



# Two day conference

## **Electrochemical Science and Technology**

4th and 5th October 2007

at

The Danish Technological Institute in Aarhus

and at

The Aarhus University

**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**  
**Kim Daasbjerg, Associate Professor, Aarhus University**  
**Lars Pleth, Head of Department, The Danish Technological Institute**  
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## **ATV•SEMAPP**

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

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## PROGRAMME

### 4<sup>th</sup> October

- 14:30 – 15:00     **Arrival to the Danish Technological Institute**  
Kongsvang Allé 29, 8000 Århus C.
- 15:00             **General Assembly in the Danish Electrochemical Society**
- 16:00             **Welcome**  
*Per Møller, professor at IPL, DTU and chairman for the Danish Electrochemical Society*
- 16:05             **Key note on Electrochemical Issues:**  
**Nano Technology – Research and Development based on knowledge in Physics and Chemistry**  
*Flemming Besenbacher, Director, Prof. Dr. Scient, iNano – Interdisciplinary Nanoscience Center, University of Aarhus*
- 16:45             **Bus-departure to the Steno Museum**
- 17:15             **Visiting the Steno Museum**  
Guided tour in the museum exhibitions. Chose either tour for scientific or for medicine history.  
Special performance in the planetarium cinema
- 19:15             **Conference Dinner**  
At Matematisk Kantine, Aarhus University, Ny Munkegade, Bygning 535, 8000 Århus C. only a few minutes walk from the Steno Museum
- 22:30             **Return to hotels by bus**

### 5<sup>th</sup> October

- 09:00             **Welcome and opening of the conference**  
*Lars Pleth Nielsen, The Danish Technological Institute and Per Møller, Technical University of Denmark*
- 09:15 – 10:35     **ORAL PRESENTATIONS**
- Spinel-type electrode materials for purification of exhaust gasses from diesel fired engines**  
*Franz Bræstrup and Kent Kammar Hansen, Fuel Cells and Solid State Chemistry Department, Risø National Laboratory, Technical University of Denmark*
- Mixed ionic and electronic cathodes for SOFC application**  
*Per Hjalmarsson, Fuel Cells and Solid State Chemistry Department, Risø National Laboratory, Technical University of Denmark*
- New method in Resolving Process. Responses in Impedance Spectra**  
*Søren Højgaard Jensen et al., Fuel Cells and Solid State Chemistry Department, Risø National Laboratory, Technical University of Denmark*
- High performance ceramic composite anodes for solid oxide fuel cells**  
*Peter Blennow et al., Fuel Cells and Solid State Chemistry Department, Risø National Laboratory, Technical University of Denmark*
- 10:35 – 10:55     **Coffee break**

|               |  |
|---------------|--|
| 10:55 – 11:55 | <p><b>Production of Synthesis Gas in Solid Oxide Electrolysis Cells</b><br/> <i>Sune D. Ebbesen et al., Fuel Cells and Solid State Chemistry Department, Risø National Laboratory, Technical University of Denmark</i></p> <p><b>Measurement of Creatinine: From lab-model to Application in the Clinical Laboratory</b><br/> <i>Susanne Thostrup Jensen and Thomas Kjær, Radiometer Medical ApS</i></p> <p><b>Formation with the use of Electrostatic Repulsion of Covalent Attached Thin Layer on Glassy Carbon Surface</b><br/> <i>Kristoffer Malmos et al., Department of Chemistry, University of Aarhus, and Interdisciplinary Nanoscience Center (iNANO), University of Aarhus</i></p>  |
| 12:00 – 13:00 | <b>Lunch</b>   |
| 13:00 – 14:00 | <p>POSTER PRESENTATIONS</p> <p><b>SEMOS: Surface Embedded Metal Oxide Sensors</b><br/> <i>Jesper Lebak Jespersen et al., Danish Technological Institute, Aarhus C. and Department of Manufacturing Engineering and Management, Technical University of Denmark</i></p> <p><b>SOFC cathode/YSZ-non-stationary TPB effects</b><br/> <i>Jimmi Nielsen and Torben Jacobsen, Department of Chemistry, Technical University of Denmark</i></p> <p><b>Metal Sulfide Nanoparticle Based Electrochemical Biosensors</b><br/> <i>Jacob Ask Hansen et al., Chemical Department, University of Aarhus and Arizona State University</i></p> <p><b>Simultaneous Electrografting of Organic Layers with different Functionalities on Carbon Electrodes</b><br/> <i>Vijaykumar S. Ijeri, Karina H. Vase, Steen U. Pedersen and Kim Saashjerg. Department of Chemistry, University of Aarhus, Denmark</i></p> <p><b>Prediction of new conditions for the fabrication of nanoporous alumina in aqueous solutions of dicarboxylic acids</b><br/> <i>S.P.V. Foghmoes, P. Morgen and E. Skou, University of Southern Denmark</i></p> <p><b>Preparation and investigation of cheap polymer electrolyte membranes for fuel cells</b><br/> <i>Mikkel Juul Larsen, University of Southern Denmark</i></p> <p><b>PEM fuel cell catalyst and carbon durability</b><br/> <i>Shuang Ma and Eivind M. Skou, Institute of Chemical Engineering, Biotechnology and Environmental Technology, University of Southern Denmark</i></p> <p><b>Microscopy studies on Pronton exchange membrane fuel cell electrodes with different ionomer contents</b><br/> <i>Shuang Ma et al., Institute of Chemical Engineering, Biotechnology and Environmental Technology, University of Southern Denmark, Institute for Materials and Surface Technology, University of Applied Sciences, Kiel and IRD Fuel Cells A/S, Denmark</i></p> <p><b>Solvent Uptake in Nafion® and EFTE-g-PSSA Membranes from Water-Alcohol Mixtures</b><br/> <i>Yue Ma, Mikkel J. Larsen, Per L. Hansen and Eivind M. Skou, Institute of Chemical Engineering, Biotechnology and Environmental Technology, University of Southern Denmark</i></p> <p><b>Electrochemical Solar Cells/Dye-Sensitized Solar Cells /DSC cells</b><br/> <i>Laursen, T., Lauritzen H., Danish Technological Institute</i></p> |

14:00 ORAL PRESENTATIONS CONTINUED

**Inhibiting effect of silver-palladium surface on silver-resistant bacteria**

*Wen-Chi Chiang et al., Department of Manufacturing Engineering and Management, Technical University of Denmark*

**Utilization of electromigration in civil and environmental engineering**

*Lisbeth M. Ottosen et al., Dept. Of Civil Engineering & Dept. Of Chemical Eng., Technical University of Denmark, and Teknologisk Institut, Taastrup, Denmark*

**Electrochemistry of artificial quinoid base 1 H-benzoimidazole-4,7-dione and its interactions with cytosine**

*Elena E. Ferapontova, Mikkel F. Jacobsen, Kurt V. Gothelf, Centre for DNA Nanotechnology, Department of Chemistry and iNANO, Aarhus University, Denmark*

**Tailoring the dimensions of one dimensional nanoporous alumina**

*S.P.V. Foghmoes, P. Morgen and E. Skou, University of Southern Denmark*

15:20 – 15:40 **Break**

15:40 – 16:00 STUDENT AWARD PRESENTATION

16:00 – 16:15 **Closing**

## Spinel-type electrode materials for purification of exhaust gasses from diesel fired engines.

*Frantz Bræstrup and Kent Kammer Hansen, Fuel Cells and Solid State Chemistry Department. Risø National Laboratory, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, DK.*

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

The purpose of this project is to find new electrode materials, based on the spinel structure ( $\text{AB}_2\text{O}_4$ ), which can be used electrochemically to reduce  $\text{NO}_x$  to  $\text{N}_2$  and/or oxidize unburned fuel and soot particles to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

Different spinel-type oxides ( $\text{MgFe}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$  and  $\text{NiMn}_2\text{O}_4$ ) have been prepared by the glycine-nitrate combustion synthesis (CNS), the citric acid combustion synthesis (CAS) and by solid state reaction. Samples prepared by GNS and CAS were calcined for 6 hours at  $1000^\circ\text{C}$ . Samples prepared by the solid state reaction were heated for 90 hours at  $900^\circ\text{C}$ . The powder was pressed, sintered and cut into cones-shaped electrodes, which were placed with the tip downwards on an Yttrium stabilized Zirconia electrolyte tube. The cone-shaped electrode was used as the working electrode (WE) and a Silver counter electrode (CE) which also acted as the reference electrode (RE) were placed inside the electrolyte tube. The cone setup is a two atmosphere setup 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 10 mV/s and 1 mV/s were performed on the different cathode materials from  $300^\circ\text{C}$  –  $600^\circ\text{C}$ . 10 mol%  $\text{O}_2$  in Ar, 1 mol% NO in Ar and 1 mol%  $\text{NO}_2$  in Ar were used as the reaction gasses with a gas flow rate of 20ml/min. The contact area between the cone and the electrolyte was determined by impedance spectroscopy. Four point DC resistivity measurements were performed on the samples from  $30^\circ\text{C}$  -  $1000^\circ\text{C}$  in air. Results show that  $\text{MgFe}_2\text{O}_4$  have a larger activity towards reduction of the NO compared to reduction of  $\text{O}_2$  at temperatures below  $500^\circ\text{C}$ .  $\text{ZnFe}_2\text{O}_4$  and  $\text{NiMn}_2\text{O}_4$  are on the other hand not active towards the reduction of  $\text{O}_2$  or NO. Instead, these spinels are possible anode materials for electrocatalytic oxidation of unburned fuel or soot particles because of there relatively high current density in the anode region. The electric conductivity of the spinels shows that  $\text{ZnFe}_2\text{O}_4$  and  $\text{NiMn}_2\text{O}_4$  are good semi-conductors already at room temperature, whereas  $\text{MgFe}_2\text{O}_4$  have a low electronic conductivity in the temperature region where the electrochemical measurements were made.

## Mixed ionic and electronic cathodes for SOFC application

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Keywords: cathodes, MIEC, oxygen reduction

The Solid oxide fuel cell (SOFC) is a device that electrochemically convert chemical energy in gases such hydrogen, natural or bio-gas into electrical energy. The principle is based upon an electrolyte that only carries oxide ions while it at the same time is electronically insulating. On both sides of this membrane two electrodes accommodate the reduction of oxygen (the cathode) and the oxidation of fuel (anode). For the reaction to be completed the electrons will be transported through an external circuit over which a voltage is measured. For the full reaction to occur efficiently a number of requirements exist for each the components. This presentation will deal with the cathode, what the requirements are and how they can be fulfilled.

The working conditions of a fuel cell are mainly defined by the electrolyte which in the case of SOFC means temperature of 600-800 °C. The high temperature limits the material choice, in reality, to oxides and to date the most popular materials belong to the perovskite family. This is due to the fact that metal ions can be combined into perovskites in a large variety with an particularly broad spectrum of physical and chemical properties. Furthermore these properties are easily tuned by full or partial substitution of metals.[1]

There exist a number of requirements on cathodes, chemically, physically and technologically. Perhaps the most important ones are the catalytic activity and the ability to conduct both electrons and ions. This last requirement can be fulfilled in two ways.[2] The traditional way is by the use of a composite containing one electronic and one ionic conducting phase, which is the situation in the standard  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3/\text{YSZ}$  (Ytria Stabilized Zirconia) cathode where LSM provides the electronic and YSZ the ionic conductivity. This will restrict the reaction zone to the so called triple phase boundary (TPB) where the two phases meet the gas phase.

Another way is to used a mixed ionic and electronic conducting (MIEC) material which has the ability to conduct both electrons and ions. An example of such a material is  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ , which has shown to possess high electro-catalytic activity towards oxygen reduction. One reason for this is the fact that its high mixed conducting property extends the reaction zone beyond the TPB and thus activates a large fraction of the surface area. [3] This presentation will report on MIECs as potential SOFC-cathode materials, advantages and disadvantages as well as an attempt to describe the electrochemical reactions occurring in such an electrode.

1. R. M. Ormerod, Chem. Soc. Rev., 32 (2003) 17.
2. S. B. Adler, Chem. Rev., 104 (2004) 4791.
3. S. B. Adler, J. A. Lane, B. C. H. Steele, J. Electrochem. Soc., 143 (1996) 3554.



## **New Method in Resolving Process Responses in Impedance Spectra**

*Søren Højgaard Jensen\*, Anne Hauch\*+, Sune Ebbesen\*, Mogens Mogensen\*, Nicolaos Bonanos\*, Torben Jacobsen+*

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Usually many reactions contribute to the overall impedance of an electrochemical cell and these may be difficult to separate in the impedance spectrum. Here, we present a method that may be helpful in identification of the individual contributions. Using differences in impedance spectra due to changes of operating parameters of a Solid Oxide Fuel Cell (SOFC) we resolve impedance arcs that otherwise would be hard or even impossible to distinguish.

## High performance ceramic composite anodes for solid oxide fuel cells

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### Abstract

Solid oxide fuel cells (SOFC) are high temperature electrochemical devices, which convert the energy of a chemical reaction directly into electrical energy. They are normally operated between 600-1000 °C. Most developers of SOFCs use anodes that are a ceramic-metallic composite (cermet) of yttria-doped zirconia (YSZ), a polycrystalline ceramic that conducts oxygen ions, and nickel. The nickel-based fuel electrodes are capable of outstanding performance in hydrogen or syngas (a mixture of H<sub>2</sub> and CO usually formed by hydrocarbon reforming). However, at elevated temperatures nickel tends to agglomerate and sinter, resulting in a degradation of the anode performance with time. The Ni-YSZ anode degrades during redox cycles [1] and impurities in the fuel stream, particularly sulphur [2], inhibit anode functionality. Therefore, it would be advantageous to develop alternative anode materials or compositions to overcome the problems associated with Ni-YSZ. In this paper, a SrTiO<sub>3</sub>-based oxide combined with Gd-doped CeO<sub>2</sub> (CGO) has been investigated as a potential fuel electrode for solid oxide fuel cells (SOFC) with Electrochemical Impedance Spectroscopy (EIS). Measurements on electrodes, in a symmetrical cell configuration, at open circuit voltage (OCV) showed that the electrochemical activity was maintained or even improved compared to the current state of the art Ni/YSZ fuel electrode in SOFC applications. Due to an apparently low activation energy of the electrode (around 0.5 – 0.7 eV), high performance was achieved at a wide range of operating temperatures, with an electrode polarization resistance of 0.12 Ωcm<sup>2</sup> and 0.44 Ωcm<sup>2</sup> in wet H<sub>2</sub> at 850 °C and 650 °C, respectively. The corresponding polarization resistances for Ni/YSZ electrodes, measured on similar sample geometry, were 0.125 Ωcm<sup>2</sup> and 0.82 Ωcm<sup>2</sup> at 850 °C and 650 °C, respectively. In addition, the ceramic composite electrode was shown to be redox stable. The electrode was actually activated with redox cycles at 650 °C. As a result of the high redox stability, the novel ceramic composite electrode is more robust to changes in the surrounding atmosphere. Based on measurements at different temperatures and various fuel gas compositions the EIS data have been fitted to the equivalent circuit LRS(RQ)1(RQ)2(RQ)3, following the circuit description codes described elsewhere [3]. Possible explanations to the physical/chemical nature of the different electrode processes are suggested and discussed.

1. Klemensø, T., Chung, C., Larsen, P. H., Mogensen, M., In: SOFC-IX, S. C. Singhal, J. Mizusaki (eds). The Electrochemical Society Proceedings, Pennington, NJ, The Electrochemical Society, (2005) 1226.
2. Y. Matsuzaki, I. Yasuda, Solid State Ionics. 132 (2000) 261.
3. B. A. Boukamp, Solid State Ionics. 169 (2004) 65.

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## Production of Synthesis Gas in Solid Oxide Electrolysis Cells

*Sune D. Ebbesen, Søren H. Jensen, Anne Hauch and Mogens Mogensen*

*Fuel Cells and Solid State Chemistry Department, Risø National Laboratory, DTU, Denmark*

During the last decade intensive research in Solid Oxide Fuel Cell (SOFC) technology has taken place world wide. These cells may also be used for electrolysis of water ( $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$ ) or  $\text{CO}_2$  ( $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$ ) [1, 2] and are then called solid oxide electrolysis cells (SOEC). SOEC's has become increasingly investigated in recent years as a green technology. The possibility for combination of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  electrolysis makes SOEC a potential low-cost option for converting renewable electricity into synthesis gas ( $\text{CO} + \text{H}_2$ ), which in turn can be used for the manufacturing of synthetic fuels such as methane, gasoline or di-methyl ether (DME).

Therefore, we have characterized SOEC performance (current-density-voltage curves and electrochemical impedance spectroscopy) and durability over many hundred hours in either  $\text{H}_2\text{O}/\text{H}_2$  or  $\text{CO}_2/\text{CO}$  mixtures.

SOEC's shows promising initial performance for both  $\text{H}_2\text{O}$  and  $\text{CO}_2$  electrolysis. Regarding durability, the cell degradation rate for  $\text{CO}_2$  electrolysis was found to be around 5 times higher compared to the degradation rate of  $\text{H}_2\text{O}$  electrolysis in a SOEC when operated at a current density of  $-0.25 \text{ A.cm}^{-2}$ , a  $\text{CO}_2/\text{CO}$  or  $\text{H}_2\text{O}/\text{H}_2$  ratio of  $2/3$  and  $850^\circ\text{C}$ . Possible reasons for the degradation, which takes place on the Ni-YSZ- $\text{CO}_2$  or Ni-YSZ- $\text{H}_2$  electrode, are being investigated by varying the electrolysis conditions (current, temperature and  $\text{H}_2\text{O}/\text{H}_2$  or  $\text{CO}_2/\text{CO}$  ratio), by thermo gravimetric analysis as well as electron microscopy on both durability tested and reference cells.

If this technology should play an important role in the future it is necessary to lower the degradation rate. Degradation mechanisms during both  $\text{H}_2\text{O}$  and  $\text{CO}_2$  electrolysis will be discussed.

Furthermore, perspectives for the full synthesis gas production process using renewable electricity will be discussed based on SOEC performance and an economic assessment.

### References

[1] A.O. Isenberg, Solid State Ionics 3-4 (1981) 431-437.

[2] W.Doenitz, R. Schmidberger, E. Steinheil, R. Streicher, Int. J. Hydrogen Energy 5 (1980) 55-63.

## Measurement of Creatinine: From lab-model to Application in the Clinical Laboratory

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Based on literature survey an amperometric biosensor based on H<sub>2</sub>O<sub>2</sub> oxidation was chosen as the sensing principle for the whole blood determination of creatinine. The sensor utilises a 3-enzyme cascade reaction transforming creatinine to creatin (Creatininase (CA)), then transforming the creatin to sarcosin (Creatinase (CI)) and finally oxidation of sarcosine by sarcosine oxidase with the simultaneous release of the H<sub>2</sub>O<sub>2</sub>. Ultimately the H<sub>2</sub>O<sub>2</sub> is detected by oxidation at an Platinum electrode.

In order to obtain reasonable measuring range and low degree of interference from oxidizable components (e.g acetaminophen) the sensor consists of 4 layers: An outer, diffusion limiting membrane governing the sensitivity, an enzyme layer in the middle, and two inner layers reducing interferences.

A major challenge in the development of the sensor was to obtain a stable, not too dense enzyme layer with a low enough thickness to allow a response within 15-20s, and still containing enough enzyme to allow a use life at about 2-4 weeks.

Another problem is learned from the fact that the total biosensor has to be based on the difference between the amount of creatinine+creatin and the amount creatin as determined from a 2-enzyme sensor with CI and SA only. Making the 2 sensors with similar measuring characteristics is not trivial.

As the sensor has to measure with a sensitivity of 5-15 nA/mM with a measuring range of creatinine of 10-1800 µM, also background correction has to be implemented in a more sophisticated way than used e.g. in our glucose sensors.

Also choice of calibrating solutions, packaging and storage conditions of the sensors, preparing sensor production, analyser software and hardware present areas to be fixed.

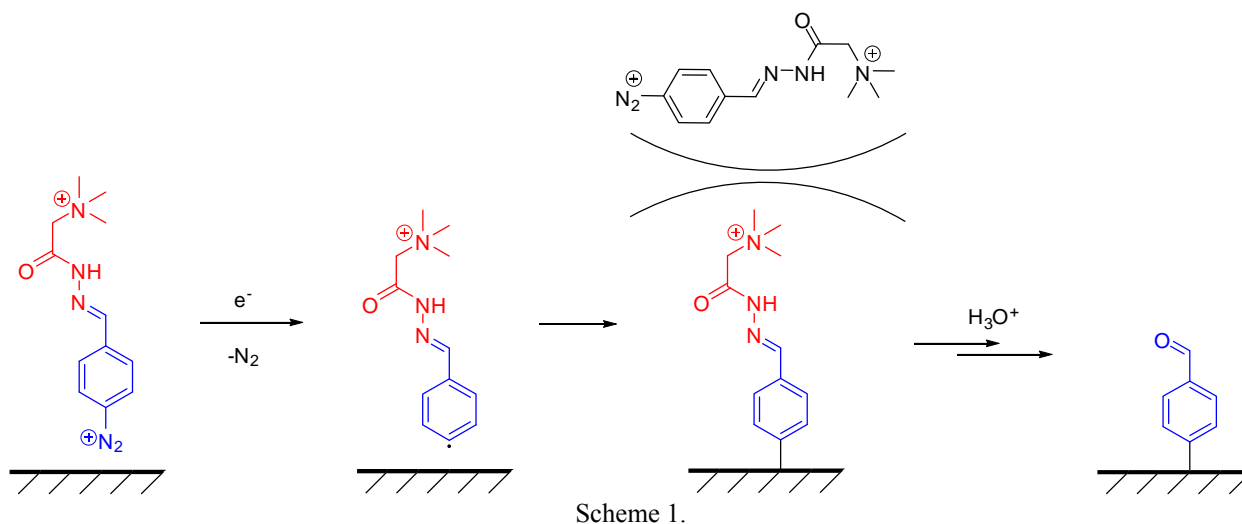
In the end a very well behaving sensor was brought to the market in 2007.

## Formation with the use of Electrostatic Repulsion of Covalent Attached Thin Layer on Glassy Carbon Surface

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One of the most widely used surface modification techniques is electrografting of aryl diazonium salts on both metals and carbon-based materials. Electroreduction of the diazonium cations results in the formation of aryl radicals and the release of dinitrogen. The aryl radical is formed in close proximity to the electrode surface, to which it creates a strong covalent bond. The highly reactive aryl radical is also capable of attacking already grafted aryl groups, and in this way multilayers are formed<sup>1</sup>.



The formation of multilayer is not desirable in some applications, such as sensors and molecular devices<sup>2</sup>. This talk presents one solution to avoid multilayer formation. Electrografting of a dicationic molecule consisting of two parts: 1) The aryl diazonium cation (Blue part, Scheme 1) and 2) a removable positively charged end group (Red part, Scheme 1). The first layer grafted on the surface has an ability to repel the other incoming diazonium cations due to the electrostatic interactions. In this way the *tert*-amine group is hindering the dication of the hydrazone diazonium salt to get sufficiently close to the surface to be reduced and thereby prevents the formation of multilayers.

The positively charged part of the resulting monolayer can then be removed by hydrolysis and the corresponding aldehyde is formed. This can again be transformed into other functional groups, and/or reacted with amines or hydrazine to incorporate other functionalities

<sup>1</sup> Karikuki, J. K.; McDermott, M. T. *Langmuir* **1999**, 15, 6534

<sup>2</sup> Nielsen, L. T.; Vase, K. H.; Dong, M.; Besenbacher, F.; Pedersen, S. U.; Daasbjerg, K. *J. Am. Chem. Soc.* **2007**, 129, 1888

## **SEMOS: Surface Embedded Metal Oxide Sensors**

*Jesper Lebak Jespersen<sup>1</sup>, Syed Talat Ali<sup>2</sup>, Lars Pleth Nielsen<sup>1</sup>, Søren Knudsen Kær<sup>3</sup>, Per Møller<sup>2</sup>*

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**Keywords:** Fuel cells, Metal Oxide Sensors, Embedded Sensors

### **Abstract:**

SEMOS is a joint project between Aalborg University, Danish Technological Institute and Danish Technical University in which micro temperature sensors and metal oxide-based gas sensors are developed and tested in a simulated fuel cell environment as well as in actual working fuel cells. Initially, sensors for measuring the temperatures in an operating HT-PEM (High Temperature-Proton Exchange Membrane) fuel cell are developed for detecting in-plane temperature variations. 5 different tracks for embedded thermal sensors are investigated. The fuel cell MEA (Membrane Electrode Assembly) is quite complex and sensors are not easily implemented in the construction. Hence sensor interface and sensor position must therefore be chosen carefully in order to make the sensors as non-intrusive as possible. Metal Oxide Sensors (MOX) for measuring H<sub>2</sub>, O<sub>2</sub> and CO concentration in a fuel cell environment is the second and main part of the project. The main challenges in developing metal oxide sensors are proper choice of the material, sensor location and fabrication technique due to lifetime and cross sensitivity issues in harsh environment where the problems like de-bonding or some kind of diffusion in the form of electrochemical migration or electro-migration due to change in the chemical composition of the sensor material may cause performance degradation of the sensor. The objective of the sensors developed in SEMOS are to aid to the fundamental understanding of the transport and degradation mechanisms occurring in PEM fuel cells. Moreover, the data from the embedded sensors can provide important validation data for numerical fuel cell models and eventually be applied to optimize the overall efficiency.

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## SOFC cathode/YSZ – non-stationary TPB effects

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### Abstract

The origin for the dynamic nature of  $(\text{La}_{0.85}\text{Sr}_{0.15})_{0.95}\text{MnO}_{3\pm\delta}$  (LSM) cathodes with activation and deactivation processes was studied by comparison between measurements on and electrode/YSZ interfacial changes of Au, LSM point electrodes and thin  $\frac{1}{2}$ -1  $\mu\text{m}$  thick LSM film electrodes on YSZ. The techniques used in the study were linear potential sweeps and long term (250-300 hours) step polarization. The electrodes were after experiments removed by dissolution and the YSZ contact areas were studied by SEM and EDS. The results show current induced YSZ morphological changes, which lead to an increase in the Three-Phase-Boundary (TPB) length and consequently an activation of the electrode. In the case of LSM electrodes a current enhanced formation of  $\text{La}_2\text{Zr}_2\text{O}_7$  was observed that can result in deactivating phenomena of LSM electrodes. The interplay between these processes can to a large extent explain the dynamic nature of LSM electrodes.

Keywords: SOFC, LSM, Gold, Non-stationary effects, Microstructure

# Metal Sulfide Nanoparticle Based Electrochemical Biosensors

Jacob A. Hansen,<sup>†</sup> Vadim V. Sumbayev,<sup>†</sup> Joseph Wang,<sup>‡</sup> Kurt V. Gothelf<sup>†</sup>

Metal sulfide nanoparticles have been applied for the design of three sensor setups for the amplification and electrochemical detection of biomolecular interactions. Two sensors were developed using a novel displacement assay, one for the detection of DNA<sup>1</sup> and one for the simultaneous detection of multiple proteins<sup>2</sup> (see Fig 1).

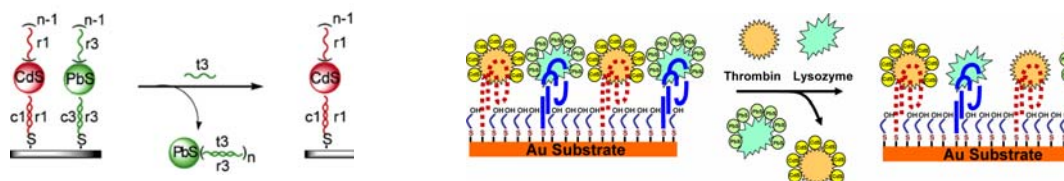


Fig 1: Displacement assays for detection of DNA or proteins. Displacement of surface bound nanoparticle conjugates via either a target, either (A) DNA or (B) proteins enables the detection of these via monitoring remaining nanoparticles at the surface

The nanoparticle conjugated reporters (DNA (A) or proteins (B)) were attached to a gold surfaces using hybridization to capture sequences (for DNA detection) or binding aptamers (for protein detection) immobilized on the gold surface via thiol-linkers. Addition of the target displaces the reporter nanoparticle conjugates from the gold surface, and thus enabling the detection of the target via stripping voltammetry by monitoring the amount of reporter nanoparticle conjugates remaining at the surface. Using this methodology we achieved sensitivities for DNA of 10amol, and for proteins 50amol, while still maintaining good selectivity.

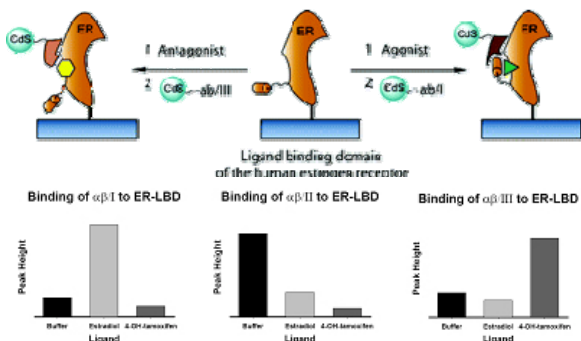


Fig 2: Three different conformations of the ligand binding domain of the human estrogen receptor (ER-LBD) are observed for the native state when binding an agonist and when binding an antagonist. By conjugating ER-LBD conformation specific peptides to CdS nanoparticles, the three different states can be identified by anodic stripping voltammetry. This electrochemical sensor can detect and distinguish the binding of different ligands to the human estrogen receptor.

As an extension of the above mentioned sensors we have developed a sensor based on the estrogen receptor (ER) as the biorecognition element for the detection of estrogenic compounds (agonists and antagonists).<sup>3</sup> Binding ligands to the ER changes its conformation. This change is reliant on the type of ligand bound and gives 3 different conformations of the ER, the native state of the ER, binding of an agonist, and binding of an antagonist. Conjugating CdS nanoparticles to small peptides recognizing the different conformations of the ER enables us to design a sensor capable of detecting and differentiating ligands binding to the ER (see Fig 2).

Keywords: Electrochemical Biosensors, Aptamers, DNA, proteins, Estrogen Receptor

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## Simultaneous electrografting of organic layers with different functionalities on carbon electrodes

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Electrochemical reduction of a wide variety of aromatic diazonium and iodonium salts on carbon electrodes leads to the covalent attachment of the corresponding aromatic moieties [1, 2].

Modification of carbon surfaces is an important objective in electrochemistry and material science from the industrial point of view to improve the mechanical properties of carbon composite materials, and active attention is currently paid to covalently modified electrodes for catalytic or analytical purposes in view of biotechnological applications [3].

Herein we report the possibility of forming covalently attached mixed layers with carboxylic and amino functionalities on carbon surfaces via electro-reduction of corresponding diazonium and iodonium salts. Mixed layers with different ratios of carboxylic and amino groups were obtained by electrolytic reduction in corresponding mixed solutions. The modified carbon electrodes were characterized by Cyclic Voltammetry and Electrochemical Impedance Spectroscopy in acetonitrile and aqueous media at different pH values. In acetonitrile, the impedance values for the grafted electrodes are all higher than those for the bare ones at all ratios and frequencies but they all present a minimum when the ratio of salts in grafting solutions is 1:1. This implies that mixed layers containing both amino and carboxy groups are formed on the electrode surfaces grafted from mixed solutions. The presence of both acidic and basic groups immobilized on a surface in close proximity allows for charge transfer to occur and make the layer less impervious. More details will be discussed in the poster.

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## Prediction of new conditions for the fabrication of nanoporous alumina in aqueous solutions of dicarboxylic acids

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**Keywords:** Anodization, nanoporous alumina, porous thin films and nanostructured surfaces.

**Abstract:** Nanoporous alumina has so far been created in two inorganic acids; sulphuric (i) and phosphoric acid (ii) as well as in a number of organic dicarboxylic acids; oxalic (iii), citric (iv), malonic and tartaric acid (v) through the tedious process of trial and error.

Here we present our recently established mathematical correlations between various parameters for the previously used acids. The correlation possesses predictive power for the essential anodization parameters of concentration and voltage. We have utilised the correlations to include malic as well as maleic acid in the range of usable acids. The availability of these two acids has extended the range of pore sizes which can be produced by this method. The correlation has also been used to supplement the conditions under which a perfect structural arrangement can be obtained in tartaric acid.

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# Preparation and investigation of cheap polymer electrolyte membranes for fuel cells

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**Keywords:** PEM, polymer electrolyte membrane, grafting, ETFE, polystyrene, crosslinking, DVB, divinylbenzene, methyl substitution, tert-butyl substitution, fuel cell, chemical stability, proton conductivity

The electrolyte of choice for low temperature polymer electrolyte fuel cells (PEFCs) has traditionally been DuPont<sup>TM</sup> Nafion<sup>®</sup> membranes or similar poly(perfluorosulfonic acid)s. The chemical structure and morphology in the hydrated state of Nafion<sup>®</sup> is shown in figure 1 from which it is seen that the material consists of hydrophilic and hydrophobic domains. This structure gives hydrated Nafion<sup>®</sup> very high proton conductivity as well as great stability.<sup>(i)</sup>

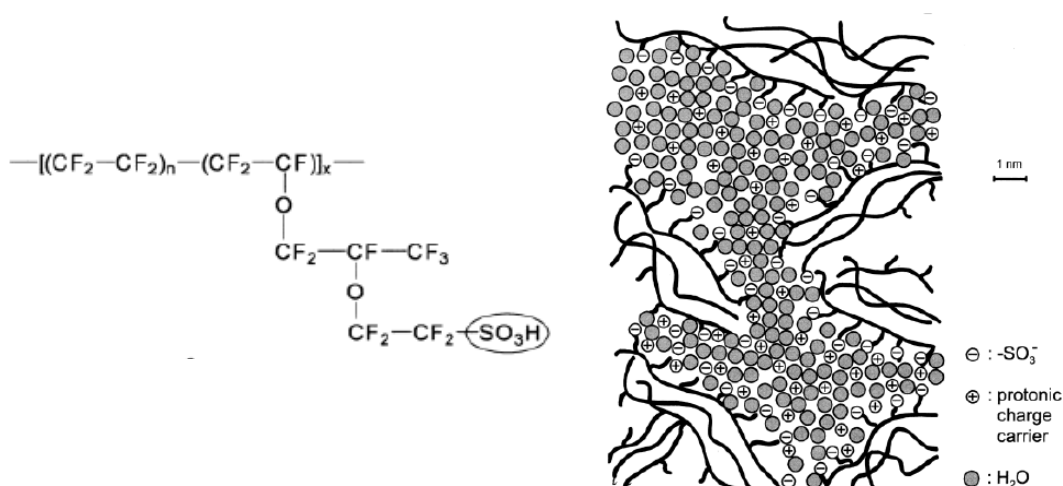


Figure 1. The chemical structure of Nafion<sup>®</sup> and its morphology in the hydrated state.

However, the poly(perfluorosulfonic acid) membranes are very expensive materials, and their high water uptake, significant methanol crossover, and relatively poor thermal stability constitute serious drawbacks with respect to their fuel cell use.<sup>(i), (ii), (iii)</sup> These aspects propel the search for cheaper and better alternatives.

In this study membrane systems consisting of a hydrophobic poly(ethylene-alt-tetrafluoroethylene) (ETFE) backbone grafted by hydrophilic poly(styrene sulfonic acid) (PSSA) have been synthesized in a three-step procedure comprising electron beam irradiation, grafting polymerization reaction, and sulfonation. The chemical structure of the resulting ETFE-g-PSSA is shown in figure 2, and it is believed that the morphology upon hydration resembles that of the poly(perfluorosulfonic acid)s. The stability of the material has been improved by crosslinking by divinylbenzene (DVB) and by inferring methyl- and tert-butyl substituents on the styrene aromatic ring.

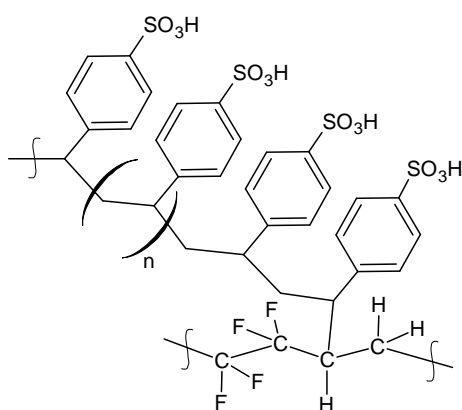


Figure 2. The chemical structure of ETFE grafted by sulfonated polystyrene (ETFE-g-PSSA).

It has been found that crosslinking by divinylbenzene clearly improves the chemical stability of both sulfonated styrene- and methylstyrene/t-butylstyrene-grafted ETFE membranes. However, the crosslinking reduces the proton conductivity due to decreased water uptake, thus downgrading the membranes' electrolytic properties. Grafting with a fraction of DVB in the order of 1-2 vol-% of the total monomers seems to be advantageous for both of the two grafting systems as a compromise between high chemical stability and good proton conductivity of the final membrane. The use of methylstyrene and t-butylstyrene as grafting monomers instead of styrene gives the resulting membranes a significantly increased chemical stability, while a reasonable proton conductivity can still be obtained. Both membrane systems show a smaller methanol uptake than water uptake.

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## **PEM fuel cell catalyst and carbon durability**

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Stability of platinum plate, platinum fine particle and platinum support carbon was studied. Platinum was treated with cyclic voltammetry in sulfuric acid solution ambient conditions; the platinum surface area and particle size were evaluated with hydrogen adsorption/desorption and X-ray powder diffraction. Platinum nano-particles' surface area was found follow a first order decay. Carbon durability was found depend on supporting catalyst properties, carbon surface area and relative humidity.

## **Microscopy studies on Pronton exchange membrane fuel cell electrodes with different ionomer contents**

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Proton Exchange Membrane (PEM) fuel cell electrodes with different ionomer contents were studied with various microscopic techniques. The morphology and surface potential were examined by Atomic Force Microscopy (AFM) and Kelvin Probe Microscopy (KPM) respectively. The particulate nature of the electrode was well displayed in the topography and phase images. The particle and pore height (Z) distribution showed the most frequent values at 30-40 nm and 20-30 nm respectively. The particle size corresponds to the size of the carbon support for the platinum catalyst. Catalyst agglomeration was observed at high ionomer content electrodes. The surface potential images showed distinct difference to the topography. The overall grain size was seen to increase, the pore volume to decrease, the surface roughness to decrease, the surface potential variation to increase and CO<sub>2</sub> permeation to increase with the increase of ionomer content in the catalyst layer. Transmission electron microscopy (TEM) was carried out on selective electrode to provide additional information. Cyclic voltammetry (CV) showed that the electrode containing 30 wt.% ionomer have maximum catalyst utilization.

# **Solvent Uptake in Nafion® and ETFE-g-PSSA Membranes from Water-Alcohol Mixtures**

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## **Abstract**

This project studies the sorption properties of DuPont™ Nafion® and synthesized poly (ethylene-alt-tetrafluoroethylene)-graft-poly(styrene sulfonic acid) (ETFE-g-PSSA) proton exchange membranes swollen in binary mixtures of water and selected alkane-mono-ols at room temperature, with emphasis on 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 <sup>1</sup>H 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.



## **Electrochemical Solar Cells / Dye-Sensitized Solar Cells / DSC cells**

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The attention paid to electrochemical solar cells / dye-sensitized solar cells / DSC cells in international R&D projects has over the last 15 years steadily increased from a limited number of widespread investigations to a worldwide massive interest from all relevant major research laboratories. The build-up of knowledge and research competence is now entering a new phase, where there is a need for a strong technological focus along with the ongoing research activities. According to our considerations, the three most critical technological aspects are at present: the encapsulation, the stability and the life expectancy for cells and panels  
the scaling up of the cell's active area, in order to reach a usable current production at cell level  
robust production technology suited for high-volume production of modules  
Consequently, these three aspects are high-lighted in the Institute's R&D work. We are working on the encapsulation and stability issues in collaboration with the University of Copenhagen and on the scale-up of active cell area and production of modules in cooperation with Mekoprint A/S and Aalborg University.

For encapsulating DSC cells and modules, a sandwich consisting of an adhesive film and the two substrates, upon which the cell is built, is assembled and subsequently laminated under careful pressure and temperature control. The adhesive film is chosen after an evaluation of the chemical stability of a range of sealants in contact with the cell's aggressive iodide electrolyte. The lamination is challenging, as the chosen film requires a sealing temperature of about 300°C.

The developed encapsulations are tested in an accelerated leakage test, in which a pressure drop is forced over the sealing's cross section, and an eventual outflow from the cell is fed directly in a mass spectrometer for analysis. The stability of the sealed cells is evaluated in field tests and accelerated tests, covering both light soaking and weather chamber. The electrical performance of the individual cells in max power point is logged every 5 minutes during the entire exposure. Subsequently, the degraded cells are subjected to careful chemical and electrical characterization. The electrical characterization is performed both at device level and locally by scanning over the cell's active area.

For developing adequate production technology for a future commercial production of DSC panels, the present laboratory production of DSC cells is transferred to a fully-automated, screen-printing line at Mekoprint A/S. Screen printing is chosen as our preferred production platform as it is suited for high-volume production of layered structures at a reasonable cost. Furthermore, printing is chosen because it allows adjustments of the prints from batch to batch, and thereby are tailor-made DSC panels viable.

# Inhibiting effect of silver-palladium surface on silver-resistant bacteria

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## KEYWORDS

bacterial inhibiting surface; silver; palladium; electric field; galvanic reaction

## ABSTRACT

In this study, silver-palladium (Ag-Pd) surfaces were designed and investigated focusing on electrochemical principles to form inhibiting effects on planktonic or/ and biofilm bacteria in water systems. This design is based on Ag coatings applied to stainless steels (or ceramic and polymers) that can be micro/ nano-structured by a treatment with Pd. In this way, a Ag-Pd surface can form an electrical field on the surface by itself. Due to the potential difference between Ag and Pd while contacting with an electrolyte, the surface can form numerous discrete anodic and cathodic areas. It is desired that when living bacteria pass or approach the designed surface, they will be inhibited in growth by electrical field and electrochemical interaction rather than Ag toxicity (Fig. 1).

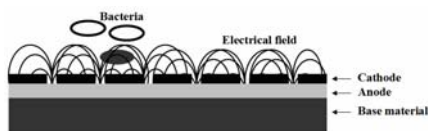
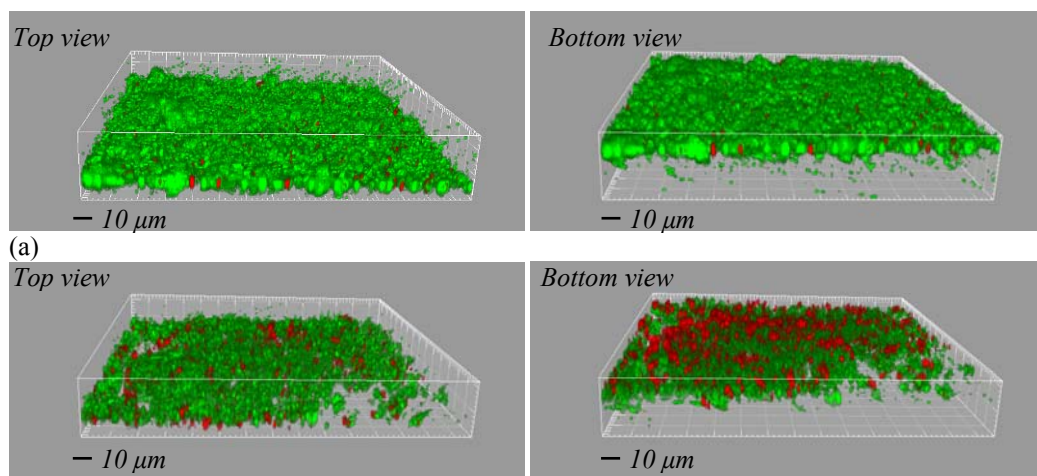


Fig. 1. An inhibiting surface and its electrical field.

It could be argued that the inhibiting effect on this Ag-Pd surface is only caused by higher local Ag ion concentration due to the galvanic reaction. Therefore, in order to clarify this issue, a Ag-resistant *Escherichia coli* (*E. coli*) strain was used for the evaluation of the inhibiting effect and inhibiting mechanism. From the top view images of confocal laser scanning microscope (CLSM) in Fig. 2, microcolonies formed on both tested surfaces. However, from the bottom view images, it shows Ag-Pd had an inhibiting effect when Ag-resistant *E. coli* attached to the surface (as compared with the Ag surface). The CLSM image of Ag-Pd also shows that dead *E. coli* can act as a protective layer for live *E. coli* against the inhibiting effect from the surface. Therefore, live *E. coli* can survive just above these dead *E. coli* and further use them as a nutrient source for microcolonies growth. Fig. 2 can be one of the clear explanations of that the inhibiting effect can be formed by electrochemical interaction or/ and electric field from the Ag-Pd surface. However, in some specific media, such as ammonium containing, undesired Ag ions release may occur. Therefore, the media, organic load, and flow pattern are important parameters determining the effectiveness of Ag-Pd surfaces.



(b)  
Fig. 2. CLSM micrographs for Ag-resistant *E. coli* on the surfaces of (a) Ag, (b) Ag-Pd. after 3 days incubation (live bacteria are green fluorescence; dead bacteria are red fluorescence).

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## Utilization of electromigration in civil and environmental engineering

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Electromigration is utilized for transport of matter in porous materials in different engineering disciplines. The present work is focused on processes related to porous materials within the fields of civil and environmental engineering.

In civil engineering electromigration is utilized for repair and maintenance purposes and most studied worldwide are the processes desalination and re-alkalisation of concrete. At BYG.DTU, however, the focus is laid on desalination of masonry especially from heritage buildings. Salt decay of masonry is a generally recognized problem in both ancient and recent buildings and no efficient method for the removal of the salts is implemented. In laboratory scale experiments it has been shown possible to reduce salt concentrations from initially damaging concentrations to harmless concentrations by application of an electric field. Also preliminary pilot tests have shown encouraging results.

On the contrary to the desalination of masonry where ions are removed, electrochemical re-impregnation of wood is based on supply of ions. In the applied electric field it is possible to supply impregnation chemicals in depth when the wood is still placed in the construction and in this way it is possible to avoid replacement of decayed wood if the treatment is done before the strength of the wood is damaged (diffusion of impregnation chemicals is often too slow). Both the rate of copper and boron supply has been significantly increased in an applied electric field compared to diffusion.

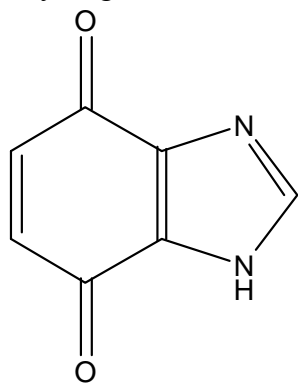
In environmental engineering electromigration is mainly used for transporting pollutants out from contaminated matrices, but also the transport of materials into the matrices can be of value in some situations. Electrokinetic soil remediation is certainly the most investigated method, but electromigration has also been tested in other matrices as sewage sludge, impregnated wood waste, harbour sediment and fly ashes at DTU. At first the solid matrix was water saturated when the electric field was applied, but later it was shown that the process was significantly faster and more stable when the waste product or the soil (fine fraction) was treated in suspension. In the case of heavy metal removal from porous materials the limiting step is most often desorption of the target elements. Mobilization is obtained by acidification, and the combination of acidification and an applied electric field is very efficient (by far more efficient than acidification alone) and low heavy metal concentrations can most often be obtained in the treated medium.

# Electrochemistry of artificial quinoid base 1H-benzoimidazole-4,7-dione and its interactions with cytosine

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Base-modified oligonucleotides are becoming increasingly popular as probes for DNA-DNA, DNA-RNA and DNA-protein recognition (Kool E.T. Acc.Chem.Res. 35(2002)936). As an alternative to fluorescent nucleobases (e.g. 2-aminopurine), sensitive to localised structural alterations, we focused our research on electrochemically active artificial nucleobases, which are potentially useful as constituents of nucleic acid sequences, capable of changing their electrochemical activity due to the biorecognition event. In this work we studied electrochemical behaviour of a synthetic guanine-mimicking redox-active base, composed of two conjugated units – an imidazol ring and a quinone redox-active part (1H-benzoimidazole-4,7-dione Q1, Figure). Q1 is unique in its combination of redox activity, and guanine-like structure (~isostere) that should allow for hydrogen bond formation with cytosine (C). The kinetics of Q1 reduction and oxidation both through quinone and imidazol moieties was studied on gold electrodes in aqueous bufer solutions, pH 2 - pH 12. Reduction and consequent oxidation of the quinone moiety proceeded through  $2e^-/2H^+$  mechanism, characteristic of other known quinones; the degree of reversibility decreased in highly acidic media. At high pHs the oxidation of imidazol moiety was followed at potentials close to those of guanine oxidation. We studied the effect of the possible hydrogen bond formation, between Q1 and C, on redox atcivity of Q1. When Q1 and C were co-adsorbed on gold from aqueous solutions, there was some indication of chemical reaction occurring between the two entities. However, when the bases were co-adsorbed from butanol and octanol solutions, a distinct shift of the Q1 redox potential in less positive direction was observed, increasing from 28 mV in aqueous media, pH 5, to 67 mV in octanol. We are currently considering a model to explain the observed potential shifts that entails hydrogen bonding between Q1 and C.



Keywords: Artificial nucleobases, electrochemistry of quinones, electrochemical detection of interactions between nucleobases, hydrogen bonding

## Tailoring the dimensions of one dimensional nanoporous alumina

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**Keywords:** Anodization, nanoporous alumina, porous thin films and nanostructured surfaces.

**Abstract:** Templates for the fabrication of nano sized structures has been investigated heavily in recent years as the properties of a material can change dramatically upon approaching the nano scale. Among these are anodized aluminium which has been known for at least 50 years (1)

A highly ordered version of anodized aluminium, which posses a hexagonal symmetry and which is of nanometer dimensions, was produced by the anodization of pure aluminium in oxalic acid as early as in 1995 by Masuda et al (2). This ordered version is known as nanoporous alumina and it has due to its high degree of symmetry, chemical tolerance and thermal robustness now emerged as a very promising candidate for the synthesis of one dimensional structures such as nano wires. There is a strong correlation between the used combinations of anodization voltage and acid and the resulting pore size of the template (3). With the present range of acids used a limited number of pore sizes are available. Additional acids are therefore essential for the tailoring of the properties of any object created by the use of this kind of template. The fabrication has, however, only been developed by the method of trial and error (4,5,6 and 7) and ways to predict additional acids and their processing parameters are thus essential.

We will here present the properties and prospects for nanoporous alumina as a template as well as a method to predict optimum processing conditions for dicarboxylic acids.

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| Martijn van Dijk, Product Manager,                                  |             |
| Steen Grønbjerg,  | 21 55 53 54 |
| <b>Radiometer Medical ApS</b>                                       | 38 27 38 27 |
| Poul Ravn Sørensen, Project Leader, Analytical Chemist              | 38 27 38 27 |
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