

# Two day conference

## Electrochemical Science and Technology

1<sup>st</sup> and 2<sup>nd</sup> October 2009

at

Roskilde University



**Organized by:**

**Danish Electrochemical Society**

In partnership with **ATV•SEMAPP**

**Organizing committee:**

Torben Lund, Associate Professor, Roskilde University

Per Møller, Professor, Technical University of Denmark

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

## Sponsors:



## Exhibition:



## Dansk Elektrokemisk Forening

v/Daniel Minzari

Institut for Mekanisk Teknologi, Danmarks Tekniske Universitet, Bygning 204, 2800 Kgs. Lyngby

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## ATV•SEMAPP

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

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ATV-SEMAPP

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PROGRAMME:

**1<sup>st</sup> October**

- 14:15 – 14:30    **Arrival to Roskilde University**  
Universitetsvej 1, Building 25, 4000 Roskilde  
- If you want to join the conference part solely, you are welcome to arrive just before the welcome at 15:45.
- 14:30 – 15:30    **General Assembly in the Danish Electrochemical Society**  
For members and guests.
- 15:45 – 15:50    **Welcome**  
*Torben Lund, Associate professor at Roskilde University and chairman for the Danish Electrochemical Society*
- 15:50 – 17:15    **Honorary Symposium for professor Henning Lund from Århus University**  
  
**Organic Electrochemistry in Denmark During the Latest 100 Years**  
*Henning Lund, Århus University*  
  
**Electrografting of Surfaces - A Radical Solution**  
Inspired by the Work of Henning Lund  
*Kim Daasbjerg, Århus University*  
  
**The One-Electron Oxidation of 1,4-Phenylenediamines and Low-Generation PAMAM Dendrimers with a 1,4-Phenylenediamine Core**  
*Ole Hammerich, University of Copenhagen*
- 17:15 – 19:00    **Check-in at hotels**
- 19:00            **Conference Dinner**  
at “Guldalder Salen”  
Hotel Prindsen  
Algade 13  
DK-4000 ROSKILDE

**2<sup>nd</sup> October**

- 09:00 – 09:05    **Opening of the conference**
- 09:05 – 10:15    **Live demonstration of selected SPM instruments**  
*Curt Sander, DME – Danish Micro Engineering*

10:15 – 10:45     **Coffee break**

### **ORAL PRESENTATIONS**

10:45 – 12:00     **Analytical and Environmental Electrochemistry**

**Effect of Process Related Contamination on Electrochemical Migration in Electronic Devices**

*Marianna Johnsen, DTU Mekanik*

**Electrodialytic upgrading of municipal solid waste incineration fly ash in pilot scale**

*Pernille Jensen, DTU Byg*

**Electropolymerisation of derivated thiophenes**

*John Mortensen, RUC*

12:00 – 13:00     **Lunch**

13:00 – 14:00

### **POSTER PRESENTATIONS**

**Platinum electrodes infiltrated with Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>2-δ</sub>**

*Anders Lund, Torben Jacobsen, Karin Vels Hansen & Mogens Mogensen  
Risø DTU*

**New Membrane Structures with Proton Conducting Properties**

*Casper Nørgaard, University of Southern Denmark*

**Electrochemical Migration of Tin in Electronics**

*Daniel Minzari, Morten Jellesen, Umadevi Rathinavelu, Marianna Johnsen and  
Rajan Ambat, DTU Mekanik*

**Parameter study on bleaching of the organic dye p-nitrosodimethylaniline (RN O) by electrochemical oxidation**

*Jens Muff & Erik G. Søgaaard, Aalborg University*

**An ESR Study of Radicals Associated With PEM Fuel Cell Electrodeodeode Materials**

*Mikkel Juul Larsen & Eivind M. Skou, University of Southern Denmark*

**Improvement of Thermal Stability and Efficiencies of Dye-sensitized Cells (DSC ) by the Application of Sterical Hindreded Pyridine Adddditives**

*Phuong Tuyet Nguyen<sup>1</sup>, Kasper Nørgaard<sup>2</sup>, Hanne Lauritzen<sup>2</sup>, Torben Lund<sup>1</sup>  
1) Roskilde University, Denmark. 2) Danish Technological Institue*

**Wetting Properties of Proton Exchange Membrane Fuel Cell Electrodes**

*Shuang Ma Andersen & Eivind Skou, University of Southern Denmark*

**Analysis of Differences in Impedance Spectra**

*Søren Højgaard Jensen, Risø DTU*

**Regioselectivity in the Reductive Bond Cleavage of Diarylalkylsulfonium Salts: Variation with Driving Force and Structure of Sulfuranyl Radical Intermediates.**

*Jack A. Kampmeier<sup>1</sup>, AKM Monsour Hoque<sup>1</sup>, Franklin D. Saeva<sup>1</sup>, Donald. K. Wedegaertner<sup>1</sup>, Pia Thomsen<sup>2</sup>, Saif Ullah<sup>2</sup>, Jacob Krake<sup>2</sup>, Torben Lund<sup>2</sup>*

*1) University of Rochester, 2) Roskilde University*

**Electrodialytic treatment of sludge ash from fluidized bed combustor**

*Marta Pazos<sup>1,2</sup>, Ricardo Barata<sup>2</sup>, Pernille Jensen<sup>2</sup>, Gunvor M. Kirkelund<sup>2</sup>, Lisbeth M. Ottosen<sup>2</sup>*

*1) Department of Chemical Engineering, University of Vigo, 36310 Vigo. Spain.*

*2) Department of Civil Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark*

**Surface patterning by Scanning ElectroChemical Microscopy**

*Mette Johnsen, Kristian Torbensen, Steen U. Pedersen and Kim Daasbjerg  
Organic Surface Chemistry, Department of Chemistry, Aarhus University,  
Aarhus, Denmark*

**ORAL PRESENTATIONS (continued)**

14:00 – 15:00      **Energy conversion**

**Solid Oxide Fuel Cells – From Fundamentals to the Market**

*Anke Hagen, Risø DTU*

**Comparison of the degradation of the polarisation resistance of symmetrical LSM-YSZ cells, with anode supported Ni-YSZ/YSZ/LSM-YSZ SOFCs**

*Iris Torres da Silva, Risø DTU*

**High Temperature and pressure alkaline electrolysis**

*Frank Allebrod, Risø DTU*

15:00 – 15:15      **Coffee break**

**ORAL PRESENTATIONS (continued)**

15:15 – 15:55      **Research on pressurized solid oxide electrolysis cells**

*Xiufu Sun, Risø DTU*

**Increasing the Coulombic Efficiency of Glucose Biofuel Cell Anodes by  
Combination of Redox Enzymes**

*Federico Tasca, Biochemistry Department, Lund University*

15:55 – 16:10     **Student Award presentations**

16:10 – 16:20     **Closing**

# ORAL PRESENTATIONS

## **Organic Electrochemistry in Denmark During the Latest 100 Years**

*Henning Lund, Århus Universitet*

### Abstract

In the survey of the organic electrochemistry in Denmark from 1920 to 2005 first the quinhydrone electrode and the synthetic work by the Clauson-Kaas group are mentioned. In the rest of the time the work of the Aarhus group, excluding surface electrochemistry later presented by Kim Daasbjerg, will be briefly presented. The work of the Copenhagen group will be discussed by Ole Hammerich. Here I shall present some of the electrochemical work in which I have been involved the latest 55 years. The following subjects will be briefly discussed: Electrochemical oxidations in acetonitrile, reduction of azomethine compounds, structure determinations, electrolysis of heterocyclic compounds, indirect reduction of halogen compounds, electron transfer in some nucleophilic reactions, determination of redox potentials of short-lived radicals, photoreduction of ketones to pinacols, electrochemical preparation of Grignard reagents, radicals generated by electro-induced hydrogen abstraction. Finally, the Sandbjerg meetings on organic electrochemistry will be briefly mentioned.

Henning Lund, Department of Chemistry, Aarhus University

# Electrografting of Surfaces – A Radical Solution Inspired by the Work of Henning Lund

Steen U. Pedersen and Kim Daasbjerg

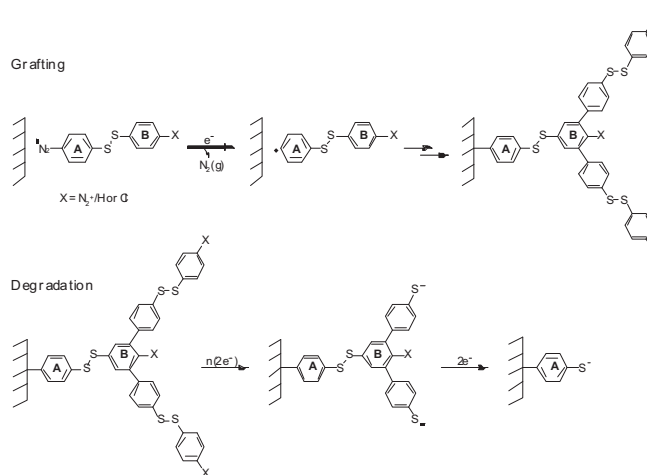
*Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Århus C, Denmark*

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Our recent research efforts are mainly concerned with the area of functionalized surfaces. The goal is to develop new tools and methodologies for creating and building molecular structures on the nanometer length scale. To ensure an extraordinarily high stability of the modified layer the organic molecules are attached covalently to the conducting surface using electrografting. This method being a fairly recent development in modified electrode research may be carried out by oxidation of amines, aliphatic alcohols, or aryl acetates, or by the widely used reductive procedure involving aryldiazonium salts [1,2].

Although the diazonium salt procedure is quite versatile the electrode derivatization is usually so effective that intertwined multilayers are formed in a difficult controllable polymerization reaction. In recent work we have developed an electrochemical approach for constructing a monolayer or near monolayer of molecules by degradation of the multilayer film formed via the electrografting of diazonium salts. Rather than controlling the grafting process the key issue becomes selecting appropriate molecular systems containing cleavable groups [3,4]. For instance, the use of disulfides leads to the formation of reactive surface-confined thiophenolates which may be exploited in further reactions to develop more advanced molecular systems [3].

Finally, our progress toward the central objective of rational design of larger covalently attached molecular systems will be described, as will initial efforts toward creating useful applications such as durable coatings (with and without switchable properties), catalytic systems, and molecular components.



**Scheme 1.** "Formation-Degradation" Approach for Forming a Monolayer of Covalently Attached Thiophenolates.

## References

- [1] Pinson, J.; Podvorica, F. *Chem. Soc. Rev.* **2005**, *34*, 429–439.
- [2] Barrière, F.; Downard, A. J. *J. Solid State Electrochem.* **2008**, *12*, 1231–1244.
- [3] Nielsen, L. T.; Vase, K. H.; Dong, M.; Besenbacher, F.; Pedersen, S. U.; Daasbjerg, K. *J. Am. Chem. Soc.* **2007**, *129*, 1888–1889.
- [4] Malmos, K. Dong, M.; Pillai, S.; Kingshott, P.; Besenbacher, F.; Pedersen, S. U.; Daasbjerg, K. *J. Am. Chem. Soc.* **2009**, *131*, 4928–4936.



# The One-Electron Oxidation of 1,4-Phenylenediamines and Low-Generation PAMAM Dendrimers with a 1,4-Phenylenediamine Core

Ole Hammerich\*, Thomas Hansen, Asbjørn Thorvildsen and Jørn B. Christensen\*

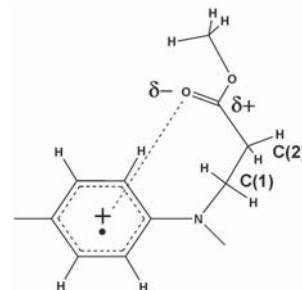
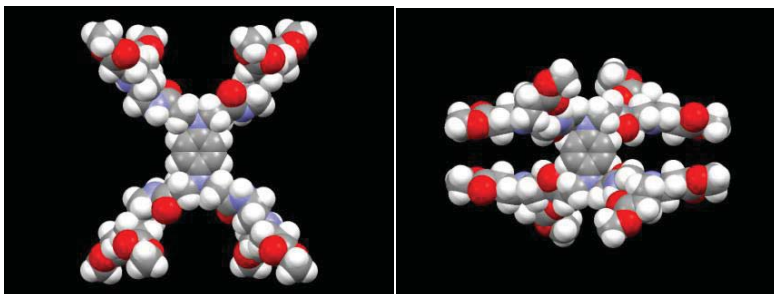
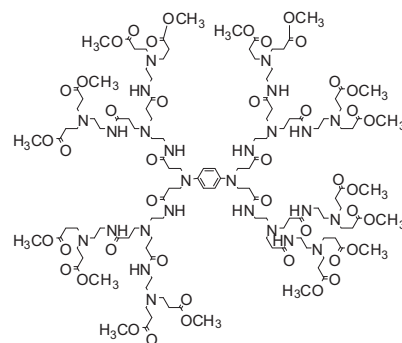
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The one-electron oxidation of 1,4-phenylenediamines (PD) were studied by cyclic voltammetry and Gaussian DFT B3LYP 6-31G(d,p) calculations. Oxidation affects the geometry close to the electro-active core only little and the conformations of the four  $N,N,N',N'$ -substituents are in most cases essentially the same for the neutral substrates and the corresponding radical cations. Plots of the experimental CV oxidation potentials,  $E_{ox}$ , vs. calculated values of  $E_{HOMO}$ ,  $IP_a$ ,  $\Delta G_{ox,gas}$  and  $\Delta G_{ox,MeCN}$ , respectively, were linear with increasing slopes approaching unity for the  $E_{ox}$  vs.  $\Delta G_{ox,MeCN}$  plot.

The one-electron oxidation of a series of low-generation (G-0.5 to G2.0) PAMAM dendrimers with a PD core were studied by differential pulse voltammetry and Gaussian DFT B3LYP 6-31G(d,p) and ONIOM DFT B3LYP 6-31G(d,p):AM1 calculations. (An example of a PAMAM-PD dendrimer is shown to the right). The dendrimers were in all cases more difficult to oxidize than the simple  $N,N,N',N'$ -tetraalkyl-PDs and became as a rule easier to oxidize with increasing dendrimer generation. Results from the DFT calculations demonstrated that the hydrogen-bond and dipolar interactions between the side-chain amide groups did not affect the geometry around the  $N$ -atom; thus, the effect of the dendrimer generation on  $E_{ox}$  is the result of local electronic and solvation effects rather than caused by a change of the geometry of the electro-active PD core imposed by the side-chains.

In contrast, the geometries (conformations) of the dendrimer side-chains were predicted by calculation to be strongly affected by oxidation as seen below (neutral to the left; radical cation in the middle). We attribute this reorientation of the side-chains upon oxidation as resulting from the attractive electrostatic interaction between the ester/amide dipoles and the positive charge at the PD core as illustrated by the structural element shown below. Potential applications of such redox induced structural changes are now being investigated.



Reference: Ole Hammerich, Thomas Hansen, Asbjørn Thorvildsen and Jørn B. Christensen. *ChemPhysChem* **2009**, 10, 1805-1824.

Keywords: dendrimers · amines · radical ions · density-functional calculations · solvent effects

**Live demonstration of selected SPM instruments**

**C-AFM, Kelvin Probing, EC Microcell, and NanoBio AFM.**

***Curt Sander, DME - Danish Micro Engineering***

**Abstract**

Introduction to fundamental configuration of TIP-sample surface interaction in Scanning Probe Microscopes (SPM). SPM technologies have the capability of three-dimensional imaging of surface topography down to molecular or atomic scale as well as n-dimensional mapping of lateral coherent surface properties in vacuum, gas, and some liquids like electrolytes and biological water (buffer solution). Measurement of sample surface electron mobility, metal corrosion and plating in electrolyte, optical properties in organic as well as inorganic materials, Raman spectroscopy for investigation on molecular scale are some of the scientific application areas for SPM technology that can be combined with all other surface characterization tools for large and small scale investigation.

**Effect of Process Related Contamination on Electrochemical Migration in Electronic Devices**  
*Marianna Johnsen, Daniel Minzari and Rajan Ambat, DTU Mekanik*

Electronic devices are becoming an increasing part of our everyday life. By making components smaller and denser, devices get more and more built-in functionalities, while mass production is ensuring reduced cost prices. Environmental concerns regarding the use of Pb in solder alloys has lead to the implementation of lead-free alternatives, but thereby a change in production parameters of the soldering process is inevitable. New contaminations are introduced during lead-free soldering, due to changes in process temperature and introduction of new flux chemistries. In order to assess and predict possible market failures, an in-depth understanding on the effect of the process related contaminations on corrosion and electrochemical migration is required. In this work, electrochemical migration has been investigated on chip capacitors with and without solder flux, which is heated to various temperatures. Solder flux alone is found to passivate tin surfaces due to the presence of adipic acid, thereby reducing the risk of migration. However, the increase in the heating process used in lead-free solders is found to release bromide from the flame retardant used in the laminate of the printed circuit board (PCB). The effect of bromide on electrochemical migration is therefore investigated using various concentrations of bromide, ranging from 1 to 250 ppm. It is found that the probability of migration increases with increasing bromide concentrations up to 50 ppm, after which the probability decrease. Potentiodynamic anodic polarization is used to gain information on the electrochemical dissolution of tin and lead-free solder in bromide and adipic acid solutions, and corrosion products are investigated using FEG-SEM, FIB-SEM, EDS and XPS.

## **Electrodialytic upgrading of municipal solid waste incineration fly ash in pilot scale**

***Pernille Erland Jensen, Gunvor Marie Kirkelund, Arne Villumsen DTU Byg***

Air pollution control (APC) residues from municipal solid waste incineration (MSWI) are classified as hazardous waste due to its high alkalinity and high content of salts and mobile heavy metals. Currently, APC residues from MSWI are generally stabilized and disposed of. Apart from being toxic, APC residues contain resources that are valuable and could be sold to the industry as secondary raw material, if the toxicity is reduced.

Electrodialysis can be used to reduce the toxicity of APC residues by removing toxic metals such as Pb, Cd, As, Ni, Cu, Cr and Zn. This work presents a pilot scale study of the feasibility of treating APC residue by electrodialysis. The electrodialysis design was based on conventional electrodialysis and several previous electrodialytic remediation studies at laboratory and bench scale and the design was adjusted to fit a high solids content feed solution (10% APC residue, 90% water).

Experiments were made in pilot scale, treating 8 kg of APC residue in the feed solution. Compared to the traditional electrodialytic remediation cell design, the APC residues were treated in a membrane stack which consists of several ionexchange membranes, concentrate and APC residue solution compartments. Experiments were made with varying remediation time and current densities and several metals were studied. The main aim was to reduce the availability of heavy metals in the APC residue by the electrodialytic treatment.

The experiments show that the removal of the soluble fraction of the metals from the feed solution into the concentrate solution occurs within hours. Leaching tests (L/S 2) of the treated APC residue shows substantially reduced leaching of heavy metals and salts compared to the untreated APC residue, e.g. Pb from 555 mg/l to 3.8 mg/l. About 50 % of the APC residue is dissolved during treatment and thus the total concentration of heavy metals in the APC residue was higher in the treated APC residue than the initial concentrations. However, the reduction in total amount of heavy metals was 20-30 %.

## Electropolymerisation of derivated thiophenes

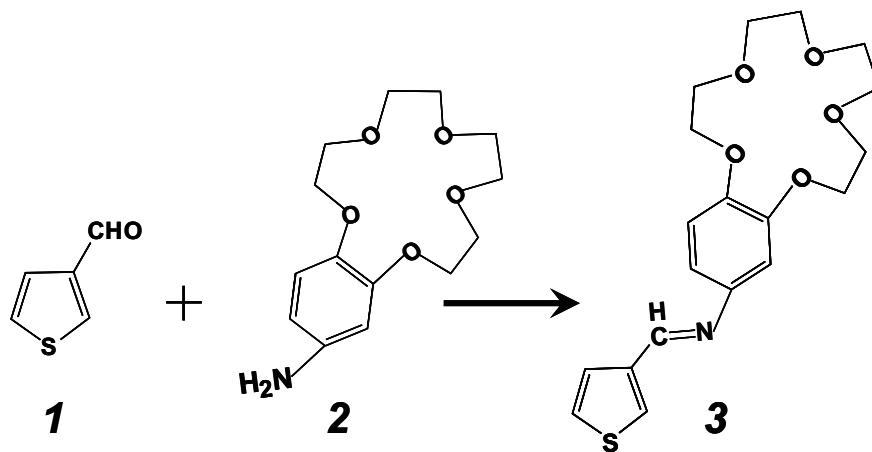
By John Mortensen and Paul Thorn, Department of Science, systems and Models, Roskilde University

### Abstract:

Chemical sensors or Ion Selective Electrodes normally suffer from known and unknown interferences from other substances than the one with the highest selectivity. Therefore it is a difficult task to use only one sensor for absolute concentration measurements, but the use of many sensors can be useful, as it is possible to make positive use of the cross selectivity of the sensors. This can be done in the concept of the electronic tongue, where the “tasting” of the solutions is done by a multisensor system with many chemical sensors. Depending on the calibration, categorisation and/or quantitative information can be gained.

Therefore it is our aim to find easy ways to produce such sensors, and one way is to incorporate an ionophore into a conducting polymer membrane and let this be the chemical sensor. The idea is to synthesise ionophores connected to a thiophene over the 3- position and subsequently electro-co-polymerise the derivated thiophenes and thiophene ending up with an active membrane.

Thiophene and 3-substituted thiophenes readily undergo electrochemical polymerisation from acetonitrile solutions. We have produced thiophene substituted ionophores for  $\text{Na}^+$  and potassium  $\text{K}^+$  of the crown ether type here 4-benzo-15-crown-5 ether)-thiophene-3-methylene-amine (BTA):



Schematic illustration of the synthesis of the BTA monomer.

BTA is subsequently electroco-polymerised with thiophene on a gold electrode and then dipped in a strong  $\text{Na}^+$  solution. Nernstian response from  $10^{-4}$  to  $10^{-1}$  M was obtained. Other ionophores for  $\text{K}^+$ , and for carbonate will be shown.

## POSTER PRESENTATIONS

### **Platinum electrodes infiltrated with Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>2-δ</sub>**

*Anders Lund<sup>a</sup>, Torben Jacobsen<sup>a</sup>, Karin Vels Hansen<sup>b</sup> & Mogens Mogensen<sup>b</sup>*

*<sup>b</sup> Fuel Cells and Solid State Chemistry Division, Risø National Laboratory for Sustainable Energy, DTU, Frederiksborgvej 399, DK-4000 Roskilde, Denmark*

*<sup>a</sup> Department of Chemistry, DTU, DK-2800 Kgs. Lyngby*

#### **Abstract**

The state of the art potentiometric oxygen gas sensors have porous platinum electrodes because of the good stability and physico chemical properties of platinum. These sensors are mainly used in combustion engines and industrial processes where the harsh environments may lead to a poisoning of the sensor electrodes. To prevent this from happening it would be interesting to make the electrodes more robust and catalytic active. Increasing the catalytic activity might also decrease the operating temperature, whereby energy may be saved. We hereby present a study of the electrochemical properties and morphology of symmetric cells with porous platinum electrodes infiltrated with Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>2-δ</sub> (20CGO). We investigated the electrochemical properties of the electrodes with electrochemical impedance spectroscopy (EIS) and the morphology with scanning electron microscopy (SEM). The EIS measurements were performed at temperatures around 600-800 °C and in various atmospheres of air mixed with N<sub>2</sub>, thereby obtaining a pO<sub>2</sub> going from 10<sup>-5</sup> to 0.2 bar. According to the EIS measurements, the polarization resistance of the infiltrated cells were decreased from 3.2 Ω cm<sup>2</sup> to 0.67 Ω cm<sup>2</sup>, depending on the surface concentration of 20CGO. The characteristic frequency increased from 3190 Hz to 17600 Hz in air at 700 °C. This indicates that CGO catalyzes the oxygen reaction. A similar tendency was found at a pO<sub>2</sub>=10<sup>-5</sup> bar and also at lower temperatures. The SEM images showed that 20CGO had partially filled the void of the porous platinum electrodes and a porous layer of 20CGO particles had been formed on the surface of the platinum particles. Infiltration with 20CGO can therefore significantly improve the electrochemical properties of platinum.

## **New Membrane Structures with Proton Conducting Properties**

**Casper Nørgaard, University of Southern Denmark**

**Subject:** Polymer Electrolyte Membranes for Fuel Cell Applications

**Keywords:** Polymer, electrolyte, membrane, PEM, fuel cell, composite, proton conductor, zirconium phosphate, ZrP.

Perfluorosulfonic acid membranes (e.g. Nafion®) are the most widely applied electrolytes in Polymer Electrolyte Membrane Fuel Cells (PEMFCs) because of their good chemical stability, mechanical properties and high proton conductivity, when well hydrated. The upper limit of operating temperature for these membranes is restricted by the loss of conductivity and dimensional stability as the temperature reaches the boiling point of water and the glass transition temperature of the polymer. At low relative humidity the membranes dehydrate, resulting in loss of conductivity and reduced dimensions. High temperature and high relative humidity can cause excessive swelling of the membranes, yielding insufficient mechanical properties and breakdown of membrane function. Moreover, in the case of the Direct Methanol Fuel Cell (DMFC), their significant methanol permeability causes loss of efficiency. Higher operating temperatures (>100 °C) are desired as they improve reaction kinetics and reduce the problem of CO poisoning the catalyst, thus allowing reduced noble metal loading in the catalyst layers of the membrane electrode assembly of the fuel cell. Moreover water and heat management can be simplified if higher operating temperature is enabled. One approach to obtain improved membranes in the aspects of applicable operating temperature and methanol permeability, which has attracted considerable attention, is the formation of composites by distributing inorganic fillers into Nafion or alternative polymers [1, 2, 3]. Improved fuel cell performance from incorporation of hygroscopic oxides or solid proton conductors (e.g. zirconium phosphates) has been reported. The poster exhibits upcoming work in the field of composite electrolyte membranes at the University of Southern Denmark, combining radiation grafted fluoropolymers [4, 5] with various inorganic additives.

**References** [1] A.M. Herring, Journal of Macromolecular Science, Part C: Polymer Reviews 46 (2006) 245-296 [2] G. Alberti, M. Casciola, Annu. Rev. Mater. Res. 33 (2003) 129-154 [3] S.R. Sogaard *et al.*, Solid State Ionics 178 (2007) 493-500 [4] L. Gubler *et al.*, Fuel Cells 5 (2005), No. 3, 317-335 [5] M.L. Larsen *et al.*, Appl. Phys. A – Materials Science & Processing 96 (2009), 3, 569-573

## **Electrochemical Migration of Tin in Electronics**

***Daniel Minzari, Morten Jellesen, Umadevi Rathinavelu, Marianna Johnsen and Rajan Ambat, DTU Mekanik***

Electrochemical migration is a corrosion phenomenon that has received increased interest during the past decades, as electronic components has become smaller, more sophisticated and as devices are being exposed to practically any environment. On modern electronic circuits, most metallic surfaces are shielded from external environment using a soldermask, though contacts and solder joints are still exposed in most cases. For this reason, tin, tin solder alloys, and gold account for most of the metallic surfaces exposed to an outside environment. Gold is of less relevance from an electrochemical migration point of view due to its nobility, and an in-depth understanding of the electrochemical migration of tin and tin solder alloys are therefore of high relevance. In this poster, the electrochemical migration phenomenon is described, and models will illustrate how parameters such as bias potential, volume of condensed droplet, distance between electrodes, and contaminations can affect electrochemical migration.



## **Parameter study on bleaching of the organic dye p-nitrosodimethylaniline (RNO) by electrochemical oxidation**

*Jens Muff & Erik G. Sogaard, Aalborg University*

Keywords: Electrochemical oxidation; hydroxyl radical scavenger; p-nitrosodimethylaniline, RNO, NDMA, pNDA, chlorine oxidation

Subject: Environmental electrochemistry

Bleaching of the organic dye p-nitrosodimethylaniline (RNO) is a method widely applied for evaluation of the oxidative performance of electrochemical water treatment systems (Comninellis, 1994; Martinez-Huitle et al. 2004; Tanaka et al. 2004). During the last 15 years, electrochemical oxidation has been developed into a strong physico-chemical oxidation technique for treatment of water utilizing hydroxyl radicals and lattice active oxygen depending on the electrode material used. The present study concerned the use of RNO as a selective probe compound for detection of hydroxyl radicals, an indirect determination method adapted from the cell biology and photobiology fields (Kraljic and Trumbore, 1965). RNO was claimed to act as a selective scavenger towards hydroxyl radicals through oxidation of the chromophore nitroso group, however, bleaching was also observed in Ti/Pt and Ti/RuO<sub>2</sub> anode systems utilizing chemisorbed lattice active oxygen (Tanaka et al. 2004) according to the generally accepted models (Comninellis 1994). In addition, several studies reports bleaching of RNO by other strong oxidant as ozone (Wabner and Grambow, 1985) and chlorine (Tanaka et al. 2004). These observations were explained by oxidation mechanisms through radical chain reactions generating intermediate hydroxyl radicals (Fukatsu and Kokot, 2001). The applied anode material was Ti/Pt90-Ir10 and experimental runs in inert 0.050 M sodium sulphate and sodium phosphate electrolytes confirmed bleaching of RNO following first order reaction kinetics. In 0.050 M sodium chloride electrolyte, the bleaching rate was much faster with a shift in kinetics to second order RNO dependence, which confirmed the oxidation of RNO by the generated hypochlorous acid/hypochlorite pair. The electrolytic formation of available free chlorine species in a 0.154 M sodium chloride electrolyte was simulated with addition of alkaline sodium hypochlorite solution in similar amount and rate, in order to compare the oxidation rate of the in-situ generated and the physically added chlorine. The rate of the chemical oxidation obeyed none of the standard kinetic expressions, but comparison of the evolution in the relative RNO concentration revealed a superior oxidation efficiency of the in-situ generated hypochlorous / hypochlorite species. In order to study the role of hydroxyl radicals in the oxidation reactions observed, tertiary butyl alcohol (t-BuOH) was added in excess to remove all hydroxyl radicals if present. In 0.050 M sodium sulphate electrolyte an almost similar evolution in the RNO concentration was found with or without the presence of 0.05 M t-BuOH stating that no hydroxyl radicals was formed by the Ti/Pt90-Ir10 anode material and that the oxidation was due entirely to lattice active oxygen MO<sub>x</sub>+1. In a similar fashion, the hydroxyl radical chain reaction proposal was rejected since neither 0.05 M nor 0.10 M t-BuOH slowed or even affected the rate of RNO oxidation in the 0.050 M sodium chloride electrolyte. As concluding remark, RNO was both oxidized by lattice active oxygen and chlorine species, and can not be regarded as a fully selective hydroxyl radical probe compound in electrochemical studies. However, it is a very applicable and easy to use compound for evaluation of the electrochemical oxidation potential, taking account of all oxidative species generated in the process.

## **References**

Comninellis, C. (1994): Electrocatalysis in the electrochemical conversion/combustion of organic

pollutants for waste water treatment. *Electrochimica Acta*, 39:11/12:1857-1862 Fukatsu, K., Kokot, S. (2001): Degradation of poly(ethylene oxide) by electro-generated active species in aqueous halide medium. *Polymer Degradation and Stability*, 72:353-359

Kraljic, I., Trumbore, C.N. (1965): p-Nitrosodimethylaniline as an OH Radical Scavenger in Radiation Chemistry. *Journal of the American Chemical Society*, 87:12:2547-2550

Martinez-Huitle, C.A., Quiroz, M.A., Comninellis, C., Ferro, S., De Battisti, A. (2004): Electrochemical incineration of chloranilic acid using Ti/IrO<sub>2</sub>, Pb/PbO<sub>2</sub> and Si/BDD electrodes. *Electrochimica Acta*, 50:949-956

Tanaka, F., Feng, C., Sugiura, N., Maekawa, T. (2004): p-Nitrosodimethylaniline (RNO)-Based Evaluation of Enhanced Oxidative Potential During Electrochemical Treatment of High-Salinity Wastewater. *Journal of the Environmental Science and Health Part A*, A39:3:773-786

Wabner, D., Grambov, C. (1985): Reactive intermediates during oxidation of water at lead dioxide and platinum electrodes. *Journal of Electroanalytical Chemistry*, 195:95-108

## **An ESR Study of Radicals Associated With PEM Fuel Cell Electrode Materials** **Mikkel Juul Larsen & Eivind M. Skou, University of Southern Denmark**

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**Keywords:** ESR, radicals, fuel cell, electrode, carbon black, carbon nanotube

Radical species in a polymer electrolyte membrane fuel cell (PEMFC) are generally unwanted as they may cause degradation of the proton-exchange membrane. A number of different radical intermediates can be generated at the platinum-loaded porous carbon (Pt/C) electrodes of a PEMFC, depending on the reaction paths. The nature of the carbonaceous catalyst-support material itself may be of some importance as to which and how many radicals are formed during the oxygen reduction and the hydrogen oxidation. Many of the radicals can be identified and quantified by electron spin resonance (ESR) spectroscopy by the use of different organic spin trap molecules; see figure 1. *Figure 1. ESR spectra of radical adducts.* The most common catalyst support is carbon black (CB), which consists of nano-sized particulates made up of smaller quasi-graphitic crystallites in a matrix of disorganized carbon. The crystallites are small (on the order of 4 parallel carbon layers thick and 20 Å in diameter) and have a quite high degree of imperfection. The content of unpaired electrons associated with broken bonds at layer edges and defects is therefore large. These radicals are resonance-stabilized and detectable by ESR spectroscopy as a relatively broad signal, owing to resonances from multiple species. Figure 2 shows the ESR signal of an as-received commercial CB (E350G, Timcal). *Figure 2. ESR spectra of CNT and raw and annealed CB.* Upon heat treatment in an oxygen-free atmosphere the crystallites grow and become more perfect. This gives rise to a decreased concentration of the radicals described above. At sufficiently high temperatures (2500-3000 °C) the structure of the crystallite becomes close to that of graphite, and a different ESR signal due to mobile electrons in conduction bands is observed. This is also shown in figure 2. With increased degree of graphitization the CB becomes more stable toward degradation in chemical and electrochemical environments. This can therefore be a beneficial treatment for PEMFC catalyst- support CBs. Another possibility is to use materials of more perfect structure, e.g. carbon nanotubes (CNTs). The ESR spectrum of a CNT is included in figure 2 and is seen to differ quite a lot from the CB spectra. Using CNTs or graphitized CBs, however, makes it more difficult to attach the catalyst particles to the support. On the other hand, if this problem can be circumvented, the absence of radicals in the support species may cause the electrode reactions to follow different paths in which a smaller amount of radical intermediates is produced. A suitable way to study the pathway of the electrode reaction is rotating ring-disc electrode (RRDE) measurements complemented by ESR spectroscopy.

### *Reference*

[1] A. Panchenko et al., *Phys. Chem. Chem. Phys.* **6** (2004) 2891-2894.

[1]

# Improvement of thermal stability and efficiencies of Dye-sensitized cells (DSC) by the application of sterical hindred pyridine additives

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Dye-sensitized solar cells (DSC) have been extensively studied in the last decade as a promising renewable energy source because of their potential inexpensive manufacturing technology compared to silicon cells.<sup>1-3</sup> The principle of the cell is shown in Fig. 1.

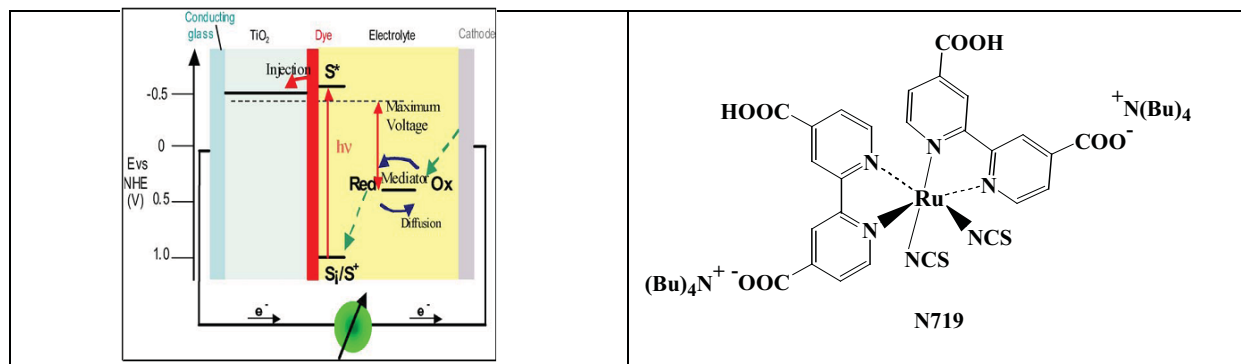
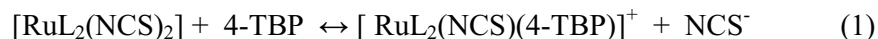


Fig. 1: Energy diagram of the DSC cell

4-*tert*-butylpyridine (4-TBP) has been extensively used as an additive in many DSC laboratories in order to increase the  $V_{oc}$  of the cell. The additive, however has the draw back that it may react thermally at high temperatures ( $> 80^{\circ}\text{C}$ ) with ruthenium dyes like N719, according to eq. (1):<sup>4</sup>



In this work we report that the negative effects on the thermal stability of the dye due to the substitution reaction (1) may be eliminated by the application of sterical hindered pyridines. No reactions were observed between N719 and the sterical hindered pyridines as 2-picoline; 2,6-lutidine; 2,3,5-colodine and 2,4,6-trimethylpyridine. Besides other additives which are 1-methylbenzimidazole; 3-picoline; 4-picoline; 3,5-lutidine react with N719 slower than 4-TBP three to four times. The thermal stability of the DSC cell is therefore anticipated to be much higher with application of these pyridines compared with the very popular 4-TBP additive. Furthermore DSC cells with the different additives are more efficient than the ones with 4-TBP.

## References

- [1] B. C. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO<sub>2</sub> films, *Nature* 353 (1991) 737.
- [2] M. Grätzel, Solar energy conversion by dye-sensitized photovoltaic cells, *Inorganic Chemistry* 44 (2005) 6841-51.
- [3] M. Grätzel, Photoelectrochemical cells, *Nature* 414 (2001) 338-44.
- [4] H. T. Nguyen, H. M. Ta, T. Lund, Thermal thiocyanate ligand substitution kinetics of the solar cell dye N719 by acetonitrile, 3-methoxypropionitrile, and 4-*tert*-butylpyridine, *Solar Energy Materials & Solar Cells* 91 (2007) 1934-42.

## Poster title: Wetting properties of Proton Exchange Membrane Fuel Cell electrodes

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### Abstract

As one of the most promising future energy provider, Proton Exchange Membrane Fuel Cells (PEMFCs) carry the merit of renewability, efficiency and cleanness<sup>1,2</sup>. Durability issue of PEMFCs is nowadays well recognized no less important as exploring alternative cheaper material or increasing cell efficiency<sup>3</sup>. Degradation of a cell can result from different factors; one of the important failure modes is the limitation of mass transport due to water management in the gas channel<sup>4</sup>. Therefore, wetting property of the electrode is a major factor influencing the transport and accumulation of water.

In this work, hydrophobicity of PEMFC GDL and electrodes were studied by means of contact angle with water droplet. Different fresh and treated GDL and electrodes were studied. Standard sample was chemically treated with 20% hydrogen peroxide at 80 °C in auto clave or electrochemically treated with potential cycles between hydrogen and oxygen evolution. Normal, reducing and advancing contact angle of the samples were compared as shown in figure 1 and 2.

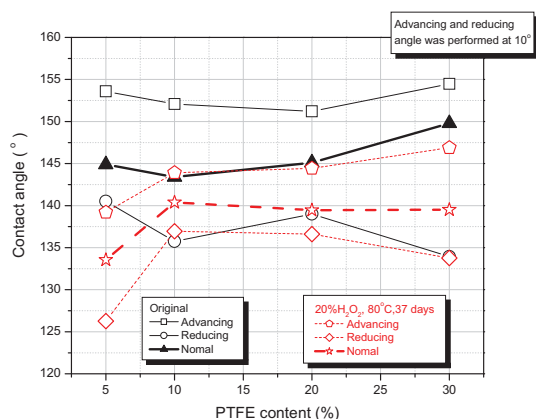


Fig. 1. Contact angles for GDLs before and after chemical treatment.

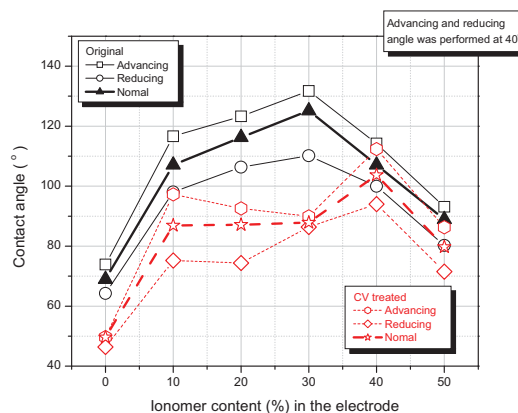


Fig. 2. Contact angle for electrode with different ionomer before and after chemical treatment.

1 Stone C. and Morrison A.E., Solid State Ionics 152: 1-13 Part A 2002.

2 Smitha B., Sridhar S. and Khan A.A., J. Membr. Sci. 259 10-26 2005.

3 Borup RL, Davey JR, Garzon FH, et al. J. Power Sources. 163 1 76-81 2006

4 Bazylak A, International journal of hydrogen energy, 34 9, 3845-3857 2009.

## **Analysis of Differences in Impedance Spectra**

*Søren Højgaard Jensen, Risø DTU*

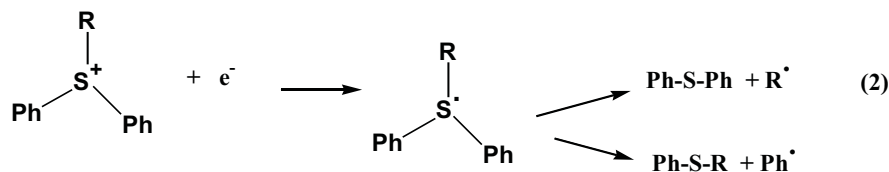
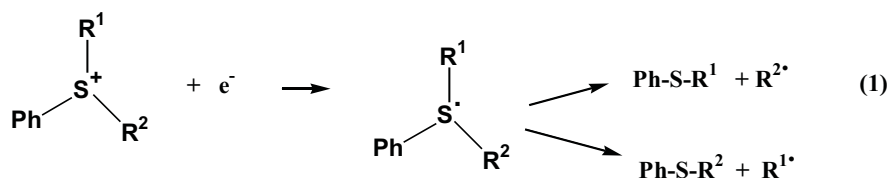
Electrochemical Impedance Spectroscopy (EIS) is extensively used to obtain information about the processes that limits the performance of fuel cells. This is often accomplished by fitting a model to the measured fuel cell impedance spectrum. Ideally, the fitting process makes the variables of the model converge to some values which can provide quantitative information about the performance limiting processes. However, several processes contribute to the fuel cell impedance and a detailed model will accordingly involve several variables. Unfortunately, this often implies that the variables converge with an unsatisfying accuracy. Usually some priori knowledge about the fuel cell is present, e.g. the anode, electrolyte and cathode are serially connected and this knowledge can be used to enhance the accuracy. Suppose we slightly change the humidity of the anode gas, the difference between two impedance spectra recorded respectively before and after the change will only involve anode processes. This means a detailed model of the impedance difference may contain fewer variables than a detailed model of the full spectra would do. Therefore, the variables may converge with higher accuracy when we model the impedance difference than when we model the full spectra.

# Regioselectivity in the Reductive Bond Cleavage of Diarylalkylsulfonium Salts: Variation with Driving Force and Structure of Sulfuranyl Radical Intermediates.<sup>1</sup>

Jack A. Kampmeier,<sup>†\*</sup> AKM Monsour Hoque,<sup>†</sup> Franklin D. Saeva,<sup>†</sup> Donald. K. Wedegaertner,<sup>†</sup> Pia Thomsen,<sup>‡</sup> Saif Ullah,<sup>‡</sup> Jacob Krake,<sup>‡</sup> Torben Lund.<sup>‡\*</sup>

<sup>†</sup>*Contribution from the Department of Chemistry, University of Rochester, Rochester, N. Y. 14627 and the* <sup>‡</sup>*Department of Science, Systems and Models, Roskilde University, P.O. Box 260, DK-4000, Denmark*

The one electron reduction of phenyldialkylsulfonium salts  $\text{Ph-S}^+\text{R}^1\text{R}^2$  gives cleavage of the weaker S-alkyl bonds in the approximate order of the stability of the resulting radicals, primary < secondary < benzyl; the phenyl group is not cleaved. In contrast, the stronger S-aryl bond may be cleaved in the one-electron reduction of diphenylalkylsulfonium salts  $\text{Ph}_2\text{S}^+\text{R}$ . We now report that the ratio  $F = [\text{PhSR}]/[\text{Ph}_2\text{S}]$  of aryl to alkyl bond cleavage in some diarylalkylsulfonium salts is a function of the potential of the reductant.



$$F = \frac{[\text{Ph-S-R}]}{[\text{Ph-S-Ph}]}$$

Ph = phenyl

R = alkyl group

R<sup>1</sup>, R<sup>2</sup> = benzyl, alkyl

## References

- 1) J. Am. Chem Soc 2009 in press.

# Electrodialytic treatment of sludge ash from fluidized bed combustor

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Sewage sludge contains several potentially hazardous compounds such as heavy metals, PCBs, PAHs, dioxins, pesticides and endocrine disruptors, pathogens and other microbiological pollutants. However, elements with high agricultural value (N, P, K, Ca...) are also present. During the last years, the fluidized bed sludge combustor (FBSC) has been considered an effective and novel alternative to treat sewage sludge. In this reactor the sludge, mostly from urban wastewater treatment (>90%) although some mixed urban and industrial sludge (<10%), is incinerated [1]. As a result, the elevated amount of sludge is reduced to a small quantity of ash and the thermal destruction of toxic organic constituents is obtained. Conversely, the removal of heavy metal is not reached. This arises as an impediment to the use of the ash as fertilizer.

Electrodialytic treatment of wastewater sludge has showed encouraging results to reduce heavy metal content [2,3]. With this technique, the electric field is used to extract heavy metals and ion exchange membranes are used to prevent the waste of current in transporting ions from one electrode towards the other.

Based on previous research, the electrodialytic treatment of sludge ash from a FBSC was studied. A detailed characterization of the sludge ash was done initially, determining that, with the exception of Cd, all heavy metals were under the limit levels of Danish legislation. Cd was thus selected as the target metal.

The experiments were carried out at constant current density ( $0.8 \text{ mA/cm}^2$ ) during 7 and 14 days, with pH control in the cathode chamber (pH 2) to improve the efficacy of the treatment. Buffering capacity, heavy metal content, sequential extraction and SEM analyses before and after the treatment were also done.

In Fig. 1 the initial Cd concentration, the mean concentrations after treatment and limiting values are shown. In both experiments the concentration of Cd was reduced. However, only after 14 days of treatment, the Cd concentration was reduced to values below the limiting concentration. Cd compounds are, compared to other heavy metals, relatively soluble and generally more

mobile [3]. For this reason, no extracting agents were used to avoid the removal of others metals and their possible interference in Cd removal. The concentration of other heavy metals was also measured after the treatment. In both experiments the concentrations were under limit values of the Danish legislation.

It can be concluded that the electrodialytic treatment is an adequate alternative to reduce the Cd concentration in FBSC ash prior to use as fertilizer.

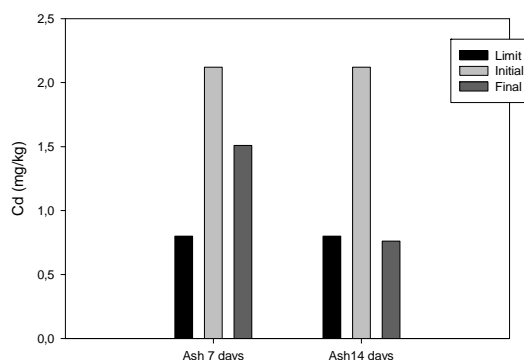


Fig. 1 Limiting Cd concentration and Cd concentrations in FCB ash before and after electrodialytic treatment.

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## References

- [1] M. Van de Velden, R. Dewil, J. Baeyens, L. Jossion, P. J. Hazard. Mater. 151 (2008) 96-102.
- [2] M.R. Jakobsen, J. Fritt-Rasmussen, S. Nielsen, L.M. Ottosen, J. Hazard. Mater. 106 (2004) 127-132.
- [3] L.M. Ottosen, A.J. Pedersen, H.K. Hansen, A.B. Ribeiro, Electrochim. Acta. 52 (2007) 3420-3426.



## **Surface patterning by Scanning ElectroChemical Microscopy**

*Mette Johnsen, Kristian Torbensen, Steen U. Pedersen and Kim Daasbjerg*

*Organic Surface Chemistry, Department of Chemistry, Aarhus University, Aarhus, Denmark*

Derivatization of surfaces (metallic and carbon) using aryl radicals generated by reduction of aryldiazonium salts have been studied thoroughly. In the past years some research effort has focused on creating micropatterns on these surfaces employing the scanning electrochemical microscopy (SECM) technique rather than carrying out an overall modification. In general, the studies utilizing electrochemistry have used the approach of generating an active species (e.g., production of a reactive aryl radical or a catalyst) in close vicinity of a surface in a spatially confined region, ultimately resulting in the creation of a microscale pattern on the surface.

In the present study we exploit a complementary process. Using a diazonium salt of a diaryl disulfide we first graft a multilayer on a surface rendering it inactive towards a chosen redox probe. This multilayer can subsequently be electrochemically cleaved via a reduction of disulfide bridges present in the grafted molecule. The precise dimension of such a cleaved area can be controlled using the two-electrode potentiometry feature of SECM. This results in the local formation of a thiol/thiolate monolayer that is now sensitive towards redox probes. In this way, the pattern created by the local reduction of the multiayer can be visualized directly exploiting the local variation in electrochemical sensitivity to a given probe. Moreover, a complementary optical image of the surface pattern can be obtained by exposing the surface to a fluorescent tag with a selective reactivity to either disulfides or thiols.

## ORAL PRESENTATION (continued)

### **Solid Oxide Fuel Cells – From Fundamentals to the Market**

*Anke Hagen, Risø DTU*

#### **Abstract**

In a solid oxide fuel cell, SOFC, the chemical energy of a fuel such as hydrogen or methane is directly converted to electricity and heat; thereby the detour via thermal energy as in conventional power production is avoided and high efficiencies can be achieved.

A number of key advantages make the SOFC technology very promising:

- High electrical efficiency
- Fuel flexibility (natural gas, hydrogen, ethanol, bio fuels, diesel,...)
- Low emissions (NO<sub>x</sub>, CO<sub>2</sub>)
- Low noise
- Modular concept (from kilowatts to megawatts)
- Well suited for combined heat and power due to a relatively high operation temperature (550-1000 °C)

Research on SOFCs has been carried out at Risø since the 1980s. Our strategy is based on accomplishing technological development based on and in parallel with fundamental research. For the effective development and commercialization of Danish SOFC technology a close collaboration with the Danish company Haldor Topsøe A/S (today Topsoe Fuel Cell A/S – TOFC, fully owned by Haldor Topsøe A/S).

Our research spans from fundamental investigations of the electrochemical properties of materials at the molecular level to the manufacture of complete cells with industrially relevant processes. An important task is to understand the correlation between composition, microstructure and performance of a component, and to implement this in predictive models. We test components such as solid oxide cells with regard to performance, stability and fuel flexibility, and they are characterized in great detail using methods such as impedance spectroscopy, scanning and transmission electron microscopy, and X-ray diffraction. Other experimental methods include thermal analysis and measurements of magnetic properties.

# Comparison of the degradation of the polarisation resistance of symmetrical LSM-YSZ cells, with anode supported Ni-YSZ/YSZ/LSM-YSZ SOFCs

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*Keywords:* SOFC, EIS, LSM, cathode

*Subject:* Solid oxide fuel cells

## Abstract

Symmetrical cells are a useful tool for screening electrode performance [1]. The goal of this study was to investigate how the results collected from symmetrical cells relate to results obtained on a corresponding full cell. Therefore, electrochemical impedance spectra (EIS) from a symmetrical cell and full cell were collected periodically over a longer period of time, at open circuit voltage and 650°C in air (cathode) and humidified (4%) hydrogen (anode).

The symmetrical cells were screen-printed lanthanum strontium manganite - yttria stabilized zirconia composite cathodes [LSM25.5-YSZ composites, where LSM25.5 =  $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{MnO}_{3\pm\delta}$  and YSZ =  $\text{ZrO}_2$  with 8 mol%  $\text{Y}_2\text{O}_3$ ] on stabilized zirconia, YSZ, electrolyte. The full cells were planar anode supported Ni-YSZ/YSZ/LSM25.5-YSZ cells. These materials have been chosen as they are of continuing interest in the field [1, 2, 3].

The impedance was affected by degradation over time in the same frequency range for both cells (~10 Hz), possibly indicating that the same physical process was affected in both types of cell. To break down the losses of the cells, equivalent circuits were applied to the EIS data from both types of cells [4, 5]. However, deconvolution of the impedance data was not straightforward. Applying slightly different  $n$ -values for the constant phase elements;  $n$ -values proposed in literature or  $n$ -values determined in this study, in an otherwise identical equivalent circuit, led to very different results for the breakdown of losses of the full cell, showing the high sensitivity of the fitting procedure. Moreover, both sets of  $n$ -values delivered unexpected and non physical breakdown of losses. Hence, further data on the symmetrical cells at different temperatures and partial oxygen pressures have been obtained. Refinement of the equivalent circuits will be done applying analysis techniques like ADIS [6] (analysis of difference in impedance spectra) and DRT [7] (distribution of relaxation times).

## References

- [1] S.C Singhal and K. Kendall, editors. High Temperature Solid Oxide Fuel Cells - Fundamentals, Design and Applications. Elsevier, 2003.
- [2] S.P. Jiang. J. Mater. Sci. 43:6799, 2008.
- [3] S.B. Adler. Chem. Rev. 104:4791, 2004.
- [4] M.J. Jørgensen, S. Primdahl, C. Bagger, and M. Mogensen. Solid State Ionics, 139:1, 2001.
- [5] R. Barfod, A. Hagen, S. Rasmousse, P.V. Hendriksen, and M. Mogensen. Fuel Cells, 6:141, 2006.
- [6] S.H. Jensen, A. Hauch, P.V. Hendriksen, M. Mogensen, N. Bonanos, and T. Jacobsen. Journal of the Electrochemical Society, 152:B1325, 2007.
- [7] H. Schichlein, A. Müller, M. Voigts, A. Krügel, and E. Ivers-Tiffée. Journal of Applied Electrochemistry, 32:875, 2002.

## **High Temperature and pressure alkaline electrolysis**

*Frank Allebrod, Sune D Ebbesen, Johan Hjelm, and Mogens Mogensen Risø DTU*

Alkaline electrolysis is a well proven technology to produce hydrogen from water with a relative high efficiency. Nevertheless there is a demand for even higher efficiencies at reduced investment costs. Increasing the operating temperatures from  $\sim 100^{\circ}\text{C}$  to temperatures up to  $250^{\circ}\text{C}$  and the operation pressure from atmosphere to pressures up to 100 bar would increase the efficiency. Potassium hydroxide, which is the most widely used electrolyte, is highly corrosive even at low temperatures. To realize high temperature operation of alkaline cells, materials that can withstand the highly corrosive environment have to be developed. Nickel and nickel alloys are very resistant towards corrosion, as well as titanium and silver. Silicon nitrides and graphite are supposed to withstand, too. Also perovskite structured oxides may be used for the electrodes, but corrosion data at the aspired temperatures, pressures and concentrations of the Potassium Hydroxide is not available for these materials. Also the influence of hydrogen and oxygen on corrosion of materials in the electrolyte is not available. It is the aim of the project to develop alkaline electrolysis cells with an operation temperature up to  $250^{\circ}\text{C}$ . The strategy for the development as well as initial results on the development will be discussed in the presentation.

## **Research on pressurized solid oxide electrolysis cells**

*Xiufu Sun, Sune D. Ebbesen, Søren H. Jensen, Mogens Mogensen, **Risø DTU***

High temperature solid oxide electrolysis cells (SOEC) are considered to be one of the most practical and promising technologies for large scale renewable fuel production. Compared to the conventional water electrolysis, high temperature solid oxide electrolysis which is operated in the temperature range of 700°C-1000°C has many advantages. The high operating temperature results in faster reaction kinetics and reduces the electric energy demand thus enabling potentially high efficiency. Furthermore, the SOEC can be used to co-electrolysis with water and CO<sub>2</sub> to produce syngas (H<sub>2</sub> + CO), which can be converted catalytically to various types of synthetic hydrocarbon fuels. Operating SOEC at high pressure may have many advantages because it is favourable for gas storage. Further, operation at high pressure allows for integration with production of synthetic hydrocarbon fuels which are normally operated at pressures exceeding 40 bars. Unfortunately, there are very limited reports on the effect of pressurising SOEC, and it is therefore necessary to study how the pressure affects the performance of the SOEC.

In order to have a further understanding the effect of pressure on SOEC, we have built a new test system at Risø DTU to investigate the SOEC under increased pressure. Here, we give a presentation of the recent research and development of SOEC at Risø DTU.

## Increasing the Coulombic Efficiency of Glucose Biofuel Cell Anodes by Combination of Redox Enzymes

Federico Tasca, Biochemistry Department, Lund University

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Enzymatic biofuel cells use redox-enzymes as catalysts at the electrodes. They can be build from cheap components, and work at room temperature. If the enzymatic reactions are specific for the anodic and cathodic processes, no membrane separating the anodic and cathodic compartment is required. Due to their potential use as implantable power sources, especially glucose-O<sub>2</sub> biofuel cells are in the focus of current research [1, 2]. In this contribution we describe a glucose biofuel cell anode based on a combination of pyranose dehydrogenase (PDH, EC 1.1.99.29) from *Agaricus meleagris* (*Am*PDH) and cellobiose dehydrogenase (CDH, EC 1.1.99.18) from the ascomycete *Myriococcum thermophilum* (*Mt*CDH), which has been studied previously with respect to biofuel cell applications [1, 3]. The combination of *Am*PDH and *Mt*CDH, leads to an anode, which is able to gain up to six electrons out of a suitable substrate molecule. In contrast to the enzymes glucose oxidase, glucose dehydrogenase, or *Mt*CDH, which oxidize glucose at the C(1) carbon to its corresponding lactone, *Am*PDH is able to oxidize glucose at the C(2) and C(3) gaining up to four electrons from one substrate molecule [4]. Among the substrates of *Am*PDH besides glucose, cellobiose, sucrose, (due to their appearance in plants) and trehalose are of primary interest for possible biofuel cell applications. Trehalose is the dominant sugar in many insects such as large grasshoppers. The ability to study implantable biofuel cells in insects could lessen the use of vertebrates, particularly mammals, in animal experiments. *Am*PDH is active at physiological conditions (PBS buffer, pH 7.4, 0.14 M NaCl), it does not react with oxygen at all and no H<sub>2</sub>O<sub>2</sub> is produced by this enzyme.  $\beta$ -D-cellobiose and cello-oligosaccharides, lactose, which have the same  $\beta$ -1,4 glycosyl linkage as cellobiose but differs in the 4-OH position of the galactose moiety, glucose and some di- and oligosaccharides, e.g., maltose (consisting of two R-1,4-linked glucose moieties), can be oxidized with high turnover rates from *Mt*CDH. *Am*PDH and *Mt*CDH were adsorbed to pyrolytic graphite electrodes in the presence of a low potential Os redox polymer (poly(vinylpyridine)-[osmium-(*N,N'*-methylated-2,2'-biimidazole)<sub>3</sub>]<sub>2+/3+</sub>) [5] and single-walled carbon nanotubes. By combining *Am*PDH and *Mt*CDH, a glucose biofuel cell anode with increased coulombic efficiency, which is defined as the coulombic output derived from a fuel compared to the total amount of fuel being consumed, has been developed.

1. F. Tasca, L. Gorton, W. Harreither, D. Haltrich, R. Ludwig, and G. Noll, Journal of Physical Chemistry C 112:13668 (2008).
2. I. Willner, Y. M. Yan, B. Willner, and R. Tel-Vered, Fuel Cells 9:7 (2009).
3. F. Tasca, L. Gorton, W. Harreither, D. Haltrich, R. Ludwig, and G. Noll, Journal of Physical Chemistry C 112:9956 (2008).
4. F. Tasca, S. Timur, R. Ludwig, D. Haltrich, J. Volc, R. Antiochia, and L. Gorton, Electroanalysis 19:294 (2007).
5. F. Mao, N. Mano, and A. Heller, Journal of the American Chemical Society 125:4951 (2003).

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