## Two day conference

## **Electrochemical Science and Technology**

5th and 6th October 2006

at

Technical University of Denmark

## 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.
Co-organizer: ATV·SEMAPP

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## **ATV·SEMAPP**

THE ACADEMY OF TECHNICAL SCIENCES - THE SOCIETY OF PROCESS- AND PRODUCTION ENGINEERING

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## **Index**:

Programme	4 – 6
Abstracts	7 – 25
Posters	26 – 34
List of participants	35 - 36

### **PROGRAMME**

5 <sup>th</sup>	Octo	her
J	Ocu	w

#### 14:30-15:00 **Arrival to DTU**

- Mødelokale 1, Building 101, Entrance A, Anker Engelunds Vej, DK-2800 Kgs. Lyngby
- If you want to join only the conference part, you are welcome to arrive just before the talk at 16:00.
- 15:00 **General Assembly** in the Danish Electrochemical Society

For members and guests.

#### 16:00 **Welcome**

Per Møller, professor at IPL, DTU and chairman for the Danish Electrochemical Society

## 16:10 Electrochemistry and Bioelectrochemistry at the Nanoscale and Single-molecule

Levels

Jens Ulstrup, Department of Chemistry, Technical University of Denmark

## 17:15 **Bus-departure to Esrum**

## 18:00 **Visiting Esrum Kloster**

Welcome reception, guided tour, Middle Ages Dinner

22:00 Return to Lyngby by bus.

#### 6<sup>th</sup> October

## 09:00 **Opening of the conference part**

Anke Hagen, Head of Program, Risø National Laboratory

#### **SESSION 1 - FUEL CELLS AND ENVIRONMENT**

Chairman: Mogens Mogensen, Fuel Cells and Solid State Chemistry Department, Risø National Laboratory.

## Novel ceramic anodes for solid oxide fuel cells investigated by cone shaped electrodes

Presentation by: Peter Blennow, Fuel Cells and Solid State Chemistry Department, Risø National Laboratory and Lund University.

09:40	Microbial fuel cell operation for generating electricity from wastewater treatment Presentation by: Booki Min, Environment & Ressources, Technical University of Denmark.
10:00	Electricity generation integrated with xylose degradation by microbial fuel cell Presentation by: Liping Huang, Environment & Resources, Technical University of Denmark and Dalian University of Technology, China.
10:20	Modelling of the Cathode Processes in a Solid Oxide Fuel Cell Presentation by: Martin Søgaard, Fuel Cells and Solid State Chemistry Department, Risø National Laboratory.
10:40	Coffee break
11:00	Electrochemical reduction of NOx Presentation by: Frantz Bræstrup, Risø National Laboratory.
11:20	Electrochemical Reduction of NO on La2-xSrxBO4 (B = Cu, Ni) having the K2NiF4 Structure  Presentation by: Vibe L. Simonsen, Fuel Cell and Solid State Chemistry Department, Risø National Laboratory.
	<b>SESSION 2 - CORROSION</b> Chairman: Rajan Ambat, IPL, Department of Manufacturing and Management, Technical University of Denmark
11:40	Intergranular Corrosion Susceptibility of Al-Mg Alloys Presentation by: Daniel Minzari (expected), Department of Manufacturing and Management, Technical University of Denmark.
12:00	Lunch
13:00	The Influence of a Magnetic Field on Chemical Dissolution of Iron Presentation by: G. Bech-Nielsen, Department of Manufacturing and Management, Technical University of Denmark.
13:20	The electrochemical behaviour of innovative hardening treatments and coatings on stainless steels exposed to erosive-corrosive conditions in the food industry Presentation by: Morten S. Jellesen, Department of Manufacturing and Management, Technical University of Denmark.
13:40	Corrosion behavior of a new biofouling inhibiting surface in some liquid solutions Presentation by: Wen-Chi Chiang, Department of Manufacturing Engineering and Management, Technical University of Denmark.

14:00	Electrochemistry at an oil/water interface for physical chemical characterization and detection of dermal drug compounds  Presentation by: Maria Deryabina, Department of Pharmaceutics and Analytical Chemistry, The Danish University of Pharmaceutical Sciences.
14:20	Coffee break
14:40	Covalent Immobilization of Alkynyl and Aryl Groups onto Glassy Carbon Surfaces by Electrochemical Reduction of Iodonium Salts Presentation by: Kim Daasbjerg, Department of Chemistry, University of Aarhus.
15:00	Electrochemically Assisted Surface Modification of Carbon Felt - Preparation, Characterization and Applications Presentation by: Steen U. Pedersen, Department of Chemistry, University of Aarhus.
15:20	Chemical Approaches for Controlling Surface Layer Thickness upon Electrografting of Aryldiazonium Salts Presentation by: Lasse Nielsen, Department of Chemistry, University of Aarhus.
15:40	Mathematical modelling of chemical equilibria in enzyme based sensors  Presentation by: Poul Ravn Sørensen, Radiometer Medical ApS (link to abstract is expected to be updated).
16:00	Potentiometric creatinine sensor (Master thesis work at DTU) Presentation by: Claus D. Rasmussen, Radiometer Medical ApS.
16:20	Closing remarks
16:30	End of conference

**SESSION 3 - SURFACES, INTERFACES AND SENSORS**Chairman: Torben Jacobsen, Department of Chemistry

## Novel ceramic anodes for solid oxide fuel cells investigated by cone shaped electrodes

Peter Blennow<sup>a,b,\*</sup>, Kent K. Hansen<sup>a</sup>, L. Reine Wallenberg<sup>b</sup>, Mogens Mogensen<sup>a</sup>

**Keywords:** Nb-doped SrTiO<sub>3</sub>, Ceramic SOFC anode, cone shaped electrodes

#### **Abstract**

Yttria-doped zirconia (YSZ), a polycrystalline ceramic that conducts oxygen ions, is used as electrolyte and a nickel-YSZ cermet is the most frequently used anode material in the current state-of-the-art solid oxide fuel cells (SOFC). However, it has many disadvantages, including the tendency of nickel to agglomerate and sinter, resulting in a degradation of the anode performance with time. The anode also degrades during redox cycles. Impurities in the fuel stream, particularly sulphur, inhibit anode functionality. Another problem is created by the use of hydrocarbons. It is widely agreed that direct feeding of dry hydrocarbons into the fuel cell must be avoided when using a Ni-based anode since Ni is an efficient catalyst for hydrocarbon cracking, resulting in coking on the electrode. The development of new fuel electrodes for solid oxide fuel cells (SOFC) capable of converting hydrocarbons without addition of steam and at the same time being tolerant to gas impurities would be a significant breakthrough.

Recently composites with doped strontium titanates have been reported to show promising electrocatalytic and conductivity results appropriate for solid oxide fuel cell (SOFC) applications.<sup>2</sup> The doped strontium titanate composite anodes were tolerant to oxygen-, carbon, and sulphur-containing atmospheres. Some n-doped titanates have also been found to be dimensionally phase stable during redox cyclings.<sup>3</sup>

In this paper the electrical and electrochemical properties of niobium-doped strontium titanate have been studied in order to investigate their potential use as part of solid oxide fuel cell (SOFC) anode materials.  $Sr_{(1-x/2)0.99}Ti_{1-x}Nb_xO_3$  and  $Sr_{0.99}Ti_{1-x}Nb_xO_3$ , where  $x=0.01,\,0.02,\,0.05,\,$  and  $0.1,\,$  have been synthesized with a modified glycine-nitrate process. The synthesized powders have been calcined and sintered in air or in 7%  $H_2$  in  $N_2$  between  $800-1400\,^{\circ}C$ . The electrical conductivity as a function of temperature and oxygen partial pressure ( $P(O_2)$ ) has been investigated for some selected samples. For  $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_{3-\delta}\sigma=125\,$  S/cm at  $1000\,^{\circ}C$  in 9%  $H_2/N_2$ . The material has a metallic character, i.e.  $\sigma$  is increased with decreased temperature. The electrochemical properties have been investigated with electrochemical impedance spectroscopy (EIS) and cyclic voltammetry using cone shaped electrodes. The EIS data were fitted to the equivalent circuit  $R_S(Q_1[R_1(RQ)_2])$ , following the circuit description codes used elsewhere 4, and possible explanations to the nature of the different electrode processes are suggested. The suitability for using cone shaped electrodes as a tool for investigating electrode materials is also discussed.

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## Microbial fuel cell operation for generating electricity from wastewater treatment

Booki Min, Finn Willy Poulsen, Anne Belinda Thomsen, and Irini Angelidaki

#### **Abstract:**

In response to a high request of renewable energy, the concept of a microbial fuel cell (MFC) has been of interest again to researchers around the world. The MFC is a device that can convert chemical energy from organic matter directly to electrical energy via microbial oxidation and chemical reduction processes. It generally composed of two chambers, an anode chamber for the oxidation of organic compounds under anaerobic condition and a cathode chamber for oxygen or ferriccyanide reduction. There are mainly two benefits comparing to other bio-renewable sources; it can extract theoretically the most energy from organic matter since no intermediate process like a combustion process is not necessary for electricity generation. The other thing is that it can treat waste, for example, domestic or animal wastewater without air pollution gas emission. However, up to now, the performance of the MFCs still remains limited for the field application. The limitation of the current MFC system could be found from a number of operational factors. In this study, we therefore develop a new configuration of a MFC, which has lower internal resistance for more power generation and can be easily applicable to the real world. We investigate key operational parameters that affect power output from simple organic compound and even more complicate organic matter such as domestic wastewater and lignocellulosic waste. The internal resistance of a MFC is measured using an impedance spectroscopy, and the removal of organic matter is demonstrated by the chemical oxygen demand (COD) or gas chromatograph (GC) measurements. We also study microbial ecology of bacteria consortia and their metabolism in the anode chamber of a MFC

# Electricity generation integrated with xylose degradation by microbial fuel cell Liping Huang <sup>1 2</sup> Booki Min <sup>1</sup> Irini Angelidaki <sup>1</sup>

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**Keywords:** microbial fuel cell; xylose; degradation

#### **Abstract:**

Large amounts of energy contained in lignocellulosic materials from agricultural residues that we refer to as waste usually remain unexploited and subject of microbial degradation. Pentoses represents a non-negligible portion of the lingo-cellulosic hydrolysates and no effective microorganisms for conversion of pentoses to bioethanol is vet found. Finding a way to investigate pentose degradation for the generation of electricity is the driving force for the development of microbial fuel cells (MFCs). In this contribution, electricity generation integrated with xylose degradation was investigated in one typical two-chamber microbial fuel cell (MFC). Voltage (1000  $\Omega$  external resistor) and coulomb increased with xylose concentration from 0.1 mM to 8.29 mM. The maximum voltage, coulomb and power generation were obtained at xylose concentration of 8.29 mM which were about 84 mV, 51.9 C and 3 mW/m2, respectively. Further increase of xylose concentration led to the decrease of voltage, coulomb and power generation, which were 71.3 mV, 36.8 C and 2.55 mW/m2, respectively at xylose concentration of 14.8 mM. The differences in coulomb yield at different substrate concentrations showed that some electrons were consumed by mechanisms other than the cathode reaction. Xylose degradation rate appeared to follow saturation kinetics as a function of xylose concentration under 10 mM with a maximum of 0.226 mmol/L·h and half-saturation constant of Ks  $\approx 3.00$  mM. A slower degradation rate under a higher xylose concentration 14.8 mM may imply the metabolism inhibition by higher concentration substrate or metabolism products which depleted some electrons, and consequently, resulting in a lower coulomb yield. This work demonstrates that optimum utilization of xylose by microorganisms in the MFC, which lead to the maximization of fuel cell performance can be carried out by adjusting initial xylose concentration.

## Modelling of the Cathode Processes in a Solid Oxide Fuel Cell

Martin Søgaard<sup>1</sup>,\*, Peter Vang Hendriksen<sup>1</sup>, Torben Jacobsen<sup>2</sup> and Mogens Mogensen<sup>1</sup>

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- 2) Department of Chemistry, Technical University of Denmark, Kemitorvet, Building 207, DK-2800 Kgs. Lyngby, Denmark

#### **Abstract**

Perovskite materials have been intensively studied for the use as cathodes in solid oxide fuel cells (SOFCs). A fuel cell is an electrochemical device that converts chemical energy into electric energy with a very high efficiency. SOFCs have several advantages compared to the traditional ways of generating electrical power. These include: High efficiency, scalability, fuel versatility and low noise operation. The SOFCs that are manufactured at Risø National Laboratory consist of a composite anode of nickel and yttria stabilized zirconia (YSZ, Zr1-xYxO2-x/2). The electrolyte is YSZ and the cathode is a composite of strontium doped lanthanum manganite (LSM) and YSZ. The factor limiting the performance of today's state of the art SOFCs is the rate of the oxygen reduction on the cathode. Yet development of improved cathodes is to a large extent based on a trial and error approach.

The oxygen reduction reaction is generally thought to occur near the 3-phase boundary where the electrolyte, cathode and gas-phase are in contact. During the last decade many studies have focussed on the introduction of mixed ionic and electronic conductivity in the cathode material. Hereby, the area where the oxygen reduction may take place can be increased and as a consequence the polarization resistance of the cathode possibly decreased.

The paper addresses how to calculate the electrode polarisation resistance (Rp) of composite electrodes with mixed ionic and electronic conductivity from the fundamental material properties, i.e. from the electrode structure, gas diffusion through the pores, the oxygen exchange kinetics and the oxygen bulk chemical diffusion coefficient. This is realised by numerical solving of the differential equations governing the oxygen reduction process.

The predicted values of Rp for the different electrode geometries are compared to values obtained from the literature and own measurements. It is shown that one can successfully describe the polarization resistance of cathodes with different microstructures. This method is thus a tool one can use for the development of cathodes with a lower polarization resistance.

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## Electrochemical reduction of NO<sub>x</sub>

Frantz Bræstrup<sup>1</sup>, Ditte Find<sup>2</sup>, Mathilde Raad Lilliedal<sup>2</sup>, Robert Petersen<sup>2</sup>, Kent Kammer Hansen<sup>1</sup> and Vibe Simonsen<sup>1</sup>.

- 1) Risø National Laboratory, Frederiksborgvej 399, 4000 Roskilde, DK.
- 2) Roskilde Universitetscenter, Universitetsvej 1, 4000 Roskilde, DK.

#### **Abstract:**

In petrol fired engines the problems with NOx, CO and unburned fuel in the exhaust gasses has been solved or reduced significantly by the use of a three-way catalytic converter. Problems though still exist in diesel fired engines where air and fuel are injected separately into the combustion chamber. Several attempts have been made to remove NOx from the exhaust gasses but so far no method has been developed without the use of reducing gasses which has to be incorporated in the vehicle.

The purpose of this project is to find new materials which can be used electrochemically to reduce NOx to N2. This will save space and reduce the fuel costs compared with methods using reducing gasses incorporated in the vehicle.

Different spinel-type oxides (AB2O4, A = Co, Ni, Cu and Zn, B = Fe) have been prepared by the glycine-nitrate combustion synthesis (GNS) as well as the solid state synthesis (SS). Samples prepared by GNS were calcined for 5 or 6 hours at temperatures ranging from 800 – 1250°C depending on samples. Samples prepared by SS were heated for 90 hours at 900°C. All samples were analyzed by X-ray powder diffraction and only CuFe2O4 showed traces of an impurity phase, which was detected as CuO.

The samples were pressed with approximately 1 ton/cm2 for 30sec into circular pellets (Ø: 10 mm, L: 20 - 30 mm) and sintered for 6 hours at 1050-1250°C depending on samples. Pellets were then cut into cone shaped electrodes having a base diameter of 7.5mm and sides with an angle of 45°. The cones, acting as the working electrode (WE), were placed on an Yttrium stabilized Zirconia electrolyte having a Silver counter electrode (CE) which also acted as the reference electrode (RE). The set-up was a two atmosphere set-up with atmospheric air at the CE/RE side of the electrolyte and reaction gas at the WE.

Cyclic voltammetry with a potential sweep rate of 10mV/s and 1mV/s were performed on the different cathode materials using a Gamry Instrument, Femtostate. 10mol% O2 in Ar and 1mol% NO in Ar were used as the reaction gasses. The gas flow was 25ml/min and controlled by a Brook Instrument 0154 mass flow controller. The contact area between the cone and the electrolyte was determined by impedance spectroscopy using the Gamry Instrument, Femtostate.

Results show that while CoFe2O4 reduces O2 better than NO, NiFe2O4 and CuFe2O4 show a larger tendency towards reducing NO instead of O2. ZnFe2O4 was more or less not reactive towards O2 or NO reduction compared to the other spinel-type oxides. Peaks were detected in the CV spectra of CuFe2O4 only when using the NO gas. This could be related to the formation of small amounts of Cu2O in the sample.

# Electrochemical Reduction of NO on $La_{2-x}Sr_xBO_4$ (B = Cu, Ni) having the $K_2NiF_4$ Structure

### Vibe L. Simonsen, Linda Nørskov, Anke Hagen and Kent Kammer

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#### **Abstract:**

Excess air is used in combustion in Diesel engines and this leads to fuel efficiencies around 30% better than in gasoline engines. A major drawback is the production of  $NO_x$  and soot particulate [1]. The existing methods for removing  $NO_x$  cannot meet the stricter regulations which are already stated for 2008 [2].

The advantage of the electrochemical method is that  $NO_x$  can be converted directly to  $N_2$  and  $O_2$  without the use of a reducing agent: The process take place in an all solid state electrochemical cell through the reactions:

Cathode: NO + 2e<sup>-</sup> 
$$\rightarrow$$
  ${}^{1}/{2}N_{2} + O^{2-}$  (cathode-electrolyte boundary)

(1)

Electrolyte:  $O^{2-}$  (cathode-electrolyte boundary)  $\rightarrow$   $O^{2-}$  (anode-electrolyte boundary)

Anode:  $O^{2-}$  (anode-electrolyte boundary)  $\rightarrow$   ${}^{1}/{2}O_{2} + 2e^{-}$ 

(3)

A possible side reaction is the reduction of oxygen at the cathode and subsequent transport through the electrolyte and oxidation at the anode, leading to low current efficiency. This study investigates the  $K_2NiF_4$  structures  $La_{2-x}Sr_xBO_4$  (B = Cu, Ni) as possible electro catalysts for selective reduction of  $NO_x$ .

The setup for screening the electrode materials is a pseudo three electrode setup with a point shaped working electrode as described by Kammer et al. [3]. The electrolyte is 10% YSZ and the counter electrode is a combined Ag counter/reference electrode placed in air.

The La<sub>2-x</sub>Sr<sub>x</sub>NiO<sub>4</sub> (x = 0, 0.05, 0.15, 0.25, 0.35, 1.0) and La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> (x = 0, 0.05, 0.15, 0.25, 0.35) electrode materials were produced inhouse using the citric acid route [4] for the nickelates and the nitrate glycine route [5] for the cuprates. The materials were checked for phase purity by XRD and pressed into pellets, before being mechanically machined into cones and placed in the setup. Cyclic voltammetry (CV) was recorded on the materials in 1% NO in Ar or 10% O<sub>2</sub> in Ar. The current response from the voltammograms depend on the contact area between the point shaped electrode and the electrolyte. By using using Newman's formula [6] in combination with impedance spectroscopy measurements the contact area can be estimated and the current response can be normalized to give a current density. Using the point electrode setup, the electrode materials can be compared in activity towards the reduction of oxygen and nitric oxide, respectively. Of the tested materials the LaSrNiO<sub>4</sub> and La<sub>2</sub>CuO<sub>4</sub> had the highest current densities and ratio of  $i_{NO}/i_{O2}$ . Increasing the temperature from 400 to 600°C led to higher current densities but the materials became approximately as good at reducing oxygen as reducing nitric oxide. The voltammograms for the two compounds are shown in figure 1.

Figure 1 shows that a reduction and an oxidation peak occur on the cuprate while the nickelate does not have this effect. The cuprate has the highest current density and the CV can be reproduced for several cycles and thus the electrode does not seem degenerate in spite of the oxidation and reduction peaks. On the other hand the change in oxidation state of Cu may lead to changes in volume and subsequently destabilize the adhesion to the electrolyte in real cells. On basis of this study LaSrNiO<sub>4</sub> seems to be the most promising electrode material tested in this study and should be operated at 400°C to optimize NO reduction as opposed to reduction of O<sub>2</sub>.

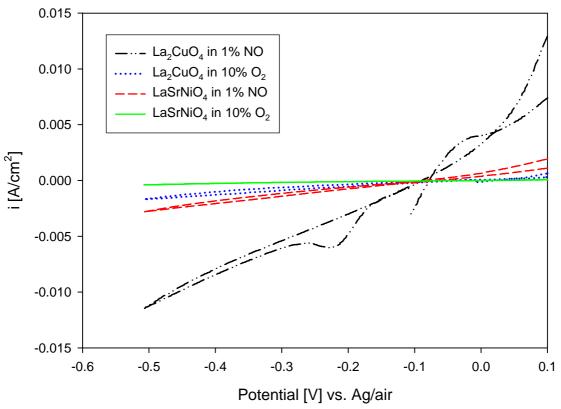


Figure 1. Cyclic voltammograms measured at  $400^{\circ}$ C and 1 mV/s for La<sub>2</sub>CuO<sub>4</sub> and LaSrNiO<sub>4</sub> in 1% NO and 10% O<sub>2</sub>, respectively.

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## **Intergranular Corrosion Susceptibility of Al-Mg Alloys**

#### D. Minzari, R. Ambat and P. Westermann,

Department of Manufacturing and Management, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

#### **Abstract:**

In response to the guidelines laid down by the Kyoto protocol on greenhouse gas emissions, the European automotive industry has committed to a 30% reduction in vehicle CO<sub>2</sub> emission by the end of 2008. One means for achieving this goal is through weight reduction, where it is generally acknowledged that each 10% reduction in total vehicle weight will allow fuel savings of approximately 6-8%. To achieve significant weight reductions, there is a growing interest in the use of low-cost, folded aluminium sheet structures in mass-production car models. Al-Mg alloys offer an attractive combination of strength, formability and corrosion resistance for structural automotive applications. From the mechanical properties point of view, it is desirable to use alloys with high magnesium content. However when more than 3 wt.% Mg is added, the alloys may become sensitized to intergranular corrosion (IGC) and stress corrosion cracking (SCC). Such alloys must be used with caution, particularly after fabrication operations like welding that may in themselves induce a degree of sensitisation to corrosion. Also there is a risk of IGC if the vehicles are used in tropical regions where the exposure temperatures are high enough to cause grain boundary precipitation over prolonged use. On the other hand exposure to de-icing salts and marine environments would be a problem in the cold climatic zones. In this work, the intergranular corrosion behaviour of Al-Mg alloys 5754 and 5182 has been investigated after sensitisation treatment at low exposure temperatures (60, 90, and 120oC) for prolonged times. Experimental investigation includes microstructural characterization, intergranular corrosion testing using phosphoric acid, electrochemical studies, and standard ASTM nitric acid mass loss test (NAMLT). Aim of the work is to make a systematic correlation between NAMLT data and IGC susceptibility after low temperature heat treatments and magnesium content in the alloy. An empirical relation between NAMLT data and IGC performance has been worked out. Electrochemical tests were performed in 3.5% NaCl solution at pH 3.0. The effect of pH on the IGC susceptibility has also been investigated for 5182 alloy. Results show that the IGC susceptibility of 5754 alloy is significantly low due to the low magnesium content, but the 5182 alloy is susceptible even after the paint-baking treatment. The susceptibility was further increased with heat treatment time and temperature. The NAMLT results showed good correlation with phosphoric acid test, however, the break down potential on the electrochemical curve was not affected until a significant level of sensitization was reached. On the other hand passive current density showed a steady increase with increasing level of sensitization..

## The Influence of a Magnetic Field on the Non-Electrochemical Dissolution of Iron

#### G. Bech-Nielsen, IPL, DTU

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**Keywords:** Chemical dissolution of iron, influence of magnetic field

#### **Abstract:**

Electrochemical dissolution of metals is well-established and accounts closely for most cases of corrosion attack. However, since about 1960 it has been shown convincingly for several metals, including iron, that also a purely chemical, potential independent dissolution takes place. For iron it has been shown that while the anodic dissolution has a positive reaction order wrt pH, the chemical dissolution has a negative one. Also influence of anions can be assumed for the chemical dissolution. L. Z. Vorkapic and D. M. Drazic<sup>1</sup> found that touching the corroding iron electrode with a magnet decreased the dissolution rate.

A model for the chemical dissolution of iron, accounting for the influence of pH and anion concentration, has been presented by G. Bech-Nielsen and J. C. Reeve<sup>2</sup>. Hower, influence of magnetic field could not be identified in this model, but a clue may be found in recent work in a different field.

A paper by H. E. Lundager Madsen<sup>3</sup> shows that smaller crystals of calcium carbonate are formed in a magnetic field, when precipitation takes place between calcium ions and hydrogen carbonate ions, but not when carbonate ions are predominant or when heavy water and deuterated chemicals are used. The effect is ascribed to faster deprotonation of the hydrogen carbonate ion as a result of quantum effects influencing closely neighbouring protons. Replacement of protons with deuterons excludes the quantum effects.

It is possible to identify a step in the model for chemical dissolution of iron<sup>1</sup>, which could be similarly influenced by a magnetic field. The model is formulated as follows:

$$Fe^0 + 2X \Leftrightarrow Fe^0(X)_2$$
 (±i)

$$Fe^{0}(X)_{2} + H_{3}O^{+}(\Leftrightarrow) Fe^{0}(X)H_{3}O^{+} + X$$
 (±2)

$$Fe^{0}(X)H_{3}O_{x=0}^{+} \Rightarrow Fe(X)H_{3}O_{x \ge d}^{+}$$
 (3)

$$Fe^{0}(X)H_{3}O^{+}_{x \geq d} + H^{+} \Rightarrow Fe^{2+}_{aq} + H_{2} + X + H_{2}O$$
 (4).

Step (i) is the common starting step for chemical and electrochemical dissolution. X is an anion. x=0 and  $x\ge d$  mean "at the iron surface" and "outside the double layer", respectively. With a low coverage of the product in (2), this step will be rate controlling, and a reaction order wrt. pH of -1

is predicted. Rate control by step (3) will arise as a result of maximum coverage by the product in (2). Then a reaction order wrt. pH of zero is predicted. A reported value of -0.45 indicates partial control by steps (2) and (3) and a rather high coverage by the product in (2). Then a magnetic field might influence reaction (-2) in a similar way as with the hydrogen carbonate ion, since the adsorbed complex contains protons at the closest distance. Thus a higher rate for reaction (-2) will decrease the rate of dissolution.

## References:

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- 2. G. Bech-Nielsen and J. C. Reeve. Dansk Kemi, 61 (1980) 261
- 3. H. E. Lundager Madsen, J. Crystal Growth 267 (2004) 251

# The electrochemical behaviour of innovative hardening treatments and coatings on stainless steels exposed to erosive-corrosive conditions in the food industry.

#### Morten S. Jellesen, Lisbeth Rischel Hilbert, Per Møller

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**Keywords:** Erosion-corrosion, food industry, stainless steel, nitriding, DLC-coating.

#### **Abstract:**

A corrosive environment, wear and the combination of corrosion and wear can cause degradation of equipment. This causes not only financial inconvenience related to renewal or repairing of damaged equipment, additionally metal release can eventually cause health risks for consumers. Some food products are known to be corrosive due to low pH, high chloride concentration, high processing temperature etc. Stainless steel is known for its corrosion resistance, but due to its poor tribological properties there is a risk of material degradation when processing equipment is exposed to combined corrosion and wear. The aim of this study was to investigate the electrochemical behaviour of carburising and nitriding hardening treatments and DLC coatings on stainless steel exposed to erosive-corrosive conditions. Electrochemical measurements have been performed in a food simulant under impingement conditions with suspended alumina particles.

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## Corrosion behavior of a new biofouling inhibiting surface in some liquid solutions

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### **Keywords**

microbe, biofilm, biofouling inhibiting surface, corrosion

#### **Abstract:**

Microbial and biofilm adhesion to the surfaces of water systems are familiar. This biofouling can cause serious problems of hygienic management. In addition, these adhesions can also affect the operation and maintenance, and accelerate the degradation of the equipment. There are different non-toxic ways to limit these problems. In this paper, some inhibiting surfaces utilizing electrochemical effects are briefly reviewed, and some aspects of the corrosion behavior of a new biofouling inhibiting surface in liquid solutions are also reported.

# Electrochemistry at an oil/water interface for physical chemical characterization and detection of dermal drug compounds

#### Maria Deryabina, Henrik Jensen, Steen Honore Hansen

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#### **Abstract:**

Electrochemistry at interfaces between two immiscible electrolyte solutions is well suited for studying physicochemical properties of drug compounds such as for example pKa values and lipophilicity as measured by the water/oil partition coefficient (i.e. log P).

In the present work two-phase partition diagrams obtained by cyclic voltammetry in 4-electrode electrochemical cell were used to characterize the drug compounds. These potential-pH diagrams show how neutral and charged species distribute according to their acid-base properties and charge and provide an accurate determination of standard partition coefficients of ionic as well as neutral species. The technique is also useful for studies on interactions of dermal drug compounds with both lipofilic and hydrophilic ligands.

The electrochemical detection principle was used as a basis for the development of a semi-miniaturized flow injection analysis setup with differential pulse amperometric (DPA) detection. The volume of the oil phase was reduced from 2 ml to 2  $\mu$ l by supporting it on PVDF membrane. The detection limits attainable with the present setup were comparable to or better than conventional detection principles.

## Covalent Immobilization of Alkynyl and Aryl Groups onto Glassy Carbon Surfaces by Electrochemical Reduction of Iodonium Salts.

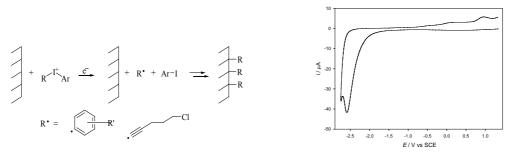
## Karina Højrup Vase, Allan Hjarbæk Holm, Steen Uttrup Pedersen, and Kim Daasbjerg

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#### **Abstract:**

Electrochemically assisted covalent modification of carbon surfaces is a fairly recent development in modified electrode research. Grafting has been accomplished by electrooxidation of amines, aliphatic alcohols, or aryl acetates, or by the widely used reductive procedure involving aryl diazonium salts. However, none of these procedures offer simple and mild conditions for the reductive attachment of alkynyl chains at carbon surfaces.

In this report we present a new procedure for electrochemically assisted grafting of carbon surfaces through reduction of iodonium salts. By this procedure aryl and alkynyl groups have been introduced onto glassy carbon (GC) electrodes. We propose that the modification mechanism outlined in Scheme 1 applies in which reduction of the iodonium salt leads to the generation of an iodoarene along with either an aryl or an alkynyl radical near the carbon surface. The radicals subsequently add to the carbon framework of the surface producing covalent C-C bonds.<sup>2</sup>



Scheme 1 Figure 1.

Cyclic voltammogram recorded of 4-bromophenyl-grafted GC electrode in 0.1 M Bu<sub>4</sub>NBF<sub>4</sub>/CH<sub>3</sub>CN

Reduction of iodonium salts containing electrochemically active moieties makes electrochemical verification of the grafting process obtainable. For instance, the presence of bromophenyl groups introduced to the carbon surface by reduction of 4,4'-dibromodiphenyliodonium bisulfate can be evidenced by recording a voltammogram in 0.1 M Bu<sub>4</sub>NBF/CH<sub>3</sub>CN (Figure 1). The voltammogram exhibits an irreversible cathodic wave at a potential close to that of bromobenzene. On the reverse oxidative sweep an anodic wave corresponding to the irreversible oxidation of bromide ions is observed. Since the unsymmetrical iodonium salts contain two possible bond cleavage sites, we have studied the possibility of controlling the exact pathway by varying the substituent on the aromatic functionality.

Further analysis of the carbon surfaces was carried out by means of X-ray photoelectron spectroscopy, polarization modulation IR reflection absorption spectroscopy, and time-of-flight secondary ion mass spectrometry.

#### References

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# Electrochemically Assisted Surface Modification of Carbon Felt - Preparation, Characterization and Applications

#### Laila Schou, Steen Uttrup Pedersen, and Kim Daasbjerg

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#### **Abstract:**

Carbon felt is a relatively new and undescribed material in modified electrode research, but has been shown to have a number of promising applications owing to its large specific surface area. While the modified carbon felts have typically been characterized by spectroscopic techniques, cyclic voltammetry analyses have rarely, and only by means of specialized equipment, been implemented. Thus, the development of a standard electrochemical set-up, for routine cyclic voltammetry analyses using carbon felt as the working electrode, has been a key topic in the present work.

The use of the RVG-4000 carbon felt, as an electrode material for electrochemical purposes, is explored. It is found to be applicable for conventional cyclic voltammetry experiments, and by reduction of the 4-nitrobenzene- and 4-(chloromethyl)benzene diazonium salts, it is shown to be possible to both modify and characterize the carbon felt surface using this technique.

Next, as the 4-(chloromethyl)phenyl modified carbon felt, obtained by reduction of the latter diazonium salt, is shown to undergo surface-solution reactions upon treatment with nucleophiles, it is investigated whether the 4-(chloromethyl)phenyl modified carbon felt may constitute a carbon-based analogue to the commercial Merrifield resin for use as a solid support in solid phase peptide synthesis (SPPS).

The successful synthesis of a simple dipeptide, see figure 1, demonstrates that the modified carbon felt can indeed be used for such a purpose, and that difficulties encountered for the commercial resin may be avoided by use of the mechanically more stable carbon felt.

#### References

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- (2) Coulon, E.; Pinson, J.; Bourzat, J.-D.; Commerçon, A.; Pulicani, J. P. *J. Org. Chem.* **2002**, *67*, 8513-8518.

## Chemical Approaches for Controlling Surface Layer Thickness upon Electrografting of Aryldiazonium Salts

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#### **Abstract:**

One of the most widely used procedures for modification of carbon-based materials and metals involves electroreduction of aryldiazonium salts. This procedure takes advantage of the fact that reactive aryl radicals produced upon reduction of the diazonium salts may form bonds to the surface. The method allows the introduction of numerous functionalities under mild conditions. The electrode derivatization is usually so effective that intertwined multi-layers are formed in polymerization reactions. Although the process to some extent may be controlled through the applied potential and electrolysis time the surface structures formed will not be well-defined.

In this work we have explored the possibilities of exerting chemical control on the constitution of the modified layer. The basic idea is outlined in the scheme shown below.

In the first step a diazonium salt of diphenyl disulfide is reduced at a glassy carbon surface to produce a multi-layer of aromatic molecules containing disulfide bridges. Because of the steric constraints at the surface the aromatic ring **B** will be much more accessible to attack by the aryl radicals formed during the grafting procedure than the inner ring **A**. Subsequently, it therefore becomes possible to obtain a thin layer of covalently attached thiophenoxides through reductive cleavage of the disulfide bonds. The reduction can be carried out electrochemically or by means of chemical reductants or nucleophiles. Depending on the reductant or nucleophile employed the thickness of the layer can be controlled quite accurately. The creation of a strong nucleophilic surface in a controlled manner also opens up for carrying out further functionalization using classical chemical procedures. Several examples thereof will be presented.

#### References

(1) Pinson, J.; Podvorica, F. Chem. Soc. Rev. 2005, 34, 429.

## Mathematical modelling of chemical equilibria in enzyme based sensors

#### Poul R. Sørensen<sup>1</sup>

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#### **Abstract:**

Although made to measure many different analytes, biosensors share common features, which have impact on the way they are/can be modeled mathematically. Thus biosensors often have enzymes trapped behind a porous membrane, which otherwise allows small molecules and ions to diffuse freely between the sample and the enzyme layer. This is a physical arrangement described in the Donnan theory. Another characteristic feature of biosensors is the production of charged reactants by the action of the enzyme. This can substantially alter the equilibrium of all other ions present, especially if the analyte concentration is high. In the mathematical model this is handled by using the Nernst-Planck diffusion equations. The correct simulation of such sensors, using the NP-equations, poses special problems with respect to initialization, since the concentrations of all charged forms of the enzyme, and all other ions present, including charged buffers, must be known before the calculation can start. A special technique was developed to handle this within the simulation program itself using an iterative approach, in which the analyte solution is used several times to 'wash' the enzyme layer to its equilibrium state.

## Potentiometric creatinine sensor

## Claus Dallerup Rasmussen<sup>a</sup>, b, Birgit Zachau-Christiansen<sup>a</sup>, Jens E.T. Andersen<sup>b</sup>

a Radiometer Medical Aps, Brønshøj, Denmark b Department of Chemistry, Technical University of Denmark

#### **Abstract:**

The aim of the present master project was to develop and characterize a creatinine biosensor that could be applied to measurements under real conditions or simulated real conditions, such as solutions resembling those of a blood matrix. The biosensor consisted of an ammonium selective electrode mounted with a nylon membrane on top. On the nylon membrane the enzyme creatinine deaminase (EC 3.5.4.21) was immobilized by applying dimethyl sulfate (DMS) to activate the nylon membrane. Glutaricdialdehyde was used as a cross-linking agent between the nylon surface and the enzyme.

The biosensors had a lower detection limit of  $0.3 \square M$  creatinine, which is approx. 50 times lower than biosensors previously described in the literature. The concentration range of linear response was found between  $2 \square M$  and 10 m M creatinine, displaying a sensitivity of  $58.78(\square 0,03) m V/decade$  (99.9%). This range fully covers creatinine concentrations that are important to clinical and biomedical investigations. The response time was determined as 31 seconds (t95). A sample volume of only  $30 \square L$  was needed for the response to reach approx. 50% of the maximum-response value and  $160 \square L$  to reach 75%. A recovery was achieved of  $100(\square 3)$ % at  $1326 \square M$  creatinine in a solution containing interferences of 170mM sodium and 8mM potassium in 25mM carbonate buffer.

The biosensors exhibited excellent storage capability, thus retaining more than 97% of the initial sensitivity after 3.5 month.

The project was carried out in the Analytical Chemistry Group at the Department of Chemistry at the Technical University of Denmark in co-operation with Radiometer Medical.

## POSTER PRESENTATIONS

## Platinum Migration at the Pt/YSZ Interface

Presentation by: Jimmi Nielsen, Technical University of Denmark.

### Localized residue detection on electronic printed circuit boards for corrosion control

Presentation by: Peter Westermann, Technical University of Denmark.

#### Using synthetically mixed BMP fuel as fuel in SOFC

Presentation by: Jens F.B.Rasmussen, Risø National Laboratory.

#### CO<sub>2</sub> Permeability in Nafion® EW1100 at Elevated Temperature

Presentation by: Shuang Ma, University of Southern Denmark, Chemistry Department.

## Solvent Uptake in Nafion® Membranes from Water-Alcohol Mixtures

Presentation by: Yue Ma, University of Southern Denmark, Department of Physics and Chemistry

## Preliminary studies of the anodization of aluminium in oxalic acid

Presented by: Søren Kristiansen, University of Southern Denmark, Department of Physics and Chemistry.

### Electrochemical characterization of LSM thin films using impedance spectroscopy

Presentation by: Malene Sørensen, University of Southern Denmark, Department of Physics and Chemistry.

### **Preparation and Analysis of New Proton Conducting Membranes**

Presentation by: Eivind Skou, based on poster made by Susanne Roslev Søgaard et al., University of Southern Denmark, Department of Physics and Chemistry.

## Platinum Migration at the Pt/YSZ Interface

## Jimmi Nielsen<sup>1</sup>, Torben Jacobsen<sup>1</sup> and Mogens Mogensen<sup>2</sup>

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2)Risø National Laboratory DK-4000 Roskilde / Denmark

Key words: SOFC, Microelectrodes, Morphology, Surface migration

#### **Abstract:**

Electrode activation, inductive hysteresis and non-linearity are well known phenomena on Pt-YSZ electrodes, and recently also regular fluctuation patterns have been reported. The oxygen electrode on YSZ surfaces is studied at Pt micro-electrodes prepared by electrochemical etching of platinum wire. The result is a well defined contact area of ~20  $\square$ m in diameter. Due to the small size and a favourable ratio between the three-phase boundary (TPB) length and the contact area, micro-electrodes should have an increased sensitivity to discrete events at the TPB. The electrode processes are studied by potential sweep, step and impedance techniques. As expected, inductive behaviour and activation during step polarization is confirmed, but furthermore a very accentuated noise pattern is seen during cathodic step polarization. Investigation of the YSZ and Pt surfaces afterwards reveals the growth of dendrite like Pt structures from the TPB. The formation of these may explain the observed noise and contribute to the explanation of the activation mechanism taking place at the platinum-YSZ interface.

## Localized residue detection on electronic printed circuit boards for corrosion control

## Peter Westermann\*, Rajan Ambat, and Per Møller

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\*Contact: s001500@student.dtu.dk

#### **Abstract:**

In recent years, corrosion of electronic systems has been a significant issue due to the development of complex systems and increasing demand for their reliability. The demand for miniaturization, multiplicity of materials used, effect of process residues together with unpredictable user environment has opened up serious corrosion problems. The miniaturization of electronic devices reduces both the size of components and the spacing between them on printed circuit boards (PCBs). Material loss of the order of  $10^{-12}$  grams can cause failures like short circuiting or current leakage in such tiny circuits; therefore even a minute environmental impact can have adverse effect on the performance of the electronic systems.

An important factor determining the susceptibility of PCB to corrosion is the residues from the manufacturing process remaining on the surface. The residues can be ionic or organic in nature resulting from the complicated PCB manufacturing process such as etching and plating. On a PCB mounted with components, the contamination brought by the components also adds to the problem. The residues interact with humid environments during application of the PCB resulting in local aggressive environments for corrosion attack. Therefore, PCB cleanliness plays a big role in controlling the corrosion in electronic devices.

Presently employed residue level test methods (such as Surface Insulation Resistance Testing) measures the conductivity of a solution before and after the PCB exposure. The change in solution conductivity after the PCB exposure is a measure of the level of residues present on the PCB surface. However, such measurements provide only the average residue levels, although at local areas the concentration can be significantly higher than the average. Therefore, an important task is to be able to detect and map the residue levels on a PCB surface in order to develop a cleaning process that will minimize the corrosion problems due to residues. This paper presents a microelectrode approach by measuring the current flow between two metal electrodes as a function of potential in a given environment. The current obtained is a function of the amount of residue present in a localized area. The resolution of the technique can be varied, but in this case the detection area was ~1 cm<sup>2</sup>. The results presented in this paper describe some of the preliminary residue mapping carried out on PCBs with various designs and components. Results indicate that the level of residues remaining on the surface depends on how complicated the PCB pattern is. In general, the areas with through holes plating had higher contamination levels compared to other areas. Also the different electronic components on the PCB have introduced some levels additional contaminants increasing the aggressiveness of the corrosive media.

## Using synthetically mixed BMP fuel as fuel in SOFC

### Jens F.B. Rasmussen\* & Anke Hagen

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#### **Keywords**

SOFC, synthetically mixed biogas, impurity

#### **Subject**

Biogas and solid oxide fuel cells

#### **Choice of presentation**

Poster

#### **Abstract**

The use of biomass produced (BMP) fuel as fuel in a planar anode supported solid oxide fuel cell (SOFC) was considered. A typical BMP fuel consists of 65% CH4 and 35% CO<sub>2</sub> as the main components, in the case where fermentation is used. However, use of this composition directly will degrade the performance of the SOFC quickly, due to graphite formation on the Ni particles. For this reason it is wise to dilute the fuel with H2O or O2

Before using diluted BMP fuel directly synthetically mixed biogas was applied. The electrochemical characterization of the fuel cell was done by use of impedance spectroscopy and iV curves. Furthermore a mass spectrometer was used to analyse the fuel inlet and outlet to the SOFC. This gave information about the similarities in gas composition between synthetically mixed gases and real BMP gas. Moreover the changes of the gases during passage of the anode of the SOFC could be investigated.

A very important component in real BMP fuel is H2S. In raw BMP fuel this typically amounts to about 200 ppm. This is a possible poison to the SOFC depending on the degree of dilution of the BMP fuel. The effect of H2S on the performance of the SOFC during long term testing is thus an ongoing investigation.

## CO<sub>2</sub> Permeability in Nafion® EW1100 at Elevated Temperature

## Shuang Ma and Eivind Skov

University of Southern Denmark

#### **Abstract:**

The permeability of carbon dioxide through Nafion® EW 1100 has been studied at different temperatures, ranging from 30 to 80 ?C. Three conditions were tested: water soaked, water vapour equilibrated and completely dry. When water is present, carbon dioxide permeability of the membrane shows a volcano shape with a maximum of 2.69\* 10-11 [cm3 (STP) cm cm-2 s-1 Pa-1] at around 50?C. In dry condition, the permeability unilaterally increases from 2.63\*10-13 to 8.41\*10-13 [cm3 (STP) cm cm-2 s-1 Pa-1]. In hydrated Nafion, the hydrophilic domain is interpreted as the major transport channel for carbon dioxide, and reduced solubility of carbon dioxide at elevated temperature is the main cause for the decline of gas permeation. Carbon dioxide permeation enhancement by methanol dissolved in Nafion is negligible in a normal operating direct methanol fuel cell.

## Solvent Uptake in Nafion® Membranes from Water-Alcohol Mixtures

#### Yue Ma, Eivind Skou, Per L. Hansen

Department of Physics and Chemistry, University of Southern Denmark, DK-5230 Odense, Denmark

#### **Abstract:**

This project studies the sorption properties of DuPontTM Nafion® proton exchange membranes (PEMs) swollen in binary mixtures of water and selected alkane-mono-ols at room temperature, in particular concerning the distribution of solvents between polymer phase and liquid phase. The experimental data of individual solvent uptake are estimated by membrane mass-difference measurements using electronic balance, and water-alcohol partitioning analyses using 1H NMR spectroscopy. A theoretical "Bag Model" is proposed at thermodynamic equilibrium condition of solvents between the two phases, which involves a modification of the Flory-Huggins model and a swelling pressure correctional term in the expressions of the chemical potentials of solvents.

## Preliminary studies of the anodization of aluminium in oxalic acid

#### Søren Kristiansen

University of Southern Denmark, Department of Physics and Chemistry.

## Per Morgen and Eivind Skou

University of Southern Denmark.

#### **Abstract:**

We have developed an alternate method to produce nanoporous aluminium oxide which uses low grade aluminium (99%) and no electropolishing but which still yields a honeycomb structure of similar quality to that seen in literature. The electropolishing has been replaced by a prolonged etching in NaOH. The pore forming process is at present not well understood and a deeper insight is hopefully obtained through this project. Applications of the pores include microelectrodes and diffraction gratings. The amount of possible applications is rapidly increasing and the material seems to be a very promising template.

# Electrochemical characterization of LSM thin films using impedance spectroscopy

#### Malene B Sørensen, Shan Lu and Eivind Skou

#### **Abstract:**

The Nyquist impedance curves of thin films of strontium doped lanthanum manganite (La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3+ $\delta$ </sub>) on alumina substrate are semicircles going through the origin. This system can be modelled with a simple equivalent circuit of a resistor and a capacitor in parallel connection. The resistance and thus conductance through the film is found, as the imaginary part of the impedance approaches zero at low frequencies.

The increase in conductance of the films measured at room temperature is correlated with the increase in film thickness as more coats are applied. The increment in conductance observed after the first coats is low compared to subsequent ones. This is interpreted as a result of substrate roughness.

A measuring cell in which the temperature and atmosphere is controlled is used to investigate the electrochemical behaviour of the LSM films at elevated temperature.

## Preparation and Analysis of New Proton Conducting Membranes for Fuel Cells

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#### **Abstract:**

A range of potential new fuel cell membranes were prepared by inserting zirconium phosphate (abbreviated ZrP below) into crosslinked ETFE-g-PSSA and PVdF-g-PSSA membranes using a slightly modified version of the ion exchange procedure described by Grot and Rajendran<sup>1</sup> and Yang *et al.*<sup>2</sup>

The ETFE based membranes represented various degrees of grafting (DOG) and degrees of sulphonation (DOS) whereas all of the PVdF based membranes had a DOG of app. 30% and a DOS of app. 90%. The product membranes were characterised with P-NMR, thermogravimetric analysis (TG), ion exchange capacity determination (IEC), impedance analysis and powder x-ray diffraction.

TG analyses of both the original ETFE-g-PSSA and PVdF-g-PSSA membrane materials and the composite membranes were performed. The thermogravimetric results revealed a surprisingly low content of ZrP in the ETFE membranes (maximum 7%) considering the high IEC values (IEC = 2). Up to 20% of ZrP was inserted into the PVdF based samples with IEC values in the range 1.8 - 2. In comparison, Nafion has an IEC of 1.0 and takes up 25 weight% of ZrP<sup>2</sup> or 35 weight% with several repetitions of the zirconium treatment procedure<sup>3</sup>.

A number of samples were impedance analysed, this revealed a slight reduction of the conductivity of the composite membranes compared to the starting materials.

The x-ray spectra contained no peaks characteristic of ZrP, thus indicating an even dispersion of the ZrP in the composite membranes.

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<sup>&</sup>lt;sup>1</sup> W.G. Grot and G. Rajendran, Membranes containing inorganic fillers and membrane and electrode assemblies and electrochemical cells employing same, US Patent 5 919 583 (6 July 1999)

<sup>&</sup>lt;sup>2</sup> Chris Yang, S. Srinivasan, A.B. Bocarsly, S. Tulyani and J.B. Benziger, A comparison of physical properties and fuel cell performance of Nafion and zirconium phosphate/Nafion composite membranes, *Journal of Membrane Science* **237** (2004) 145-161.

<sup>&</sup>lt;sup>3</sup> F. Bauer and M. Willert-Porada, Microstructural characterization of Zr-phosphate-Nafion® membranes for direct methanol fuel cell (DMFC) applications, *Journal of Membrane Science* **233** (2004) 141-149

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