particularly appealing because of its low cost and high abundance. Different iron-based catalysts such as iron phthalocyanine, iron acetate, Cl-FeIII tetramethoxyphenylporphyrin, iron ethylenediamine-tetraacetic acid [4-5] have been explored as cathodic catalysts for MFC applications demonstrating that Fe-containing species are promising candidates as ORR catalysts. In this study, catalysts containing iron chelates of ethylenediamine-N,N’-bis(2-hydroxyphenylacetic acid) and diethylene triamine pentaacetic acid supported on multiwalled carbon nanotubes or Carbon Vulcan were prepared and characterized.

II. EXPERIMENTAL AND DISCUSSION

Multi-walled carbon nanotubes (CNT), sodium ferric ethylenediamine-N,N’-bis(2-hydroxyphenylacetic acid) (Fe EDDHA), and diethylene triamine pentaacetic acid pentasodium salt solution (DTPA) were purchased by Aldrich.

Solutions of Iron containing precursors were prepared either dissolving sodium Fe EDDHA or a mixture of sodium DTPA and FeCl3·6H2O in water. Carbon Vulcan XC-72R or purified CNTs were added to the solution. The mixture was stirred for 0.5 h, filtered and the resulting wet solid dried at 70 ºC overnight. The powder was ground, placed in a ceramic vessel and heated to 800 ºC for 1.5 h under argon to obtain the catalysts which labeling is indicated in Table 1.

Commercial platinum 10 wt. % on carbon Vulcan (Pt/C) was obtained by Quintech and used as reference. Cyclic voltamograms (CV) were measured by a Potentiostat VMP3 (Bio Logic Science Instruments) at room temperature in 50 mM phosphate buffer solution (pH=7) saturated with either nitrogen or oxygen gas, with a scan rate of 10 mVs⁻¹. Single-chamber
air-cathode MFCs were assembled: the anode consists of graphite fiber brush with titanium wire as core. No catalyst was applied to the fiber brush anode. The cathode was prepared as previously reported [6]. Domestic wastewater (DW) samples were collected from a wastewater treatment plant in Canegrate (Italy) and were characterized before and after MFC tests. For MFC tests, DW was used as both inoculum and substrate.

Figure 1 shows the CV curves of the two families of iron-chelated catalysts: FeE and FeD, deposited either on carbon Vulcan (C) or on multiwalled carbon nanotubes (CNT). Under oxygen purging, the peak due to ORR can be clearly recognized, indicating that the iron-chelated catalysts are active towards oxygen and have a more positive reduction peak with respect to the substrates. The potential and current density of the ORR peaks for the different samples is listed in Table 1. On the basis of its highest oxygen reduction voltage (Ep), the best iron-chelated catalyst appears to be FeE/CNT (Ep = -0.017 V).

TABLE I
Catalysts labeling, potential (E_p), and current (I_p) peak

<table>
<thead>
<tr>
<th>Sample</th>
<th>Label</th>
<th>E_p (V vs. SCE)</th>
<th>I_p (mA/cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaFe/EDDHA/CNTs</td>
<td>FeE/CNT</td>
<td>-0.017</td>
<td>-0.702</td>
</tr>
<tr>
<td>NaFe/EDDHA/C</td>
<td>FeE/C</td>
<td>-0.114</td>
<td>-0.587</td>
</tr>
<tr>
<td>NaFe/DTPA/CNTs</td>
<td>FeD/CNT</td>
<td>-0.220</td>
<td>-0.396</td>
</tr>
<tr>
<td>NaFe/DTPA/C</td>
<td>FeD/C</td>
<td>-0.288</td>
<td>-0.396</td>
</tr>
</tbody>
</table>

To compare the performance of FeE/CNT with a reference Pt/C cathode, two air-cathode single-chamber MFCs equipped with the same anode were assembled. The cells were operated in parallel in batch mode feeding on domestic wastewater (DW) and acetate. Figure 2 shows the resulting polarization and power density curves. Power density decreases slightly when FeE/CNT is used to substitute the commercial Pt/C catalyst (127 mWm^2 vs 226 mWm^2). No substantial difference was observed in the current density generated by the two MFCs: the measured value being 1100 mA/m^2 for the cell containing the iron-based cathode and 1300 mA/m^2 for the one assembled with the reference Pt/C catalyst.

Figure 2: Polarization (E-I) and power density (PD) curves of MFCs fed with domestic wastewater and equipped with Pt/C and FeE/CNT cathodes.

III. CONCLUSION
This study presents the development of low-cost iron-chelated catalysts with high catalytic activity towards oxygen reduction reaction (ORR) for microbial fuel cell (MFC) applications. The electrocatalysts were prepared using either EDDHA or DTPA as chelating agent. Carbon Vulcan and multiwalled carbon nanotubes (CNTs) were used as catalyst support. Cyclic voltammetry experiments indicated that, among the two families (EDDHA- and DTPA-based) of prepared catalysts, the most active is NaFeEDDHA supported on CNTs (FeE/CNT).

The FeE/CNT catalyst was assembled in a MFC fed with domestic wastewater. The results obtained demonstrated that FeE/CNT was active as cathodic catalyst and its performance was just slightly lower than that of Pt/C catalysts.

ACKNOWLEDGMENT
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Abstract – Oxygen reducing microbial cathodes were made from garden compost leachate, under polarization at two different potentials, -0.4 V and +0.1 V versus SCE and characterized by chronoamperometry and cyclic voltammetry. Two redox systems were identified in the biofilms formed at +0.1 V but only one in the biofilms formed at -0.4 V. Analysis of the bacterial communities revealed a lower biodiversity in the biofilms formed at +0.1 V compared to those obtained at -0.4 V. This study evidenced both an adaptation of the bacterial communities electroactivity to the applied potential and that a high applied potential allows a higher selection of electroactive microorganisms.

Index Terms – Compost Leachate, Microbial Electrocatalysis, Oxygen Reducing Biocathode, Pyrosequencing.

I. INTRODUCTION

Microbial Fuel Cells (MFCs) were early identified as a mean to valorize wastes that contain high quantity of dissolved organic matter to produce electricity. Researchers’ interest quickly focused in designing efficient microbial anodes. In this context, microbial anodes formed from compost leachate were developed and optimized in our group (PhD. Thesis of D. Pocaznoi). These bioanodes demonstrate current densities among the highest observed to this date, reaching 35A m^-2 under constant polarization (-0.2 V versus SCE) delivering up to 6 W m^-2 power density when used in air-cathode MFC [1]. However, in respect to the performance displayed by the bioanode, it soon appeared that the long-term functioning of the MFC was limited by the abiotic air-breathing cathode. Indeed, traditional abiotic cathodes are often subject to catalyst poisoning, water flooding or microbial fouling by the microorganisms presents in the natural complex media used in MFCs.

To solve this problem, an alternative would be to use microbial oxygen reducing cathodes. Such biocathodes, involving aerobic microorganisms naturally present in the medium, have been already formed and described in other complex media such as wastewaters, sewage sludges [2], industrial effluents or seawater [3], but few examples have been realized from soils like garden compost or derived leachates [4]. Here, we report the design under two different applied potentials of biocathodes formed from garden compost leachate. We focused our work on the electrochemical characterization of biocathodes by chronoamperometry and cyclic voltammetry, together with an analysis of their respective microbial population by 16S-DNA pyrosequencing.

II. ELECTROCHEMICAL CHARACTERIZATION

Two different constant potentials, -0.4 V and +0.1 V versus saturated calomel electrode (SCE) were used to form the biocathodes. Five biocathodes were formed independently at each potential, in ten independent reactors. Biocathodes formed at each potential demonstrated reproducible electrochemical behavior and similar performances, so the different values of initial lag times (time needed to observe initial catalytic current) and current densities detailed infra are mean values from each set of five reactors.

A. Electrodes formation under polarization

When -0.4 V was applied, a reductive current started to be observed after 2 days and reached -0.18 A m^-2 on the third day of polarization. It remained stable to the end of the experiment (14 days). A longer initial lag time of 7 days was observed with the cathodes polarized at +0.1 V. The reductive current observed then increased slowly to reach -0.24 A m^-2 on the 12th day of polarization. For all cathodes formed at -0.4 and +0.1 V, the current density was enhanced when air bubbling was applied into the bioelectrochemical cell, reaching -0.36 A m^-2 under air bubbling. The highest (absolute value) current density of -0.63 A m^-2 was observed with one of the reactor polarized at +0.1 V under oxygen bubbling. A contrario, addition of a nitrogen bubbling to chase oxygen out of the electrochemical
cell led to current suppression, which clearly proved that the catalyzed reaction was effectively the oxygen reduction.

B. Voltammetric characterization

Cyclic voltammograms realized on biocathodes formed at -0.4 V after they reached a steady state current production revealed a single signal for oxygen reduction centered around -0.2 V that presented a current plateau of -0.24 A m⁻². The same signal (potential and current density) was first observed with the cathodes formed at +0.1 V before day 7, as visible on the voltammogram in red on figure 1.

![Cyclic voltammograms recorded at 1 mVs⁻¹ with biocathodes formed at +0.1 V at t = 0 (dashed black), t = 4 days (red), t = 11 days (blue)](image)

It seems that the redox specie(s) responsible(s) for this common signal is (are) ubiquitously present(s) among the bacteria in both biofilms formed at -0.4 and +0.1 V. This signal, however, decreased in activity after day 7 as another signal, centered around +0.2 V appeared and increased, as visible on the voltammogram in blue on figure 1. It displayed a current density of -0.22 A m⁻² on day 13. This signal is responsible for the reductive current observed by chronoamperometry at +0.1 V. When oxygen was bubbling in the cell, however, both signals (-0.2 and +0.2 V) were enhanced.

From these experiments, it seems that the redox couple at +0.2 V, which appeared later in biofilms which generated otherwise an identical behavior, is more an adaptive answer to a higher applied potential than the manifestation of a difference in the biofilm microbial population.

III. POPULATION ANALYSIS

Bacterial communities present into the biofilm colonizing the electrodes and in the bulk of the compost leachate were analyzed comparing 16S-DNA sequences obtained by pyrosequencing. The analysis revealed the presence of a great diversity of phyla, as means up to 387 and 449 operational taxonomic units (OTUs) were numbered respectively in the biofilms and in the leachate bulk, for a total number of OTUs evidenced of 2295 for the 10 biofilms. No dominant microbial species was clearly evidenced, contrary to what happened basically on bioanodes [5].

From the statistical analysis, three levels of selection were evidenced. First, more species are numbered into the biofilms than in the bulk of the leachate. Second, considering the populations in the biofilms, less species are observed when the electrodes were polarized at +0.1 V (349 OTUs) compared to -0.4 V (448 OTUs). Third, the populations represented in the biofilms formed at +0.1 V tend to be more dominated by a few species (Simpson index 0.88) than the ones presents in the biofilms formed at -0.4 V (Simpson index 0.97). Finally, among our ten electrodes, those that produce higher current densities correspond to those that demonstrate a lower bacterial diversity.

IV. CONCLUSION

Several oxygen reducing biocathodes were formed from compost leachate inoculum at two different polarization potentials that demonstrate rather similar performances. However, a clear selection of bacterial species was operated when a higher potential was applied, which manifests by both an adaptive answer and a decrease in the number of microbial species detected in the biofilms.

ACKNOWLEDGMENT

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3D THERMOMECHANICAL LONG-TERM BEHAVIOUR OF SOLID OXIDE FUEL CELLS, OPERATING IN FURNACE: A COMBINED MULTIPHYSICS AND SUB-MODELLING APPROACH

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Electrochemical Process Engineering (IEK-3)
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Abstract - Long-term structural reliability of fuel cells depend on the thermomechanically induced stress-strain behaviour. These are especially affected by the operation environment. Most of the research and development studies, as well as laboratory studies are performed within furnaces rather than operating in a real system environment. However, the thermomechanical response of fuel cells operating in the furnace, especially the long-term behaviour is not fully understood, yet. The present study utilises a full scale three dimensional planar type 6-cell SOFC short stack model to shed light on the thermomechanical response of high temperature fuel cells operating in furnace environments. The effect of using different fuel gases on the thermomechanical response of the fuel cells is elucidated. A sub-model of a critical fuel cell region has been used for this purpose. Experimentally determined data has been used for boundary conditions and validation purposes.

I. INTRODUCTION

Increasing the long-term reliability of solid oxide fuel cells has been a challenging task. The optimisation attempts aim to improve the life duration of the fuel cells. However, the high temperatures, which fuel cells are subject to, lead to difficulties. Thermomechanical issues during different process stages will initiate problems; especially, hermeticity difficulties (1-6). The solid oxide fuel cells operate unlike other fuel cells at temperatures around 800°C-1000°C. To reach these extremes, the fuel cell stacks are pre-heated electrically in a furnace, or through hot air via channels of the interconnector plates. Computational modelling has been an invaluable tool to study and improve our understanding of the processes; the fuel cells are going through. Studies show that most of the published work focuses on the analysis of fuel cells, operating in system environments (7-11). However, most of the conducted research utilises the furnace as the environment in which the fuel cells operate. Thus, it is exceedingly important to understand and improve the knowledge of the thermomechanical fuel cell response when operating in a furnace. In a previous study, the comparison to the system environment has been given (13). The present study aids to shed light on the long term thermomechanical response of fuel cells operating in a furnace environment. Moreover, the effect of different supply gases on the thermomechanical fuel cell behaviour is elucidated. A 3D multiphysics model has been employed to determine the 3D thermodfluid flow including radiation and the thermomechanical stress-strain behaviour of the fuel cell. Experimentally determined data has been used to investigate the effect of fuel gas operations of H2, CH4 77% and CH4 38% within a furnace. A sub-model of the whole stack has been used to investigate the long-term behaviour at the critical locations.

II. NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>x, y, z</td>
<td>cartesian coordinates</td>
<td>m</td>
</tr>
<tr>
<td>( \vec{u} )</td>
<td>velocity vector</td>
<td>m/s</td>
</tr>
<tr>
<td>k</td>
<td>thermal conductivity</td>
<td>W/mK</td>
</tr>
<tr>
<td>E</td>
<td>modulus of elasticity</td>
<td>MPa</td>
</tr>
<tr>
<td>H</td>
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<td>J/kg</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>strain</td>
<td>-</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>stress</td>
<td>MPa</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>thermal expansion coefficient</td>
<td>10^{-6}/K</td>
</tr>
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III. ABBREVIATIONS

CFD computational fluid dynamics
SOFC solid oxide fuel cell
FEM finite element method

The coupled computational fluid dynamics (CFD) and computational structural mechanics (FEM) model accounts for the experimentally determined rate-dependent creep strain (13), rate-independent elastoplasticity (14), as well as the temperature dependent material properties. Thermal radiation is considered, in addition to the conjugate heat transfer. Figure 1 depicts the employed computer model. The model has the typical fuel cell components such as interconnector plates (with channels) frames, sealants, cell and wire-mesh.

![Figure 1: Computer model of the SOFC short stack.](image)

The results are validated using creep strain data from the literature and in-house post-mortem images. The study gives an insight about the stress-strain behaviour of the fuel cell operating in different environments and the long-term thermomechanical response at the vicinity of critical section.

ACKNOWLEDGMENTS

The technical staff of the SOFC Research Group, Forschungszentrum Jülich is gratefully acknowledged for their support.

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OPTIMIZATION OF HEATING-UP PROCESS IN SOFC STACKS TO REDUCE THERMOMECHANICALLY INDUCED STRESSES BY MEANS OF SIMULATION TOOLS

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Abstract - A 3D computational model for multi-physical analysis is created, in order to evaluate the thermally induced stresses in a lightweight solid oxide fuel cell (SOFC) stack. The model is focused on SOFCs for Auxiliary Power Unit (APU) applications. Using the introduced model it is possible to obtain the thermal response to various boundary conditions based on Computational Fluid Dynamics (CFD) analysis in a reasonable computational time. In a further step the computed temperature fields are transferred to a Finite Element (FE) Model for purposes of thermo-mechanical investigations. Based on CFD analysis, temperature profiles are calculated during a complete process cycle, consisting of transient heating-up from room temperature to an operating temperature of 750 °C, steady state operation and finally transient cooling down to room temperature. In the FE structural analysis the cooling down step after assembling is also taken into account. This step is performed with a uniform temperature distribution in the fuel cell stack. During the other steps the existing temperature gradient is taken into consideration. The resulting temperature fields are transferred from the CFD post-processor to the FE Model of the solid stack. Thermo-mechanical analyses are then carried out at various time steps with small increments during the process cycle.

I. ABBREVIATIONS

SOFC  solid oxide fuel cell
APU   auxiliary power unit
CFD   computational fluid dynamics
FE    finite element

II. INTRODUCTION

Short SOFC stacks are increasingly utilized in APU applications for electric power generation due to their compactness, lightweight, environmental compatibility and multi-fuel capability. Challenges in employing SOFCs are related to the heating-up process, in general from room temperature to an operating temperature between 800 °C and 1000 °C that must be carried out in a short time. Non-uniform temperature distributions with high thermal gradients in the solid structure and dissimilar mechanical and thermal behavior of the used materials induce locally high thermal stresses that could lead to cracks, affecting the functionality of the fuel cell stack or cause the fail of its components. In order to reduce these effects, it is desirable to study the influence of the process boundary conditions on the resulting temperature field in the solid structure and consequently on the induced thermal stresses.

Detailed reviews including various CFD approaches that are based on thermo-fluid and or electrochemical processes have been elucidated from several authors in previous studies (1-8). In our previous studies, the importance of predicting the thermo-mechanically induced stress has been elucidated (9, 10). Those have been mainly focused on larger sized full scale stacks and the localization of the high stress regions. The main objective of the current work is to create a 3D model for multi-physical analysis of a full SOFC stack used in APU applications to predict the maximum stresses that occur during a process cycle and to obtain optimized thermal CFD boundary conditions to reduce these stresses. The Model is validated based on experimental observations. Model geometry and simulated process stages are presented in Figures 1 and 2.
The simulation results show that the maximum stresses occur during the heating-up stage and in some cases at the end of this step of the process cycle. This is mainly due to the highly non-uniform distribution of the temperature field in the fuel cell stack. For purposes of process optimization the CFD-Model is utilized to investigate the effects of the time rate of change of the gas inlet temperatures during the heating-up stage, where air is used as heating medium. In the study the total duration of the heating-up phase as well as the initial and final temperatures of the hot gases are fixed and the temperature rate of change is varied. The resulting distributions of the temperature fields at different time instants are compared. The analysis shows that the induced maximum stresses are related to the difference between the maximum and minimum temperature in the solid stack during the cycle.

ACKNOWLEDGMENTS

The technical staff of the SOFC Research Group, Forschungszentrum Jülich is gratefully acknowledged for their support.

REFERENCES

**MFC FROM RESEARCH TO APPLICATION: STANDARDS NEEDS**

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**Abstract** – Microbial fuel cell is a relatively young technology that in the last few years received increasing interest. Today a validation of MFC technology is requested if we like to attract funds for MFC transaction from research to application. Consequently, in front of its peculiarities, this technology must be compared with more old and well know fuel cell technologies, and other energy technologies. But looking at the existing literature few efforts have been made to define comparison criteria, or to develop a standard allowing the comparison of results obtained in different laboratories. In this work an analysis of issues and possible solution for this comparison is made. A proposal for a standard approach to MFC characterization is done.

**Index Terms** – Microbial Fuel Cell, standards, testing protocols.

**I. INTRODUCTION**

Microbial fuel cells (MFCs), like other bioelectrochemical systems, are new technologies that require expertise in a variety of scientific and technological areas, ranging from electrochemistry to biological wastewater treatment and engineering. Up to now large part of research was mainly centered on basic aspects of MFC and was conducted in prevalence by biologist and biochemistry research groups. Now the desire of transition from basic research to application and to large scale devise realization require the interaction with other research field. Then we have to compare both our lexicon and our experimental protocols with these of other technologies to implement our capability in communication of our results.

In addition to this we have also to select a reference protocol to compare our results. In fact up to now MFCs have been tested with a variety of different protocols that create difficulties in comparing different results. And this damages the capacity in developing new knowledge on MFC.

We all know that each researcher usually write his protocol in the laboratory book and he is, in some way, green-eyed of this protocol. But to carry out the comparison of results obtained by different laboratories we need a reference standard. Usually, when a new technology appears new protocols and standards are developed starting from these developed for similar previous existing technologies. This is the case also for MFCs.

In this work a process for developing a reference MFC testing protocol is proposed for discussion. The experience matured in Polymer Electrolyte Fuel Cell testing procedures and standards is used as reference point. The idea is to contribute to MFC technology development by triggering an open dialogue between researchers involved in this field. A dialogue addressed to the definition of a worldwide accepted methodology on MFC characterization.

**II. A WAY FOR A SHARED MFC TEST PROTOCOL**

The total paper length should not exceed TWO (2) pages. Papers longer than 2 pages are not acceptable.

A. Target application choice

What is the reference application for MFC?

This is (in appearance) a stupid question. Are we sure of this?

The name recalls Fuel Cell, then power generation. Are we sure that the power generation is the main target of MFC?

MFC are able to extract power from wastewater, so that probably the main target will be the wastewater treatment.

The question is not secondary because this choice will influence both the lexicon we have to use, the experimental approach and the target to be selected.

In any case MFC are an electrochemical device than we must remember that, both looking at power generation and wastewater treatment, results maximization must pass through electrochemistry optimization. But in the first case we must
maximize the power output, in the second one the purity of the exit water.

B. Critical information

At third year of my study in physics one of my teachers says: “in a scientific paper you must put an experimental part. This experimental part must be so detailed to allow anyone scientist to repeat exactly your experiment for confirming or reject your results”. Today many papers don’t respect this ethic principle, especially paper concerning research in fields having commercial potentialities. MFC are not so close to commercialization to require a knowhow protection.

In any case, there are certain data and critical information that should be included in every MFC study, as much as possible, to allow a realistic results comparison.

Looking at fuel cells standards, we can consider: surface area of the electrodes, electrolyte/culture media solution conductivity, power densities normalized to electrode surface area and/or volume.

About experimental techniques we could consider standard electrochemical techniques but adapting these to biological systems. Moreover we must choose what of the electrochemical techniques are useful for MFC characterization and reference protocols for their application.

For example i/V (polarization) curve is helpful? And in which way it must be acquired to be useful for us??

Thereafter we must define a set of testing conditions to be reported. A set could be extracted from FC standard procedures: working temperature, density of reactants (in our case nutrients for bacteria), reference hardware (the testing cell and the test rig), electrodes specifications, and electrolyte specifications, just looking at the most common.

C. Proposal for a reference cell

The necessity of a reference cell is a consequence of the experience, carried out in all electrochemical devices including fuel cells, that the cell architecture strongly influence the power output of the system. In MFC the electrolyte has very low conductivity and then also small differences in distance between anode and cathode could introduce a difference in results. Moreover large part of the experiments is carried out in bottle without an electrolyte circulation, then with conductivity and nutrient concentration changing in time. The cells differ from one laboratory to other both in volume, in architecture and materials; some studies are conducted using buffer substrates/electrolytes other using raw wastewater, i.e. media having totally different conductivities. In addition, sometime selected bacteria strains are used in other cases not selected strains are considered. In which way we could compare the results of these studies? In which way we can translate these results to engineers/industry for scale up and application?

To solve a part of these questions, these related to a standard hardware, a planar cell described below is proposed as possible laboratory reference cell.

Planar configuration is considered because this configuration is easily stackable. Moreover this configuration allows a simple calculation of the ion and electron paths. Finally this is the standard configuration for low temperature fuel cells, in particular direct methanol fuel cells that could be considered as reference for us because use a liquid feeding at the anode side.

A plastic separator will allows to fix the distance between anode and cathode, i.e. will allows a simple calculation of cell internal resistance. This separator will allows also the use of the cell both in batch and in flow configuration, and could be easily adapted both for membrane and membrane-less configuration.

Another problem revealed in the MFC is the current collection. Simple electric contact with the electrode support (carbon cloth, carbon paper and so on) by clamp will result in additional resistance. Moreover it is well known, from FC studies, that contact resistance between carbon materials and metals could vary strongly from one metal to another. Moreover this metal must be stable against the MFC environment. So that a golden wire network or a gold thin sheet are suggested for current collection. Also contact pressure between current collector and electrode materials is important for reducing the electric contact resistance, and the planar configuration allows a good distribution of the pressure over all the cell components by a simple and well tested clamping system.

Another important point in MFC is the definition of the active area to be considered as reference for calculating performances and produced power density. Using a planar configuration with electrodes of the same geometrical surface, this question has simple solution. A square shape with 25 cm2 surface area electrodes is suggested in analogy with polymer electrolyte fuel cells (both hydrogen and direct methanol fueled).

III. CONCLUSION

Looking at the open questions in MFC study, a way for the definition of standard approach to MFC testing is proposed in analogy with the work carried out on low temperature fuel cells. A scheme for a reference cell in planar configuration is done. The author like to invite the colleagues in considering the realization of a comparative study by producing a number of identical cell and testing these in a round robin test conducted by different laboratories.

ACKNOWLEDGMENT

The author likes to thank Carlo Santoro and Pierangela Christiani for the interesting discussions about MFC and their testing.
Abstract – The characterization of a meromictic lake in the north of Italy with a description of a “white cloud” phenomenon due to manganese chemistry is here for the first time described. The careful determination of the dependence of physico-chemical parameters on the depth of the lake, explains this phenomenon. A crucial parameter is the chemical composition of the rocks forming the basin of the lake. The particular interactions between pH, temperature, chemistry, redox potential, oxygen concentration make this lake a natural lab for microbial fuel cell experimentation, especially for environment-depollution purposes.

Index Terms – Microbial Fuel Cells, meromictic lake, heavy-metal depollution, MIC

I. INTRODUCTION

A Microbial Fuelcell (MFC) is a flexible technology with manifold fields of application for environmental purposes as well as energetic ones. The promising possibility of environmental depollution from naturally present heavy-metals by MFC electrochemical technology are studied in this contribution. A careful investigation of an alpine lake, in the north of Italy (Idro lake) gives access to new possibilities for the implementation of MFCs in a real natural environment. The development of a microbial community over a cathode catalyzing reactions involving oxygen reduction is connected with the development of a microbial community over the anode, catalyzing reactions involving Mn species. The presence of distinct zones for the two reactants gives access to this on-field application.

A. A meromictic Lake

The meromictic lake under study is the lake of Idro, situated approximately 40 km north from Brescia, Italy. It’s a typical alpine glacial lake with a surface of 10.9 km$^2$, and maximum depth of 120 m. Its conformation and behavior ascribes this lake as a meromictic lake. Generally, many different stratifications are present in a meromictic lake (Fig. 1), summarized in: a) mixolimnion, in which water circulates, distributing oxygen in the whole layer; b) chemocline, in which O$_2$ concentration goes to negligible values, and c) monimolimnion, where the water is stagnant. The natural presence of the net separation between the aerobic and anaerobic area make the lake affine to a massive MFC, although the concentration of nutrient and fuel in a lake is generally lower than that used for the experimentation of MFCs.

Fig. 1. Scheme of a typical meromictic lake, with the three main characteristic stratifications: mixolimnion, chemocline, and monimolimnion.

A peculiarity of this lake is the presence of a cloudy white layer, detected at 40-70 m by scuba divers and never reported in literature. The hydrographic basin is mostly composed of dolomite, the typical rock of the Alpi mountains. The general chemical composition is Mg(Ca)CO$_3$, but it could include impurities as Iron and Manganese.

B. Chemical-physical parameters measurements

A measurement campaign was devoted to ascertain the profile of some chemical parameters of the lacustrine water...
at different depths, to detect the chemical variations. A combined sensor for redox potential and sulphide concentration, handmade, was also utilized. Other physicochemical profiles (pH, oxygen concentration, temperature, conductivity) were measured with a commercial multiparameters probe. A preliminary experiment permitted the reproduction of the “white cloud” effect in laboratory. The results brought to the development of a hypothesis on the very particular chemistry of the Idro lake. Finally, a laboratory experiment was conducted to prove the effective possibility of depuration of the lake from heavy metals identified (Tab 1, 2) by means of MFC technology.

II. RESULTS AND DISCUSSION

A. Sensors response

From the measurement done in May 2013, temperature decreases shows a thermocline starting right after 6-8 m deep (20°C), and finishing at around 30 m (6°C). The temperature remained fixed at 6°C down to the bottom of the lake after the thermocline. The redox potential and the sulphide sensors showed a similar but opposite sinusoidal behavior, underlying a sudden inflexion around 50 m. The sulphide sensor started with very low concentrations (high potential) near the surface, and very high concentrations under the redox transition at 49 m of deep. Oxygen concentration shows the total depletion of O2 just before the redox transition, around 43 m of deep.

B. Chemical analysis: the Mn concentration

Some chemical analyses of the water sampled on 09/07/2013 at different deep are reported in the Table 1. The same analyses conducted on the filtered samples (0.45 µ filter) are reported in the Table 2. Chemocline is the stratification where the most of the chemicals undergo a modification in their concentrations. This is particularly visible for Mn ion, going from negligible values in the mixolimnium, up to 0.8 mgL⁻¹ in the water particulate of chemocline, decreasing in the monimolimnium.

Table 1: Chemical analyses of elements dissolved in water sampled on 09/05/2013

<table>
<thead>
<tr>
<th>Deep</th>
<th>Ca</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
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<tr>
<td></td>
<td>µgL⁻¹</td>
<td>µgL⁻¹</td>
<td>mgL⁻¹</td>
<td>µgL⁻¹</td>
<td>µgL⁻¹</td>
<td>µgL⁻¹</td>
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<tr>
<td>20 m</td>
<td>44.0</td>
<td>3.14</td>
<td>14.9</td>
<td>&lt;1</td>
<td>&lt;0.0</td>
<td>13.5</td>
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<td>40 m</td>
<td>50.6</td>
<td>4.26</td>
<td>16.2</td>
<td>&lt;1</td>
<td>0.06</td>
<td>21.7</td>
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<tr>
<td>48 m</td>
<td>59.0</td>
<td>2.16</td>
<td>16.4</td>
<td>&lt;1</td>
<td>0.09</td>
<td>25.8</td>
</tr>
<tr>
<td>48 m</td>
<td>60.2</td>
<td>1.44</td>
<td>17.1</td>
<td>&lt;1</td>
<td>0.10</td>
<td>26.9</td>
</tr>
<tr>
<td>54 m</td>
<td>66.1</td>
<td>12.1</td>
<td>17.6</td>
<td>&lt;1</td>
<td>0.13</td>
<td>28.7</td>
</tr>
<tr>
<td>60 m</td>
<td>65.7</td>
<td>28.4</td>
<td>17.9</td>
<td>&lt;1</td>
<td>0.05</td>
<td>30.1</td>
</tr>
</tbody>
</table>

C. The “white cloud” explanation

Laboratory experimentations were conducted, based on the chemical analyses. The redox potential showed that in the transition zone, a great concentration of Mn has to be in the Mn(II) form (Mn(OH)₂, most probable compound).

Table 2: Chemical analyses of the filtered particulates in water sampled on 09/05/2013

<table>
<thead>
<tr>
<th>Deep</th>
<th>Ca</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µgL⁻¹</td>
<td>µgL⁻¹</td>
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<td>µgL⁻¹</td>
<td>µgL⁻¹</td>
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<tr>
<td>40 m</td>
<td>33.3</td>
<td>n.d</td>
<td>15.9</td>
<td>359</td>
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<tr>
<td>46 m</td>
<td>62.2</td>
<td>n.d</td>
<td>13.2</td>
<td>1</td>
<td>1.6</td>
<td>12.9</td>
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<tr>
<td>48 m</td>
<td>141</td>
<td>1. n.d</td>
<td>26.1</td>
<td>675</td>
<td>2</td>
<td>7.4</td>
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<tr>
<td>54 m</td>
<td>103</td>
<td>2. n.d</td>
<td>22.3</td>
<td>493</td>
<td>8</td>
<td>22.0</td>
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<tr>
<td>60 m</td>
<td>87.9</td>
<td>52.9</td>
<td>25.5</td>
<td>45.3</td>
<td>23.4</td>
<td>23.0</td>
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</table>

In the upper zone, redox, pH and oxygen sensors indicate MnO₂ as the most relevant trace species. In the lower zone, acidic solution of Mn²⁺ is the predominant element. The “white cloud” effect may thus due to Mn(II) hydroxide accumulation in the oxygen-depleted zone, with dynamic transformations from white to brown (Fig. 3) if mixolimnium mixes with chemocline, and from white to colorless if chemocline mixes with monimolimnium.

In this scenario, microbial fuel cells (MFC) might produce power by utilizing the microbial capacity of catalyzing the oxygen reduction at the cathode, and the Mn(OH)₂ oxidation at the anode, as well as organics. Other type of MFC might develop power by reduction of Mn³⁺ by bacteria catalyses [1].

Fig. 3. The “white cloud” effect. Reproduction in laboratory-scale. White Mn(OH)₂ on the left, and oxidized brown MnO₂ on the right.

III. CONCLUSION

Manganese long-term accumulation was demonstrated to be the chemical generating the “white cloud” effect in the Idro lake. Redox and sulphide measurements confirmed that the phenomenon occurs in the chemocline, characterizing the lake. The stratification of the lake poses a new interesting applications for MFCs. MFC technology can potentially perform the treatment and removal of Mn as well as other trace elements that could affect the seasonal biota in the lake.


Acknowledgment: This work has been financed by the FSE-Lombardia.
MICROBIAL FUEL CELLS EXPERIMENTATION AT MILAN-NOSEDO WASTEWATER TREATMENT PLANT

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Abstract – The wastewater treatment plant of Nosedo, in Milan, is here described and presented, emphasizing the different chemical and biological environments eligible for microbial fuel cells (MFC) experiments. As a first step in the integration of MFCs in the wastewater treatment processes, the results of preliminary experiments are here reported. The influence of electrocatalytic surface extent is firstly evaluated, showing the possibility of scale-up processes.

Index Terms – Single Chamber Microbial Fuel cell, wastewater plant, renewable energy, depuration treatments.

I. INTRODUCTION

The Wastewater Treatment Plant of Milano-Nosedo is the last phase in a complex system that collects wastewater from the central and eastern part of the city of Milan, serving the Nosedo sewer outfall and the “Ampliamento Est” main sewer.

At the end of the process, the purified water is returned to the irrigation system serving the surrounding countryside. The main characteristics of the plant are listed below.

- Total surface area involved: 40 ha
- Area occupied by the plant: 16 ha
- Population served: 1 250 000 p.e. (population equivalent)
- Average flow rate treated in dry weather conditions: 5000 L/sec, 150 000 000 m³/year treated wastewater.
- Maximum flow rate treated in wet weather conditions: 15 000 000 L/sec.

Water line: sewage streams are transferred to the plant through different main sewers, which merge to constitute the two flows to be purified. Both flows undergo a coarse screening, followed by a fine screening. After a grit and grease removal phase, the wastewater is pumped up for biological processing, which allows to remove the organic pollutants load (COD and BOD) and the content of other nutrient substances (nitrogen and phosphorous).

This treatment includes the denitrification and oxidation-nitrification sections, followed by final sludge settling. In order
to complete the biological treatment, systems for active sludge and mixed liquor recirculation are also present. Subsequently, wastewater is filtered through sand filters, disinfected and conveyed back into the existing hydrographical system: the Nosedo effluent, Roggia Vettabbia and Redefossi channels.

**Sludge line:** Sludge processing basically consists of phases of stabilisation and reduction of the sludge volumes.

**Air extraction and deodorization:** The processing facilities are fitted with an air extraction system connected with a deodorisation section, in order to remove unpleasant odours.

**Power electricity consumption:** It is known that, from literature and on-field practice in wastewater treatment, more than 30% of the management costs is due to electrical consumption. As an example, electrical energy consumption vary from 0.4 to 0.7 kWh/m³, depending on the type and dimensions of the plant. If conventional active sludges plants with anaerobic digestion are employed, then up to 40 kWh/PE*y can be consumed, and if aerobic digestion is employed the power consumption raises up to 70 kWh/PE*y. Aerobic sections show the highest power consumptions (50-65% of the total), followed by the sludges treatment line (20%) and the first water uplift (15%) (Fig. 1). If “forced” treatments are applied, energy demand can further increase [1].

**Microbial Fuelcells:** In the as-described wastewater plant, many different chemical and biological micro-systems are present at the same time. Aerobic and anaerobic conditions are contemporarily met inside each aerobic and anaerobic treatment pools. Moreover, despite a low COD (~350 ppm) at the inlet, the presence of activated sludge and the local concentration phenomena produce a favorable environment for the development of bioanodes and biocathodes of a single chamber microbial fuelcell (SCMFC). The main aims of the experimentation were thus to develop practical SCMFCs for the contemporary: a) production of micro-powers, b) anaerobic organics digestion, c) nutrients removal (phosphates, nitrates, heavy metals). All these targets can be achieved with the use of SCMFCs.

**II. RESULTS AND DISCUSSION**

Practical, small-scale on-field SCMFCs were produced with different electrode dimensions. Materials of the electrodes were both carbon cloth. The first data of power production is reported in Fig. 2. Two exemplificative SCMFCs were immersed in the anaerobic treatment pools. As reported in figure, the two cells were different in the electrode surface dimension, being 0.0225 m² the smaller, and 0.25 m² the bigger.

Power production starts at less than two days from the immersion in the solution. After a first period of about one week, the microbial biofilm starts to generate power at an increased rate for both cells, reaching a stable plateau of 0.1 mW for the small, and more than 2 mW for the big SCMFC. Oscillations of the power production are due to environmental temperature variations and sediments aggregation on the anodic electrode. Normalization of the average power production by the electrode surface extent, gives approximately 10 mW/m² for both SCMFCs. The scale-up process does not depress the power production. For mechanical and fouling reasons, the small SCMFCs were chosen to build a multiple array of cells. At the same time, different cell designs are under study.

![Fig. 2. Electrical power production of two exemplificative SCMFCs exposed in anaerobic pools.](image.png)

**III. CONCLUSION**

The preliminary results of the on-field application of SCMFCs in a wastewater treatment plant are presented. The particular environmental conditions in the treatment pools permits the development of SCMFCs producing power. Evaluation of different electrode sizes and scale-up feasibility, produced a first prototype of multi-array SCMFCs for the extensive application in the plant.

**References**


**ACKNOWLEDGMENT**

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