



Two day conference

Electrochemical Science and Technology

2nd and 3rd October 2008

at

The Syddanske Forskerparker, Odense

Arranged by:

Danish Electrochemical Society

In cooperation with the organizing committee:

Rajan Ambat, Associate Professor, Technical University of Denmark

Anke Hagen, Senior Scientist, Head of Program, Risø National Laboratory

Per Møller, Professor, Technical University of Denmark

Eivind Skou, Lektor, Inst.for Kemi, Bio- og Miljøtekn, Syddansk Universitet

Co-organised by: **ATV•SEMAPP and Aluminium Danmark**

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v/Daniel Minzari

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ATV•SEMAPP

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PROGRAMME:

2nd October

- 14:30 – 15:00 **Arrival to Aluminium Danmark, Syddanske Forskerparker**
Forskerparken 10 (Reception, Centerbuilding), 5230 Odense M, tlf. 63 15 71 00.
- If you want to join the conference part solely, you are welcome to arrive just before the welcome at 16:00.
- 15:00 – 16:00 **General Assembly in the Danish Electrochemical Society**
For members and guests.
- 16:00 – 16:05 **Welcome**
Per Møller, professor at DTU Mekanik and chairman of the Danish Electrochemical Society
- 16:05 – 16:45 **Key note on Electrochemical Issues**
Jens Dahl Jensen, Siemens AG, Corporate Technology, Coatings and Microsensors
Whether in the fabrication or the characterisation of coatings, in the solution of corrosion-problems or in the conversion of chemical energy into electricity: Electrochemistry is present in nearly every product we meet.
This opening presentation is meant as an appetizer for all participants involved in electrochemistry research and goes to show how many industrial applications actually benefit from the latest knowledge gained within the field of electrochemistry.
Using examples taken directly from the latest and most innovative Siemens products
all participants are shown where and why electrochemistry is brought to work in our modern day and age.
Dr. Jens Dahl Jensen studied chemistry, materials sciences and surface technology at DTU from 1990 to 1996.
With a masters thesis on electrodeposition of magnetostrictive sensor materials carried out at the Daimler-Chrysler research labs in Ulm Germany, he was employed at the Institute for Product Development at DTU Copenhagen, which remained his home-base for nearly 7 years.
During this period Dr. Jensen stayed 12 months as a guest-researcher at Loughborough University UK with Prof. David Gabe and did his PhD on "Engineering of Metal Microstructures" at Linköping University in Sweden.
Since May 2004 Jens Dahl Jensen has been employed by Siemens Corporate Technology in Berlin, as program manager for the group Innovative Films & Nanotechnology Coatings.
- Aluminium Danmark and Electrochemical Issues**
Short intro to **Aluminium Danmark**
Jim Hansen, Aluminium Danmark
- 19:10 – 21:00 **Dinner**
Restaurant Kvægtorvet, Odense C.
Restaurant Kvægtorvet
Rugårdsvej 25
5000 Odense C

3rd October

09:00 – 09:15 **Opening of the conference**

ORAL PRESENTATION

09:15 – 10:35 **1. Fuel/Solar Cells**

Quantification of in situ Temperature Measurement on a Single cell PBI-based PEM fuel cell

Syed Talat Ali^{1*}, Jesper Lebak Jespersen², Lars Pleth Nielsen², Claus Mathiasen²,

Søren Knudsen Kær³ and Per Møller¹ ¹Technical University of Denmark, Department of Mechanical Engineering, 2800 Kgs. Lyngby

²Danish Technological Institute, Kongsvang Allé 29, 8000 Aarhus C

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Impact of air humidity on performance and durability of Solid-Oxide-Fuel-Cell's

Jimmi Nielsen, Anke HagenRisø, Afdelingen for Brændselsceller og Faststofkemi

Study of the use of biogas as fuel in solid oxide fuel cells

Jens F. B. Rasmussen¹, Anke Hagen¹ ¹Risø DTU, Fuel Cells and Solid State Chemistry Department, Frederiksborgvej 399, DK-4000 Roskilde

Recent progress in high temperature PEM fuel cells

J. O. Jensen^{1*}, Q. Li¹, C. Pan¹, V. Bandur¹, L. N. Cleemann¹, N. J. Bjerrum¹, M. Nilsson², T. Steenberg², S. Yde-Andersen³, T. De Rycke³. ¹Department of Chemistry, Technical University of Denmark,

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10:35 – 10:55 **Coffee break**

10:55 – 12:15 **1. Fuel/Solar Cells (continued)**

Dye degradation chemistry and stability of Dye Sensitized Solar Cells

Torben Lund ¹Department of Science, Systems and Models, Roskilde University.

². Materials and Methods

Study of Electrochemical Induced Migration on Electronic Chip Resistors by Use of Novel Electrochemical Cell Set-up

Daniel Minzari *, Morten S. Jellesen, Per Møller and Rajan Ambat
Department of Mechanical Engineering, Technical University of Denmark

Electrochemical re-impregnation of wood in structures

Lisbeth M. Ottosen, Inge Rørig-Dalgaard, DTU Civil Engineering

Corrosion of friction stir welding in aluminium (preliminary title)

Manthana Jariyaboon and Rajan Ambat
Department of Mechanical Engineering, Technical University of Denmark

12:15 – 13:15 **Lunch**

POSTER PRESENTATIONS

13:15 – 14:15 **Simultaneous Electrografting of Different Grafting Agents to Form Mixed Organic Layers**

Marcel Ceccato, V. S. Ijeri, K. H. Vase, Steen Uttrup Pedersen and Kim Daasbjerg
Department of Chemistry, University of Aarhus, Langelandsgade 140, 8000 Aarhus C

Monitoring pO₂ and pCO₂ with Radiometers Tiny-Teddy

Ole Munch Hansen, TC R&D and Birgit Zachau-Christiansen ABL R&D
Radiometer Medical ApS

Comparison of acetate, glucose and xylose in microbial fuel cells with humic acid as mediator

Anders Thygesen*¹, Finn Willy Poulsen ², Booki Min³, Irini Angelidaki³, Anne Belinda Thomsen ¹: Biosystems Department, National Lab. for Sustainable Energy, Technical University of Denmark, TUD.
²: Fuel Cell and Solid State chemistry Department, National Lab. for Sustainable Energy, TUD.
³: Department of Environmental Engineering, TUD.

Registered for poster presentation (no title submitted at the registering time) Anne-Mette Charlotte Nørgaard, PhD. Studerende
Risø, Fuel Cells and Solid State Chemistry Department

Stability of radicals in electron-irradiated fluoropolymer film for the preparation of graft copolymer fuel cell electrolyte membranes

Mikkel Juul Larsen , Yue Ma , Huan Qian , Hans Toftlund, Peter B. Lund , Eivind M. Skou
Institute of Chemical Engineering, Biotechnology and Environmental Technology, University of Southern Denmark

Polymer Electrolyte Membranes Prepared by Radiation Grafting and Sulfonation

Yue Ma Institute of Chemical Engineering, Biotechnology and Environmental Technology, University of Southern Denmark

PEMFC Durability Studies

Shuang Ma and Eivind M. Skou Institute of Chemical Engineering, Biotechnology and Environmental Technology, University of Southern Denmark

Characterizing Carbon NanoTube Supported Platinum Catalyst by Electrochemistry

Sune Veltze Institute of Chemical Engineering, Biotechnology and Environmental Technology, University of Southern Denmark

Towards super clean materials for solid oxide cells

Thomas Andersen (a), Mogens Mogensen (b) & Ib Chorkendorff (a)

a. Center for Individual Nanoparticle Functionality (CINF), Technical University of Denmark

b. Fuel Cells and Solid State Chemistry Department, Risø National Laboratory, Technical University of Denmark

Study of Green Compounds as Corrosion Inhibitors

A. Patcharinwittaya, Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400 Thailand and

M. Jariyaboon, Surface Science and Engineering Capability Building Unit, Faculty of Science, Mahidol University, Salaya, Nakornpatom, 73170 Thailand.

ORAL PRESENTATIONS CONTINUED

14:15 – 14:55 **3. Environmental Electrochemistry**

Removal of NO_x with porous cell stack

Rebecka Maria Larsen Werchmeister, Mogens Mogensen, Kent Kammer Hansen, Fuel Cells and Solid State Chemistry Department
Risø National Laboratory for Sustainable Energy, Technical University of Denmark – DTU

Electrochemical degradation of PAH compounds in process water

Jens Muff, Erik G. Søgaard Esbjerg Institute of Technology, Aalborg University
Niels Bohrs Vej 8, DK-6700 Esbjerg, Denmark

14:55 – 15:15 **Break**

15:15 – 15:45 **STUDENT AWARD PRESENTATION**

15:45 – 16:00 **Closing**

ORAL PRESENTATIONS

1) Quantification of *in situ* Temperature Measurement on a Single cell PBI-based PEM fuel cell

Authors:

Syed Talat Ali^{1*}, Jesper Lebkæk Jespersen², Lars Pleth Nielsen², Claus Mathiasen², Søren Knudsen Kær³ and Per Møller¹

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Abstract:

Recently, high temperature PBI-based fuel cell membranes have attracted much attention, due to high stability against impurities such as e.g.: CO-poisoning. Furthermore, no water management is needed and the system is characterized by and the working temperature can easily be managed. Durability, reliability and costs are the decisive factors when commercializing fuel cells on an industrial platform. High local internal temperatures forms critical conditions that accelerates degradation and lower the overall efficiency as well as life time of the fuel cell.

Obtaining *in situ* temperature data is a challenging task without disturbing the performance of the fuel cell. This work presents local measurements of in plane temperature variation and along-thechannel variations of the MEA under various operating conditions, without interfering with the overall fuel cell performance.

Two sensor approaches were implemented: (i) twisted wire thermocouples embedded in the anode and cathode flow plates, and (ii) sensors embedded on seals using PVD technique. The twisted wire thermocouples were used to detect in-plane temperature variations whereas the PVD-sensors on seals were utilized to measure the temperature as close as possible to the MEA under working conditions to ensure a correct monitoring of the MEA-temperature. In order to avoid leaching of phosphoric acid by water condensation the cell temperature should be kept above 110 °C.

The correlation between quantified temperature variation and AC impedance spectroscopy was correlated with the measured fuel cell performance.

2) Impact of air humidity on performance and durability of Solid-Oxide-Fuel-Cell's

Jimmi Nielsen, Anke Hagen

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For commercialization of solid oxide fuel cells (SOFC's) it is desirable to acquire knowledge about the impact of impurities in fuel and ambient air on durability and performance of SOFC's. An unavoidable and obvious parameter to study is humidity, which can be regarded as a characteristic 'impurity' in air. The removal of water from air prior to the SOFC is possible, but causes extra costs. The aim of the present study has been to investigate whether humidity has an effect on performance and durability of Risø-2G SOFCs and if so to which extent. The relevance of such a study not only applies to SOFC's but also other applications of electroceramic SOFC cathode materials such as gas cleaning and gas separation membranes etc.

In the talk results will be presented which show that the presence of water can enhance the cathode degradation significant and hence the overall cell degradation under current load. Two clear effects of air humidification were observed an immediate apparent reversible transient upon humidification and a significant larger than without humidification long term degradation. The magnitude of the transient upon humidification and the following degradation rate was found to be dependent on both the degree of humidification and the applied current load (cathode polarization). A classical poisoning effect of water with a blocking of active sites was ruled out since no effect of humidification on the impedance determined polarization resistance at open circuit voltage (OCV) was found. The origin of this unexpected effect of water is unclear and requires further studies.

3) Study of the use of biogas as fuel in solid oxide fuel cells

Jens F. B. Rasmussen^{1,}, Anke Hagen¹*

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1st September, 2008

Abstract

In recent years the interest for using biogas derived from biomass as fuel in solid oxide fuel cells (SOFCs) has increased. SOFCs can use the carbon-containing biogas as fuel due to their high operation temperature (850°C) and the fact that a catalyst (Ni) is present in the anode. At the SOFC operation temperature the carbon-containing fuel is converted to hydrogen and carbon monoxide, which are both fuels for the SOFC. However, impurities such as H₂S are also present in the biogas. H₂S is known to passivate the active sites on Ni catalysts. It is thus very important to determine how the electrochemistry and carbon-compound conversion in the anode are affected by H₂S, and how the effects can be lowered or at best eliminated. Single SOFC testing was carried out. The SOFC performance was characterized with use of impedance spectroscopy and electrical measurements. The main conclusions were that H₂S primarily chemisorbs at the active Ni sites in the anode. The steam reforming of the carbon compounds was affected more severely than the electrochemistry by the sulfur-poisoning. In an H₂/H₂O-fuelled SOFC tested at 850°C and 1 Acm⁻² current load, the sulfur-poisoning (2-100 ppm) lowered the performance of the SOFC reversibly. Replacing the fuel by a CH₄-containing gas, an H₂S concentration not higher than 7-9 ppm is acceptable during a 24 h period. Long term testing of SOFCs with a CH₄-containing fuel, where 2 ppm H₂S was added to the fuel for 500 h, showed that a Ni-YSZ anode-based SOFC degraded both before the H₂S was added and during the addition. Using a Ni-ScYSZ anodebased SOFC instead resulted in a better performance before H₂S was added and a better cell voltage stability during H₂S addition. This indicated that introducing scandium (Sc) in the electrolyte material can improve both the tolerance towards sulfur- and carbon-poisoning.

Keywords

SOFC, sulfur, poisoning

Subject

Testing of solid oxide fuel cells

Preferred type of presentation

Oral

4) Recent progress in high temperature pem fuel cells

J. O. Jensen^{1}, Q. Li¹, C. Pan¹, V. Bandur¹, L. N. Cleemann¹,
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ABSTRACT

Recent progress with polymer fuel cells (PEMFC) at elevated temperature will be presented. The development of a blend fuel cell membrane and a stack for operation at 170°C are described briefly as well as the development of an auxiliary power unit consisting of a diesel reforming system and a high temperature PEMFC stack. All results were obtained during the EU project “Further Improvement and System Integration of High Temperature Polymer Electrolyte Membrane Fuel Cells” (FURIM, SES6-CT-2004-502782) under the FP6. The project was an integrated project addressing both fundamental materials development and the construction of a fully integrated system with a diesel reformer and a high temperature PEMFC stack operated without CO purification. All membranes, cells, stacks and reformer components were manufactured within the project.

5) Dye degradation chemistry and stability of Dye Sensitized Solar Cells

Torben Lund Department of Science, Systems and Models, Roskilde University.

In 1991 Michael Grätzel introduced the dye sensitized nano crystalline titan dioxide solar cells (DSC or Grätzel cell) with a remarkable solar to electricity efficiency of 7 %.^{1,2} During the last 5 years the DSC field has exploded and a number of commercial company's world wide has begun production of DSC solar panels, i.e. G24i located in Cardiff. Even though the efficiency of the best DSC cells (11%) is still a factor of two less than the best silicon solar cells, the DSC production technology are relative simple and production costs low. The DSC cells may be applied on glass, polymers or steel and therefore have a very broad application range.

Besides efficiency and low price stability of the solar cell is a very important parameter. As the dye is one of the key elements in the DSC cells its essential to understand "what can go wrong" with the dye during solar cell operation and how to avoid or minimize possible side reactions.

After a general DSC introduction I will report on our DSC research in Roskilde which focus on the understanding of the DSC degradation chemistry of some of the most popular ruthenium dyes used in DSC cells.³⁻⁶

References

- [1] B. O'Regan and M. Grätzel, *Nature*, 1991, 353, 737-740.
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- [3] G. Hansen, B. Gervang and T. Lund, *Inorganic Chemistry*, 2003. 42, 5545-5550.
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- [6] H. T. Nguyen, H.M. Ta and T. Lund, *Solar Energy Materials & Solar Cells*, 2007, 91, 1934-1942.

6) Study of Electrochemical Induced Migration on Electronic Chip Resistors by Use of Novel Electrochemical Cell Set-up

*Daniel Minzari *, Morten S. Jellesen, Per Møller and Rajan Ambat*

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Corrosion reliability of electronic devices is of major concern today due to multimaterial combinations combined with miniaturization, together with globalization in production application. A significant problem is the ElectroChemical Migration (ECM) of many metals on PCBs such as e.g.: Cu, Sn, Pb, Ag [1,4]. ECM is the phenomena where metal ions dissolve from the anode and deposit at the cathode in forming dendrites. Eventually the dendrites will fill the gap between the anode and the cathode causing electrical short and device failure. It can lead to periodic or permanent failures, and can be extremely difficult to detect when performing traditional failure analysis of complex electronic circuits [4]. Failure analyses of electronic products reveal that ECM is a common problem in electronic circuits [5]. Presently very little is known about the influence of various factors on ECM and related irreversible defect mechanisms.

This presentation focuses on the investigation of ECM on passive components by applying a novel Single Component ElectroChemical Migration (SCECM) setup where condensing environment on a PCB is simulated, and the effect of various contaminations can be investigated. The advantage of this setup is that experiments can be done directly on the components, thereby eliminating the uncontrolled parameters originating from solder process and PCB laminates.

Effect that chloride and some selected organic contaminants has on ECM has been investigated and are summarized and discussed. FEG-SEM and FIB-SEM investigations were carried out for microstructural analysis of dendrites.

The dissolution of metal ions (mainly tin) at high voltage or chloride solutions results in the formation of hydroxides of tin, reducing the probability of ECM. The impact of the chemistry, hereunder especially the local pH at the anode and cathode on the level of ECM will be further discussed. The morphology of the dendrites was observed to depend on the solution chemistry.

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7) Electrochemical re-impregnation of wood in structures

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When wood in structures starts to decay, the only choices today are surface treatment or replacement of damaged wood. Replacement is not a preferred option in e.g. heritage buildings or constructions where this action is very costly due to the placement of the wood (hard to reach wood). In Denmark the climate is expected to change towards warmer and more humid conditions and this will initiate decay of more wood in structures than today in the present climate and there will be an increasing demand for efficient re-impregnation methods. Surface treatment suffers from not offering a fast protection. Such treatment is based on diffusion of the preservative into the wood and this transport is often in the range of few mm per month and when the decay reaches deeper into the wood such treatment is insufficient. Methods where holes are drilled in the wood for supply of wood preservative have been developed to protect the wood in depth, but still the diffusion rate is limited and the decay is not always efficiently stopped.

Boron and/or copper based preservatives are most often used for surface treatment.

At DTU Civil Engineering projects are carried out to develop electrochemical reimpregnation methods. It has shown possible to increase the penetration rate of preservatives in wood by applying an electric DC field where boron or copper is transported into the wood by electromigration. Compared to diffusion has shown possible to increase the transport rate of boron significantly. In this process the boron was supplied at the wood surface by brushing as boric-tartaric acid, which forms negatively charged complexes at the pH of wood (pH 4-5) and these complexes were electromigrating into the wood towards the anode. Also the transport rate of copper can be increased by application of an electric field. Here the copper source was Celcure AC800 (a copper-amine preservative from Osmose) that was placed as a liquid compartment at the end of the wood piece. The copper was present in positively charged complexes and was transported into the wood towards the cathode. Another setup for electrochemical re-impregnation with Cu originating from a Cu-nail (which serves as anode) has also shown promising. The cathode was a steel screw. The general advantage of electrochemical re-impregnation is faster transport of the preservative into the wood. The advantage of supplying copper from an anode-nail compared to the former mentioned electrochemical re-impregnation methods is that full access to the wood surface is not necessary, only access for placing the nail in the wood is needed. That means that the method can be used in situations where surface treatment is impossible e.g. where the wood serves as bearing material for artwork, where the wood hidden behind other building components, or in places where the decay is significant in depth compared to at the visible surface.

8) Corrosion Behaviour of Friction Stir Welded AA2024–T351

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Abstract

The effect of welding parameters (rotation and travel speeds) on corrosion behaviour of friction stir welds (FSW) 2024-T351 aluminium alloys was investigated by gel visualisation, immersion tests and local electrochemical measurements. The location of the weld region with highest susceptibility to corrosion was controlled by rotation speed. The intergranular attack was found in the nugget region for low rotation speed welds, whereas for higher rotation speed welds, attack occurred predominantly in the heat-affected zone. The sensitisation at grain boundaries led to the increase in anodic reactivity in the weld zone and the precipitation of S-phase particles enhanced the cathodic reactivity in the nugget region. Cryogenic CO₂ cooling was applied to FSW in order to reduce temperature during welding, and thus improve the corrosion resistance of the weld. It was found that cryogenic cooling had no effect on the degree of anodic reactivity in the weld region. However, it did decrease the width of the reactive heat-affected zone.

9) Removal of NO_x with porous cell stack

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Keywords: deNO_x, porous cell stack, LSM

In the heat of combustions engines NO_x is formed from N₂ and O₂, but it is dangerous to the environment and the health and should therefore be eliminated. This is done by a three way catalyst for an engine running with low air to fuel ratio, but this approach cannot be used for more fuel efficient engines running with high air to fuel ratio, as the excess oxygen is poisoning the traditional three way catalyst. Some materials can catalyse the direct decomposition of NO_x, but the activity is low. An electrochemical cell can be used to remove NO_x: the principle is to reduce NO_x molecules at the cathode, transport oxygen ions through the electrolyte and form O₂ at the anode. Contact between gas molecules and electrode is crucial and porous cells, where the gas flows through the cell was made in order to achieve better contact and thereby activity, which could be measured in changes of the composition of the gas stream. An 11 layer porous cell stack was made by tape casting and laminating with interchanging layers of La_{0.85}Sr_{0.15}MnO₃/Ce_{0.9}Gd_{0.1}O₂ (LSM/CGO) as composite electrode and CGO as electrolyte. Argon gas containing 1000 ppm NO was lead through the cell and the cell showed catalytic conversion of NO without polarisation in the temperature interval of 350 to 450 °C. When a potential of 0.7 V was applied over each cell the activity increased, with the highest activity observed at 400 °C, where complete conversion was obtained. Then 4 % O₂ was added to the gas stream to simulate the real conditions in the exhaust, and as expected this decreased the activity of the cell stack.

10) Electrochemical degradation of PAH compounds in model solutions and process water from removal of harbor sediment

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Keywords: Electrochemical oxidation, Polycyclic aromatic hydrocarbons (PAHs), Water treatment

Subject: Environmental electrochemistry, electrochemical water treatment

The present study has investigated the possibility to apply electrochemical oxidation in treatment of polycyclic aromatic hydrocarbons (PAHs) in water. PAHs are byproducts of incomplete combustion or hydrolysis of organic materials with recalcitrant and strong mutagenic/carcinogenic properties [1]. The family of PAH pollutants has been found widespread with high concentrations in different water bodies all over the world, and the compounds pose even at very low concentrations a great threat to ecological and human health due to their benzene analog structures. PAHs are hydrophobic compounds and their persistence in the environment is mainly due to their low water solubility [2]. Once PAHs enter into the water systems, it is difficult to remediate these by conventional methods, as PAHs are essential recalcitrant, persistent, and non-reactive in water [1]. Electrochemical oxidation of organic pollutants in contaminated water has in the recent years showed to be a versatile, non-selective, and efficient technique in the abatement of a wide range of organic pollutants [3]. The contaminated water is simply passed through electrodes in an electrochemical cell, where the organics are oxidized directly on the anode surface and/or indirectly by electrochemically generated oxidants, the removal rate and efficiency depending on several parameters as electrode material, electrolyte composition, pH etc [4]. The electrochemical oxidation of the PAHs compounds naphthalene, flouranthene, and pyrene in water has in the present work been investigated in model solutions considering variations in experimental parameters as current density, electrolyte composition, and electrolyte concentrations. The investigation has been performed in a batch recirculation experimental setup at constant temperature with a commercial cell of tubular design with Ti/Pt90-Ir10 anode and SS 316 cathode operated at galvanostatic conditions. The three investigated electrolytes were Na₂SO₄, NaNO₃, and NaCl, the concentration range was 0.6-1.4 M, and the current densities were 50-200 mAcm⁻². All three of the subjected PAHs were nicely degraded during the electrochemical treatment, and all of the conducted experiments confirmed that the removal rate of the two-ring structured naphthalene was significantly faster with regards to the specific charge added, compared to the four-ring structured compounds flouranthene and pyrene. In an inert electrolyte solution (0.1 M Na₂SO₄) all three PAHs were degraded by directly electron transfer at the anode surface. The removal rate was reduced in 0.1 M NaNO₃, but significantly increased in 0.1 M NaCl, where indirectly oxidation by hypochlorite, formed by the electrolysis of chloride, showed a clear positive effect. Reducing the NaCl concentration at constants current density decreased the removal rate of all three PAHs showing the importance of the indirect oxidation mechanism. Surprisingly, a lowering of the current density increased the removal rates in all investigated electrolyte solutions, most distinct with flouranthene and pyrene. This observation is believed to be due to a higher current efficiency of the PAH oxidation at the lower applied voltages with regards to the water oxidation side reaction. The present investigation is still ongoing, and further experiments are going to be performed; cyclic voltammetry in order to study the influence of the electrolyte composition and concentration on the oxidation potentials of the PAH compounds, and experiments clarifying the risk of formation of unwanted chloro-organic byproducts. However, the initial work has shown that the electrochemical oxidation technique has a significant potential in treating water contaminated with PAH compounds. Introductory proof of concept experiments has been performed with process water, used in the process of removing sediment from harbors, and even in very low concentrations, a wide range of PAH compounds are removed by the electrochemical treatment, to concentrations below the detection limit (0.010 µg/L-1).

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POSTER PRESENTATIONS

1) Simultaneous Electrografting of Different Grafting Agents to Form Mixed Organic Layers

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The most promising methodologies for modifying surfaces are based on the reduction of aryl diazonium, diaryliodonium, or triarylsulfonium salts.¹⁻⁵ The reduction may be carried out by means of electrochemistry or it may take place in a spontaneous but rather slow reaction initiated by the electronic interactions between the surface and the salt.

Derivatization of metals and carbon is an important tool in the design of new functional materials. The final surfaces are not roughened and monolayer or multilayer coverages can be obtained.

The covalently attached organic groups impart different properties to carbon surfaces. In this work we set out to look if it is possible to simultaneously attach two different functional groups from two different classes of precursors in a single electrolysis step. We investigated, by means of Redox Probes and the Electrochemical Impedance Spectroscopy (EIS), how the surface properties vary with different initial ratios of the two compounds. Moreover, the possibility of controlling and adjusting the reactivity of the surface towards further grafting in acidic condition has been explored.

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2) Monitoring pO_2 and pCO_2 with Radiometers Tiny-Teddy

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Continuous measurement of pO_2 and pCO_2 can be critical for the treatment of critically ill patients. Especially for neonates a non-invasive and non-blood-sampling monitoring method is a great advantage. Measuring these parameters by trans-cutaneous electrochemical sensors gives values comparable to arterial pCO_2 , while the measurement of pO_2 is more dependent on the blood perfusion, but still it can be used as a guide of *changes* in oxygen delivery to the tissue.

Radiometer has developed a combined sensor, which utilises a Clark electrode as the oxygen sensor and a Severinghaus pCO_2 sensor. The Clark electrode measures the current from diffusion controlled oxygen reduction, while the Severinghaus sensor measures the pH change in a bicarbonate electrolyte at a solid state pH electrode after equilibration through a polymer membrane. Another sensor, containing only the Clark electrode, is used for measurements of the oxygen supply to the tissue, when monitoring wound healing and making decisions on where to place an amputation. The sensors can be used for 2 years, but needs a new membrane every 7 days.

Recently Radiometer has introduced the Tiny Teddy, which comprises a miniaturization of the original combined sensor together with a more easy-to-handle mounting of new, diffusion limiting membranes on the sensor. The small sensor is easier to mount on the neonates, and the advantage of an improved membranefixation tool is a more reliable performance. The small size and the redesigned membrane have also allowed for an optimization of the calibration stability of the sensor.

3) Comparison of acetate, glucose and xylose in microbial fuel cells with humic acid as Mediator

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Power production with acetate, xylose and glucose was investigated in two-chamber microbial fuel cells (MFC) to compare these substrates. Humic acid (HA) was tested as a model compound for hydrolysed lignin and was expected to have a mediating effect due to the phenol structure. Na-acetate resulted in the highest voltage (550-600 mV) and power density (120 mW/m², 48 cm² anode surface). Usage of glucose and xylose resulted in maximum power densities of 28 mW/m² and 32 mW/m² at a lower voltage level of 380 mV and 414 mV, respectively. With glucose and xylose as substrate the maximum power density increased versus HA-concentration to 52 mW/m² and 42 mW/m², respectively at 2 g HA/l. pH decreased with glucose and xylose as substrate from 6.7 to 5 due to formation of acetic acid and propionic acid by fermentation reactions.

4) Advanced SPM method for electrochemical characterization of fuel cell materials

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Abstract: The CAHT-SPM (controlled atmosphere high temperature scanning probe microscope) is a new in-situ, high temperature SPM microscope being applied for the measurements on fuel cell components. The CAHT-SPM works on the same principles as a standard AFM (atomic force microscope). The CAHT-SPM is, in contrast to a standard AFM, equipped with a furnace (for heating the sample to high temperatures, from 500 °C -700 °C), gas in- and out-lets and a possibility for the connection of electrical measuring instruments.

The special features of the CAHT-SPM allow the study of the processes in the electrodes on a micro scale. The knowledge of these processes would enable the identification of the areas of the electrode where performance problems occur

The special environment of the CAHT-SPM demands special types of probes which must be electrically conducting and chemically stable at the high temperatures and in the relevant atmospheres. Different types of metal and ceramic probe materials have been investigated for this purpose.

Topographical and electrical (maps of conductivity) images have been acquired at 500°C on different samples and point impedance measurements have been initiated. Investigation of in situ images of the reduction of anodic symmetrical cells has been successfully performed.

5) Stability of radicals in electron-irradiated fluoropolymer film for the preparation of graft copolymer fuel cell electrolyte membranes

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Preparation of cheap polymer electrolyte membranes (PEM) for low- and intermediate-temperature fuels cell by pre-irradiation grafting has attracted much attention in the recent two decades. This method is a convenient way of producing low-cost membranes, and it offers the opportunity to tailor the final membrane with respect to properties such as proton conductivity, strength, and permeability. It comprises the following three-step procedure: 1) generation of radicals in a fluoropolymer base film, 2) grafting of the film by radical-initialized chain polymerization of styrene, and 3) sulfonation of the polystyrene chains [1]. As base film poly-(ethylene-*alt*-tetrafluoroethylene) (ETFE) is well suited due to its alternating sequence of hydrocarbon and fluorocarbon units. Generation of radicals can be obtained by irradiation of the film by γ -rays or accelerated electrons, and the radicals thus formed may be peroxy or alkyl radicals depending on the atmosphere the film is exposed to [2].

In this study the stability of radicals generated in ETFE film by electron irradiation has been investigated. The nature and relative content of the radicals in irradiated film samples have been determined by electron spin resonance (ESR) spectroscopy. The figure below shows the relative content as a function of time of peroxy radicals generated in ETFE film by irradiation in the presence of air. The radicals are seen to decay over time which is likely due to recombination. The decay rate is dependent on storage temperature, so that the radical content decreases more quickly when the film sample is stored at room temperature (RT) than when kept in liquid nitrogen. However, even cryogenic storage leads to considerable decay. A similar trend of radical decay upon storage in liquid nitrogen has also been evidenced by a decrease in the grafting yield with increased pre-grafting storage time of the irradiated film. Another very interesting result is that no radicals were detected after grafting. This indicates that no radicals are left in the final membrane, which may be an important durability issue as far as radical-induced membrane degradation during fuel cell operation is concerned.

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6) Polymer Electrolyte Membranes Prepared by Radiation Grafting and Sulfonation

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7) PEMFC Durability Studies

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Abstract

Fuel cell technology is seeing to enter energy supplying market with high competency. As the most promising energy resource, Proton Exchange Membrane fuel cell (PEMFC) is well recognized as the ultimate household and portable energy provider [1, 2]. The durability and performance of fuel cells have a major impact on the most important challenges facing fuel cell commercialization including cost, mass production, system integration, functionality, and reliability. Many efforts have been focused on improvement of the initial PEM FC performance and decreasing the cost; however systematic studies on the durability and lifetime targets are rather rare and in the stage of further development.

At IKBM, University of Southern Denmark, PEMFC durabilities were studied from noble metal dissolution and Nafion® membrane chemical stability.

PEMFC electrodes were treated with Cyclic Voltammetry (CV). Noble metal detection was achieved with Atomic Adsorption Spectroscopy (AAS). The platinum catalyst dissolution was found in the order of magnitude 10^{-6} mol/L, and it increases exponentially with increase of potential. Similar behavior was also found on ruthenium catalyst until it is depleted from the electrode. Furthermore, ruthenium dissolution was seen two orders of magnitude higher than platinum in acidic medium. X-Ray Diffraction (XRD) also confirmed faster loss of Ru in the catalyst.

Nafion® membrane chemical stability studies were summarized for both ferrous ions absent and participating situations. The results are compared from weight loss, ThermoGravimetry (TG), Ion Selective Electrode (ISE) and ^{19}F Nuclei Magnetic Resonance spectroscopy (^{19}F -NMR). The membrane degradation was seen assisted by hydrogen peroxide and enhanced by ferrous ions.

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8) Characterizing Carbon NanoTube Supported Platinum Catalyst by Electrochemistry

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9) Towards super clean materials for solid oxide cells

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Intrinsic impurities in yttria-stabilised zirconia (YSZ), used e.g. as electrolyte in solid oxide fuel cells (SOFCs), segregate to the surface of YSZ during operating conditions [1-3]. The segregation is driven by the lower surface free energy of impurity oxides compared to the bulk components and changes the reaction conditions of the three phase boundary (TPB). This study focuses on the removal and characterization of these impurities to study how fast the electrochemical processes can occur when such impurities are removed. As model system a 9 mol% YSZ single crystal is chosen. The single crystal YSZ is heated in vacuum by alternating current to temperatures around 1300 °C to increase segregation rates. The temperature of the crystal was measured indirectly by the ionic conductivity of the crystal which was measured for a representative sample. The segregated impurities of the crystal are to be studied with respect both to composition, segregation rates and atmosphere dependence by in-situ x-ray photoelectron spectroscopy (XPS). Two different strategies of cleaning YSZ are proposed. These include chemical cleaning of the single crystal by getters and sputtering of the crystal at high temperature. The two proposed cleaning methods will be carried out in parallel to find the most suitable method. Electrochemical impedance spectroscopy will be used to characterize and compare the crystals before cleaning and after cleaning.

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10) Study of Green Compounds as Corrosion Inhibitors

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Abstract

Two natural extracts, *Garcinia Mangostana* (shell) and *Piper Sammentosum* (leave), were used as corrosion inhibitors for C-steel in 0.5 M HCl. The corrosion inhibition efficiency was studied using weight loss measurement and potentiodynamic polarization technique. Both extracts exhibited a similar behaviour. The corrosion rate of C-steel can dramatically be reduced with the presence of the extracts. The inhibition efficiency increased with an increase in the amount of the extracts. In addition, it was found that the inhibition efficiency of *Piper Sammentosum* extract is better than that of *Garcinia Mangostana* extract. At concentration of 2g/l, the inhibition efficiency of *Piper Sammentosum* extract is 93.2% corresponding to the corrosion rate of 7.8×10^{-4} mm/year whereas the inhibition efficiency of *Garcinia Mangostana* extract is 84.6% corresponding to the corrosion rate of 1.7×10^{-3} mm/year. The potentiodynamic polarization curves showed that both extracts decreased anodic and cathodic processes. The effect of temperature on the corrosion inhibition efficiency of the extracts was also investigated.

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