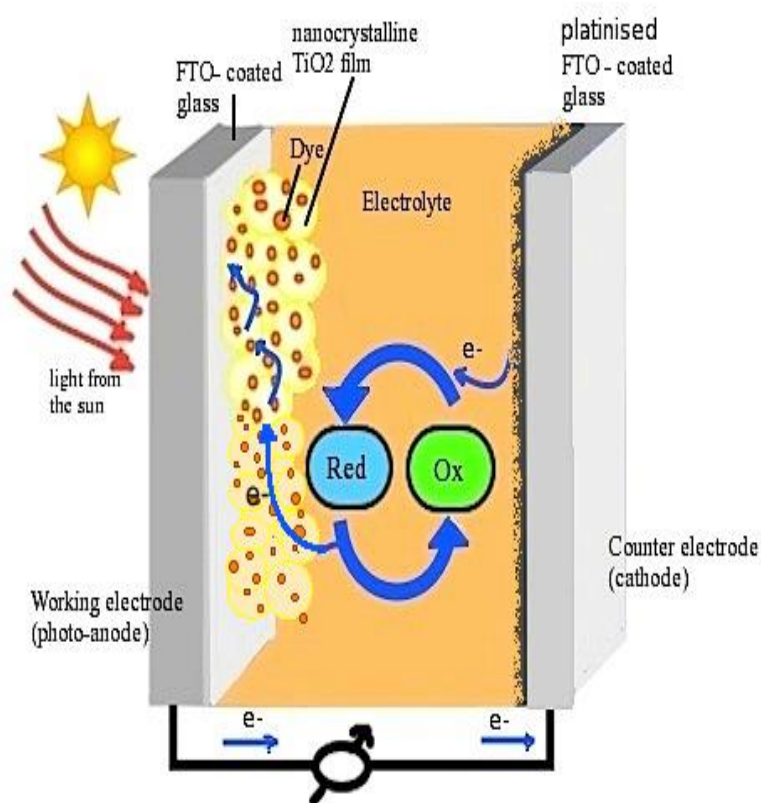




Electrochemical Science and Technology Conference 2013

3-4 October, Sørup Herregaard , Ringsted.



Lars Kloo, 2013, Figure from abstract 4



Participation list

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Electrochemical Science and Technology Conference 2013

We are glad to welcome all of the 42 participants to the Danish Electrochemical Society's two day conference on Electrochemical Science and Technology at the conference centre Sørup Herregaard near Ringsted, October 3-4, 2013. This year program contains 15 oral and 15 poster presentations covering a broad range of aspects of electrochemistry. The conference program has 5 invited oral presentations with the main talks given by Prof. Nina Balke, Oak Ridge National Laboratory, USA and Prof. Lars Kloo, KTH Stockholm. One of the objectives of the conference is to generate a forum for exchange of knowledge and to strengthen the collaboration between industry and academia. For the first time the conference is arranged on a conference place including accommodation. We hope the nice location and surroundings of Sørup Herregaard will inspire to good discussions and networking between the participants and all of you will have an interesting and informative conference.

On behalf of the board of the Danish Electrochemical Society,
Torben Lund & Johan Hjelm
(Chairman) (Member of the DEF board)

Program Thursday 3/10

15.00-16.00	General Assembly in the Danish Electrochemical Society
16.05-17.00	Invited speaker: <i>Nina Balke</i> , Oak Ridge National Laboratory: Looking at Electrochemistry on a Nanoascale
17.00-17.15	Break
17.15-17.45	Invited speaker: <i>Søren Dahl</i> , Haldor Topsoe A/S: Battery Materials – an Industrial R&D Perspective
17.45-18.15	Invited speaker: <i>Peter Vang Hendriksen</i> , DTU Energy Conversion: Solid Oxide Cells and Membranes – SOFC/SOEC/Oxygen membranes
19.00-	Dinner

Program Friday 4/10

9.00-9.05	Introduction
9.05-10.00	Invited speaker: <i>Lars Kloo</i> , Royal Technical College (KTH): The Photoelectrochemical Cell – On the Fundamentals and Current Research Directions
10.00-10.30	Invited speaker: <i>Jens Oluf Jensen</i> , DTU Energy Conversion: Degradation Issues of High Temperature PEM Fuel Cells
10.30-10.50	Break



Oral presentations session 1

- 10.50-11.10 *Mathias Arenz*, i-Nano KU: The Particle Proximity Effect and its Influence on the Oxygen Reduction Reaction
- 11.10-11.30 *Ioannis Spanos*, Nano-science Center: Advances Towards Optimizing the Oxygen Reduction Reaction - A Comparative Study of Different Synthesis Approaches for $\text{Pt}_x\text{Co}_{1-x}$ Alloys
- 11.30-11.50 *Yang Hu*, Department of Energy Conversion: A New Type of Non-Platinum Oxygen Reduction Electrocatalyst
- 11.50-12.10 *Frank Allebrod*, Department of Energy Conversion: High Temperature and Pressure Alkaline Electrolysis
- 12.10-13.10 Lunch

Oral presentations session 2

- 13.10-13.30 *Karin Vels Hansen*, Department of Energy Conversion: In Situ Surface Reduction of $\text{NiO-YSZ-Al}_2\text{O}_3$
- 13.30-14.00 *Losif Fromondi*, Metrohm Autolab B.V: Electrochemical Characterization of the Photovoltaic Cells by Using the New Led Kit from Metrohm-Autolab + Measuring Raw Signals in Electrochemical Impedance Spectroscopy
- 14.00-14.20 *Jimmi Nielsen*, DTU Energy Conversion: Impedance of Porous SOFC Electrodes
- 14.20-15.20 Poster session (*Steinar Birgisson, Martin S ndergaard, Esben Dam + Iosif Fromondi, Krzysztof P. Kowalski, Rasmus Rode Mosb k, Kristian S rensen, Wan Chen, Helena I. Gomes, Guotao Sun, Karin Vels Hansen*)

Oral presentations session 3

- 15.20-15.40 *Al-Monsur Jiaul Haque*, I-nano KU: Surface Functionalization by Electrografting of Aryldiazonium Salts and its Application to Develop Biosensors
- 15.40-16.00 *Jing Shao*, Department of Energy Conversion: Electrochemical NO_x Reduction on an LSM/CGO Symmetric Cell Modified by NO_x Adsorbents
- 16.00-16:15 Closing remarks and evaluation



Inv1: LOOKING AT ELECTROCHEMISTRY ON THE NANOASCALE

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The functionality of energy storage and generation systems like Li-ion batteries or fuel cells is not only based on but also limited by the flow of ions through the device. To understand device limitations and to draw a roadmap to optimize device properties, the ionic flow has to be studied on relevant length scales of grain sizes, structural defects, and local inhomogeneities, i.e. over tens of nanometers. Knowledge of the interplay between the ionic flow, material properties, and microstructure can be used to optimize the device properties, for example to maximize energy density, increase charging/discharging rates, and improve cycling life for Li-ion batteries for applications in electric vehicles and aerospace.

Here, we present how Scanning Probe Microscopy (SPM) can be used to measure ionic transport properties on the nanoscale and extract spatially resolved maps of ionic transport based on local volume changes instead of current. This universal approach is demonstrated for electrode materials used in electrochemical supercapacitors, Li-ion batteries, and fuel cells. We will focus on the characterization of ionic transport in electrode materials in ambient and liquid environment.

We will demonstrate how the ion insertion kinetics are measured for porous carbon-based electrodes for electrochemical supercapacitors and how these kinetics are influenced by the electrode pore size. We will discuss how to measure the nanoscale transport properties such as activation energy and diffusivity for Li-ion battery thin film cathodes and will explore how the ionic transport is influenced by the electrode microstructure such as grain orientation, step edges, and mechanically induced defects. Additionally, we will demonstrate the application of SPM for oxygen conductors. Theoretical calculations are shown to support the experimental data and to give insight into the signal generating mechanism.

Support was provided by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division, Scientific User Facilities Division, and by the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center.



Inv2: Battery Materials – an industrial R&D perspective

Søren Dahl, Haldor Topsøe A/S, Nymøllevej 55, 2800 Kgs. Lyngby

Building on its expertise in development and production of functional inorganic materials for heterogeneous catalysts Haldor Topsøe is looking at the business prospective of becoming a future supplier of battery materials for Li-ion batteries and future battery technologies.

From an R&D perspective the presentation will describe some of the questions that are critical to evaluate in such a process. The aim is as soon as possible to get into a serious dialog with cell manufactures in order to learn what they require from a new battery materials supplier.

With emphasis on some of the collaboration projects we are involved in with external partners; some examples of our R&D work will also be given.



Inv 3: Solid Oxide Cells and Oxygen Membranes; opportunities and challenges

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Keywords: SOFC, SOEC, ITM, Oxygen transport membranes

Solid oxide fuel cells (SOFCs) are all solid state devices which can convert chemical energy in a fuel (e.g. methane or hydrogen) to electricity and heat with high electrical efficiency. For more than two decades Denmark has had a very strong R&D effort in the area involving industries (Haldor Topsøe A/S, Topsoe Fuel Cell) as well as academia. Department of Energy Conversion and Storage, DTU (formerly Department of Fuel Cells and Solid State Chemistry, Risø DTU) is a key player in the area. In recent years operating the same type of cells in “electrolysis mode” (running the reverse process of converting electricity and heat to chemical energy) e.g. for production of hydrogen by steam splitting has received increased attention. This is due to the fact, that if available at the right time and scale, electrolysis could become a key technology in the transition to 100 % sustainable energy systems by providing an opportunity for storage of “surplus” electricity from fluctuating sources like wind and solar and also in providing sustainable fuels for the transport sector.

Dense oxygen membranes are devices which in many respects are similar to SOFC/SOECs. If the electrolyte of the SOFC is substituted by a mixed conducting material conducting both oxide ions and electrons, the device can be used for separation of oxygen from air with high selectivity. The device is simpler than the fuel cell, as external circuitry is not needed. Such a device may be used for production of pure oxygen with lower energy consumption than with today’s technology based on either cryogenic distillation or pressure swing. Pure oxygen is an important chemical used in large quantities for steel and glass making. Oxygen membranes could also find future use in gasification of biomass and in oxyfuel schemes for coal fired power plants targeting CO₂ capture and storage.

The presentation will address opportunities for these three technologies in the future energy system and address current challenges in their development. Specifically, the value of accurate and reliable characterization techniques in the technology development will be discussed and examples of new and promising methodologies for electrochemical characterization presented.

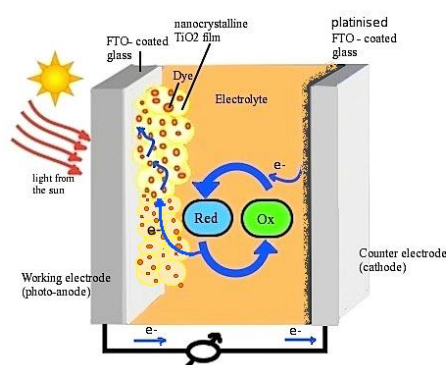


Inv 4: The photoelectrochemical cell – On the fundamentals and current research directions

Lars Kloo

Applied Physical Chemistry, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

The photoelectrochemical cell, the so-called Grätzel cell, is in essence an electrochemical cell. It consists of only three components; two electrodes and an electrolyte, just like a battery or a fuel cell. The difference from other electrochemical devices is that (at least) one of the electrodes is made photosensitive, thus generating energy-rich electrons and the energy difference between the electrodes that drives the device. A key concept of the photoelectrochemical cell is dye sensitization, just like in the old type of photography. However, in the photoelectrochemical cell it is not AgBr that is sensitized in order to respond to light of different colours. Instead, it is a wide bandgap semiconductor functioning as the support for a dye, which typically is expected to absorb as much of the solar emission wavelengths as possible, that is sensitized. The function of the dye molecules has rendered this type of solar cell its general denotation, a dye-sensitized solar cell (DSSC).



The research field obtained a boost by a pioneering publication by O'Regan and Grätzel in 1991 [1], where the use of a nanostructured, a mesoporous, form of titania as the wide bandgap support lifted conversion efficiencies from below 1% to above 7% in one swoop. The major leap in performance suddenly transformed the DSSC from a purely academic research field into a potential future commercial solar cell technology. Today, more than 3500 papers are published in refereed journals and more than 300 patents made public each year [2]. The field as such has also diversified, like a growing tree branch bifurcating into smaller branches upon growth. It now shows strong research efforts within for instance quantum-dot sensitized (qdDSSC) and various types of solid state (ssDSSC) solar cells. Today, the world records of conversion efficiencies are around 13% for liquid cells and around 15% for solid state cells with the potential to reach at least 18% in the near future. The two currently most active branches of research involve one-electron redox electrolytes in liquid cells and inorganic (so-called perovskites) hole-conducting/absorbing systems in solid state cells. The current lecture has the ambition to give an insight into the fundamentals of the DSSC, the challenges – such as long-term stability - still to be met and offer a snapshot of the current status of the research field as a whole.

1. B. O'Regan, M. Grätzel, *Nature*. **1991**, 353, 737-740.
2. A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **2010**, 110, 6595-6663.



Inv 5: Degradation issues of high temperature PEM fuel cells

*Jens Oluf Jensen, Department of Energy Conversion and Storage, Technical University of Denmark,
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High temperature PEM fuel cells (HT-PEMFC) operate at temperatures around 160°C in contrast to conventional PEMFC which cannot work at above 80-90 °C. The increased temperature makes the cells less demanding for high purity fuel and the handling of heat and water becomes very simple. This allows for a simplification of the system surrounding the cells and makes a marked cost reduction possible. HT-PEMFC is a field where Danish researchers and entrepreneurs have taken active part in the development since the very beginning in the mid nineties. Today the companies Danish Power Systems and Serenergy are in the process of bringing the technology to market as cells and stacks respectively.

One of the major challenges today is to improve and verify a long lifetime under different operating conditions. The HT-PEMFC has many materials and degradation mechanisms in common with the conventional PEM fuel cells, but a number of issues like the higher temperature and the content of phosphoric acid in the membrane impose additional challenges. A number of finding as well as an overall status will be given in the presentation.



O1: THE PARTICLE PROXIMITY EFFECT AND ITS INFLUENCE ON THE OXYGEN REDUCTION REACTION

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The main fundamental problems of polymer electrolyte membrane fuel cells (PEMFCs) to date are a low practical efficiency due to the high overpotential for the oxygen reduction reaction (ORR), the high amount of noble metal catalyst in use, and the degradation of the catalyst in a fuel cell during operation.

In order to develop improved catalysts a detailed understanding of the electrochemical interface is required - especially to clarify the relationship between the interface structure and the activity. In this study we discuss our recent work concerning the particle proximity effect. The investigated catalysts are model catalysts as well catalysts synthesised according to a recently developed "tool box principle" that allows for systematic investigations [1].

[1] J. Speder, L. Altmann, M. Roefzaad, M. Bäumer, J.J.K. Kirkensgaard, K. Mortensen, M. Arenz; "Pt based PEMFC catalysts prepared from colloidal particle suspensions – a toolbox for model studies"; Phys. Chem. Chem. Phys., 2013, 15, 3602



O2: ADVANCES TOWARDS OPTIMIZING THE OXYGEN REDUCTION REACTION: A COMPARATIVE STUDY OF DIFFERENT SYNTHESIS APPROACHES FOR $\text{Pt}_x\text{Co}_{1-x}$ ALLOYS.

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Due to their high activity for the oxygen reduction reaction (ORR), Pt based alloys are of considerable interest as catalysts for polymer electrolyte fuel cells (PEMFC). In this work we present a systematic study comparing different impregnating and colloidal (modified Ethylene Glycol based approach) synthesis protocols for preparing well-distributed and highly active $\text{Pt}_x\text{Co}_{1-x}$ alloy nanoparticles (NPs) supported on a commercial carbon black support. It is shown how individual synthesis steps, such as heating and pre-leaching influences the catalysts. In particular we focus on the effect of the Co content on the catalysts electrocatalytic performance, stability and physical properties (strain, ligand effect). Additionally we compare advantages and disadvantages of Small Angle X-ray Scattering (SAXS) over traditional Transmission Electron Microscopy (TEM) measurements for the physical characterization of catalysts.



O3: A NEW TYPE OF NON-PLATINUM OXYGEN REDUCTION ELECTROCATALYST

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Highly active catalyst for oxygen-reduction reaction (ORR) is undoubtedly essential for the practical application of fuel cells. Although precious metal group catalysts (e.g. Pt/C) show excellent activity, their limited supply and prohibitive cost preclude the large-scale use in fuel cells. Here we report a new type of non-Pt ORR catalyst, synthesized via a one-pot dry-autoclaving approach. Benefited from a unique structure, the catalyst shows excellent electrocatalytic activity and durability for the ORR. Compared with the commercial Pt/C catalyst, it exhibits the same onset and half-wave ORR potentials, better methanol tolerance and durability in 0.1 M KOH solution. In 0.1 M HClO₄ solution it also displays a high ORR activity and excellent durability.



O4: HIGH TEMPERATURE AND PRESSURE ALKALINE ELECTROLYSIS

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Alkaline electrolyzers have proven to operate reliable for decades on a large scale, but in order to become commercially attractive and compete against conventional technologies for hydrogen production, the production and investment costs have to be reduced. This may occur by increasing the operational temperature and pressure to produce pressurized hydrogen at high rate ($\text{m}^3 \text{H}_2 \cdot \text{h}^{-1} \cdot \text{m}^{-2}$ cell area) and high electrical efficiency.

This work describes an exploratory technical study of the possibility to produce hydrogen and oxygen with a new type of alkaline electrolysis cell at high temperatures and pressures. Two measurement systems were built to perform measurements under high pressures and at elevated temperatures of up to 95 bar and 250 °C, respectively. The conductivity of aqueous KOH and aqueous KOH immobilized in a porous SrTiO_3 structure were investigated at elevated temperatures and high concentrations of the electrolyte using the van der Pauw method in combination with electrochemical impedance spectroscopy (EIS). Conductivity values as high as 2.9 S cm^{-1} for 45 wt% KOH aqueous KOH and 0.84 S cm^{-1} for the immobilized KOH of the same concentration were measured at 200 °C. Porous SrTiO_3 was used for immobilization of aqueous KOH solutions. Electrolysis cells with this electrolyte and metal foam based gas diffusion electrodes were successfully demonstrated at temperatures up to 250 °C at 40 bar. Different electro-catalysts were tested in order to reduce the oxygen and hydrogen overpotentials. Current densities of 1.1 A cm^{-2} and 2.3 A cm^{-2} have been measured at a cell voltage of 1.5 V and 1.75 V, respectively, without noble metal catalysts. Electrical efficiencies of almost 99 % at 1.1 A cm^{-2} and 85 % at 2.3 A cm^{-2} were obtained.



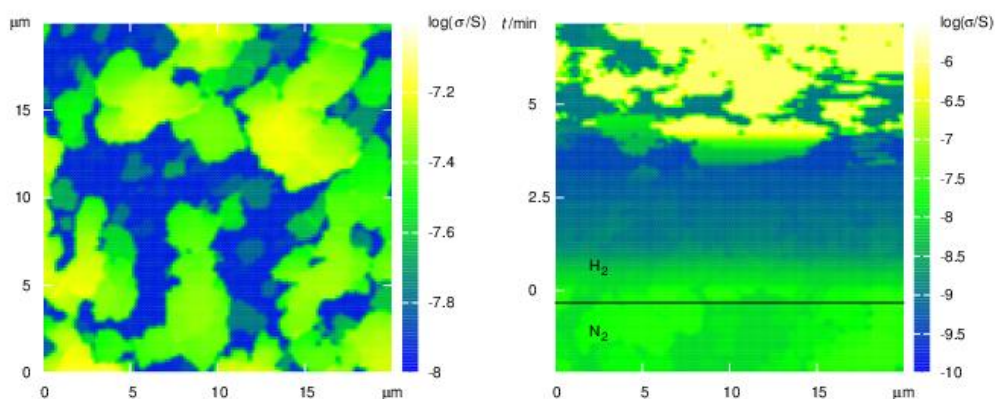
O5: IN SITU SURFACE REDUCTION OF NiO-YSZ-Al₂O₃

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In situ reductions of NiO-YSZ-Al₂O₃ composites into Ni-YSZ-Al₂O₃ cermets were carried out at 312-525 °C in a controlled atmosphere high temperature scanning probe microscope (CAHT-SPM) in dry and humidified 9% H₂ in N₂. It was possible to follow reductions by simultaneous contact mode scanning of topography and conductance. After the introduction of hydrogen, a decrease in conductance was observed indicating reduction of Ni³⁺. Later a sharp increase of the conductance is seen showing the formation of metallic Ni. The incubation time from introduction of hydrogen and until conducting Ni appeared followed the Arrhenius equation. The Arrhenius plot showed a difference in activation energy between high and low temperatures for samples reduced in a dry atmosphere. A strong retarding effect of steam on the nucleation time of Ni particles was observed.



Left: The NiO-YSZ-Al₂O₃ surface conductance before reduction.
Right: The surface conductance during reduction



O6: MEASURING RAW SIGNALS IN ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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Electrochemical Impedance Spectroscopy (EIS) involves the study of the variation of the impedance of an electrochemical system with the frequency of a small-amplitude AC perturbation. In practice, the time-domain of the input and output signals are converted into a complex quantity that is a function of a frequency. The input and the resulting output signals are hardware and software processed to yield a frequency dependent transfer function.

The Nyquist, Bode phase and Bode modulus plots are the most often used data plots in impedance spectroscopy. These plots are representations of calculated (processed) data. Because of this, it is difficult for the user to evaluate in real time or after the measurement if the measured data fulfills all the necessary conditions required for a valid EIS measurement. Moreover, if the Nyquist and Bode plots do not show the expected behavior of the system, it is difficult for the user to pinpoint the cause of the problem (e.g. noise in the system, lack of sensitivity etc.).

This presentation describes the advantage of recording the raw time domain data for each individual frequency during an electrochemical impedance measurement.



O7: Impedance of porous SOFC electrodes

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For further improvement, optimization and understanding of degradation mechanisms of porous Solid Oxide Fuel Cell (SOFC) electrodes such as e.g. the classic LSM:YSZ cathode or Ni:YSZ anode a basic understanding of the kinetics/mechanisms is important and hence the impedance spectra, which can provide such valuable information.

Impedance evaluation of such porous electrodes has despite 20-30 years of extensive research primarily been done by a fairly primitive approach consisting of a sufficient number of serial combinations of a constant phase element (CPE) in parallel with a resistor (RQ) (see e.g. the reviews [1-2]). In the present study we translate classic porous electrode theory (PET), originally developed by de Levie [3] and recently reviewed by A. Lasia [4] for a porous solid electrode in a liquid electrolyte, to the SOFC situation with a solid porous electrode and a gas phase. The translated PET model describes the co-limited situation of oxide ion conductance in the YSZ or CGO network of the composite SOFC electrode and the reaction of the electrocatalyst. The impedance of various SOFC electrodes are presented and evaluated in terms of the framework of the PET model. Fig. 1 shows the impedance and PET fits and impedance shape change as a function of temperature for a LSM:CGO composite cathode on a CGO electrolyte. The PET model has beside the ability to account for impedance shape changes as a function of temperature and a better fit than (RQ) combinations, the advantages of being able to determine parameters such as utilization thickness of the electrode and is in principle able to distinguish between a degradation due to the electrochemical reaction or the oxygen ionic conductivity within the oxygen ionic conducting material network of the electrode. Such diagnostic possibilities are highly desirable for further improvement of SOFC performance and long term durability.

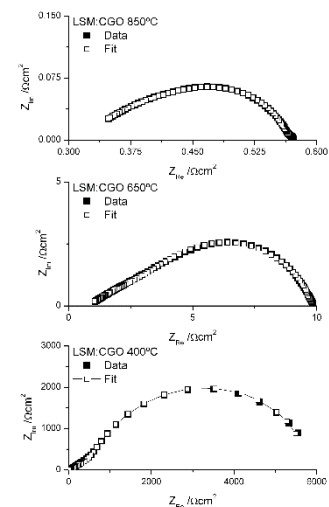


Fig. 1: EIS data and PET fits of a LSM:CGO cathode on a CGO electrolyte.

[1] M.J. Jørgensen, M. Mogensen, J. Electrochem. Soc. 148(5) (2001) A433.

[2] S. P. Jiang, J. Mater. Sci 43 (2008) 6799.

[3] R. de Levie in: P. Delahay (Eds.), Advances in Electrochemistry and Electrochemical engineering, 6 Interscience New York (1967) 329.



O8: SURFACE FUNCTIONALIZATION BY ELECTROGRAFTING OF ARYLDIAZONIUM SALTS AND ITS APPLICATION TO DEVELOP BIOSENSORS

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The formation of anchoring organic layers on electrode surfaces with desired chemical and electrochemical functions is a frequently followed procedure and a critical component in the development of biosensors and bioelectronics. Among the various methods used to form such organic layers on the electrode surfaces, the electrografting of aryldiazonium salts, introduced by Delamar et al.,¹ has become one of the best methods for surface modification because it offers many advantages compared with other methods, for example, self-assembled monolayers (SAMs). The advances are ease of synthesis of aryldiazonium salts with a wide range of functional groups and the rapid formation of stable organic layers on various surfaces such as carbon, silicon, metals, and metal oxides.¹⁻⁴ In this presentation, we present the synthesis and use of several aryldiazonium salts for functionalization of electrode surfaces, and to develop biosensors for different target molecules including antigens and neurotransmitters.^{3,4} We report the use of 1,3-dithiane, aldehyde, and amine-functionalized aryldiazonium salts for highly selective functionalization and multi-analyte detection on indium-tin-oxide (ITO) microarray electrode surfaces, producing reusable bio-functionalized surfaces, and an electrochemically reduced graphene oxide-based electrochemical immunosensor for ultrasensitive antigen detection.⁴

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O9: ELECTROCHEMICAL NO_x REDUCTION ON AN LSM/CGO SYMMETRIC CELL MODIFIED BY NO_x ADSORBENTS

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This study investigated the effect of modifying a (La_{0.85}Sr_{0.15})_{0.99}MnO₃ (LSM)/Ce_{0.9}Gd_{0.1}O_{1.95} (CGO) symmetric cell by NO_x adsorbents on the electrochemical reduction of NO_x under O₂-rich conditions. The modification was based on a full ceramic cell structure without any noble metals. Three cells were prepared and tested: a blank cell, a cell impregnated with BaO, and a cell coated with a BaO/Pt/Al₂O₃ layer. The electrochemical reduction of NO_x on the three cells was studied by conversion measurement, degradation testing, microstructure characterization, and electrochemical impedance spectroscopy (EIS). The modification, either by impregnating the BaO into the electrode or by coating the Ba/Pt/Al₂O₃ layer on the surface of the electrode, significantly increased the activity and selectivity of the NO_x reduction on the LSM/CGO symmetric cell. The cell with the BaO/Pt/Al₂O₃ layer exhibited a preferable performance at low temperatures (350 and 400 °C) and low voltages (1.5 to 2 V), although its performance was relatively poor at elevated temperatures and voltages. The impedance analysis revealed that modification with the NO_x adsorbents greatly enhanced the electrode activity. This activity enhancement was mainly due to the decrease in the resistance of the low-frequency processes, which were ascribed to adsorption, diffusion, and transfer of O₂ species and NO_x species at or near the triple phase boundary (TPB) region and the formation of the reaction intermediate NO₂. The BaO impregnation improved the adsorption of NO_x on the LSM/CGO electrode by selectively trapping NO₂ in the form of nitrate over the BaO sites and provided availability for a direct reduction of the stored nitrate. The BaO-Pt-Al₂O₃ layer enhanced the NO_x adsorption and promoted the formation of NO₂ due to the NO oxidation ability of the Pt catalyst, but hindered the gas diffusion to the reaction sites. For lowering the operation temperature and minimizing the power consumption, adding an adsorption layer was shown to be the optimum approach for modifying the electrochemical cell by NO_x adsorbents. The square-wave (SV) polarization can balance the trapping and reduction rates of NO_x species on the electrochemical cells as to further improve the NO_x reduction relative to the direct current (DC) polarization.



P1: ELECTROCHEMICAL CHARACTERIZATION OF THE PHOTOVOLTAIC CELLS BY USING THE NEW LED KIT FROM METROHM-AUTOLAB.

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Dye-sensitized solar cells (DSSC), a viable alternatives to the silicon based photovoltaic devices, are currently subject of intense research in the framework of renewable energies as a low-cost photovoltaic (PV) device. Electricity generated from a PV produces zero emissions, is modular, and can produce energy anywhere the sun shines.

In this presentation, the new LED kit from Metrohm Autolab will be presented with the possibility of applying the specific techniques used for the characterization of the DSSC: i-V characteristics, electrochemical impedance spectroscopy (EIS), Intensity Modulated Photocurrent Spectroscopy (IMPS) and Intensity Modulated Photovoltage Spectroscopy (IMVS). Also, the total integration (control and data recording) of the Avantes Spectrometers in the Nova software will be presented.

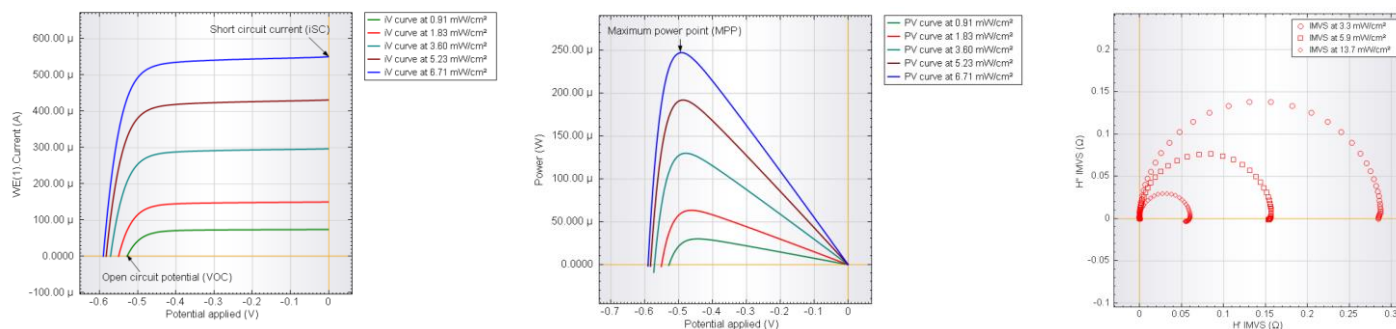


Figure 1 – Examples of i-V plot (left), power plots (middle) and IMVS plots measured on the same sample, at different light intensities by using the Autolab LED kit.



P2: COMPARISON OF THE NEW IRON DOSAGE METHODS FOR DRINKING WATER PRODUCTION

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Arsenic is considered as one of the most concerned pollutants in the world due to its adverse health effects. Therefore, its content in drinking water has been recommended to be limited to 10 µg/L (WHO 2006). One of the conventional methods for arsenic removal is based on the addition of ferrous salts that remove it with in a coprecipitation process. Recently, an extra focus has been put on other possibilities to add iron ions during the process, which can be done with help of zero-valent iron (ZVI) or electrolytic iron dissolution. Both techniques have been implemented for removal of heavy metals and arsenic and showed to be useful for this purpose (Kowalski and Søgaard 2012). ZVI is driven by spontaneous redox reactions, which limits its control and therefore optimization. However, in case of iron electrodisolution, where process is driven by the applied current to the sacrifice anode, it can be controlled, which brings main advantage in large scale water processing. However, both techniques have limitations, which results in different area of implementation. The aim of this work is to compare and evaluate new iron dosage methods by comparing the water treatment plants where ZVI and iron electrodisolution has been implemented for arsenic removal, as it is shown on the Figure 1.

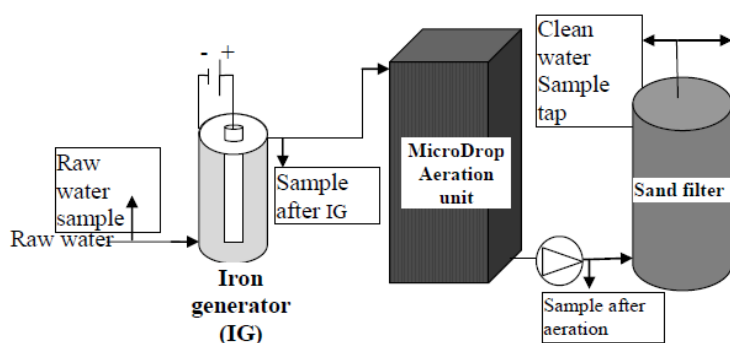


Figure 1 Incorporation of the iron electrodisolution into simple arsenic removal process

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P3: SOLID OXIDE FUEL CELL STACK DIAGNOSTICS

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As solid oxide fuel cell (SOFC) technology is moving closer to a commercial break through, lifetime limiting factors, determination of the limits of safe operation and methods to measure the “state-of-health” of operating cells and stacks are becoming of increasing interest. This requires application of advanced methods for detailed electrochemical characterization during operation.

An experimental stack with low ohmic resistance from Topsoe Fuel Cell A/S was characterized in detail using electrochemical impedance spectroscopy. A 13-cell experimental SOFC stack was tested during 2,500 hours of continuous operation with hydrogen as fuel with 52% fuel utilization and constant current load (0.2 A cm^{-2}) at 750°C . Stack interconnects were coated with six different coatings to prevent chromium poisoning on the cathode side. Four repeating units with different coatings were selected for detailed impedance analysis. Electrochemical Impedance Spectroscopy allowed a distinction to be made in terms of the degradation between the four repeating unit types that is not possible from IV-data only.



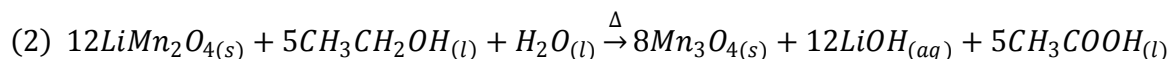
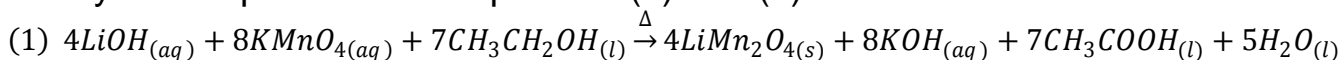
P4: IN-SITU SYNCHROTRON PXRD STUDY OF SPINEL LiMn_2O_4 NANOCRYSTAL FORMATION

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Many solvothermal reactions have a great potential for environmentally friendly and easily scalable way for producing nanocrystalline materials on an industrial scale. Here we study hydrothermal formation of spinel LiMn_2O_4 which is a well-known cathode material for Li-ion batteries. The LiMn_2O_4 nanoparticles are formed by reducing KMnO_4 in an aqueous solution containing Li-ions. The reducing agent is an alcohol (here ethanol) and the reaction takes place under high pressure and temperature. The LiMn_2O_4 nanocrystals are unstable towards further reduction to Mn_3O_4 nanocrystals. Possible reaction route for this system is presented in equations (1) and (2).



Our group has developed an experimental technique for in-situ measurements of solvothermal reactions under sub- and supercritical conditions [Becker et al, J. Appl. Crystallogr. (2010) 43]. The technique uses synchrotron X-ray radiation to measure time resolved powder x-ray diffraction patterns while the reaction is happening thereby giving real time information on crystalline phase formation, particle sizes and other structural properties for the reaction being studied.

In-situ measurements at different reaction temperatures have been conducted to see how the formation rate and particle growth is affected by temperature while the precursor concentration is kept constant. The precursor solution is an aqueous solution with Li:Mn:EtOH molar ratio of approximately 1:2:7 and the reactions conditions are constant temperature at 220°C, 260°C, 300°C, 350°C and 400°C at 250 bar.

First results show the formation of the LiMn_2O_4 and Mn_3O_4 phases, the growth of the nanocrystals of each phase and evolution of structural properties (such as unit cell constants) as a function of reaction time. Further analysis will involve estimation of reaction rate constants and activation energies for each of the reactions for better understanding of the hydrothermal reaction system.



P5: TiO₂ NANOPARTICLES FOR LI-ION BATTERIES

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For several years TiO₂ has been considered a very promising alternative to graphite as anode material in Li-ion batteries.¹ TiO₂ exists in several crystal structures of which anatase, rutile and TiO₂(B) are the most promising for Li-ion batteries. The maximum theoretical capacity of TiO₂ in various polymorphs is 335 mAh/g compared with 372 mAh/g for graphite and 175 mAh/g for Li₄Ti₅O₁₂. The potential for Li-insertion/extraction in TiO₂ is in the range of 1.0-2.5 V vs. Li-Li⁺, whereas the working potential of graphite is below 0.2 V. While the higher working potential results in lower energy density, it also implies that the formation of solid-electrolyte interface (SEI) layer is avoided, and thus may give increased safety, stability and cycle and shelf life. Furthermore, TiO₂ exhibits good low-temperature properties² and the good rate performance of TiO₂ nanoparticles may give superior power density compared with graphite. Depending on the synthesis and processing the price of TiO₂ and graphite may be comparable, and therefore TiO₂ could soon find its way into commercial Li-ion batteries.

In this work TiO₂ anatase and rutile nanoparticles are synthesized by facile, scalable, low-temperature and hydrothermal methods. The structural properties, including particle size, morphology, crystallinity and specific surface area are investigated by Rietveld refinement of Powder X-ray Diffractograms (PXRD), Transmission Electron Microscopy (TEM) and the Brunauer-Emmett-Teller method (BET). The structural properties are related to the electrochemical Li-insertion/extraction at various currents in half-cells, with Li as counter electrode.

Furthermore, in-situ X-ray diffraction is performed on half-cells while charging/discharging.

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P6: CHARACTERISATION AND MODIFICATION OF GERMAN SILVER SURFACES

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In this work modification of German silver (i.e. a copper alloy with nickel and zinc) surfaces by means of electrografting of aryldiazonium salts is presented. The aim is to prepare polymer brushes on these surfaces to, ultimately, create watertight junctions between the metal and a given polymer coating.

First, elemental surface analysis of German silver was recorded by X-ray photoelectron spectroscopy. A great variation was seen from sample to sample, but, in general, the amount of copper, nickel and zinc was found to be 31.7:36.6:31.7 with traces of calcium, sodium and chloride detected.

Surface modification was then attempted with 9,10-dioxo-9,10-dihydroanthracene-2-diazonium tetrafluoroborate on cylindrical rods (d = 1.0 mm; l = 6.0 mm). The electrografting was accomplished in a cyclic voltammetric procedure using a specialized holder for the rods to optimize a homogeneous grafting of the curved surface as much as possible (Figure 1). Importantly, a linear relationship between the polymer layer thickness—measured by ellipsometry in dry state—and the number of voltammetric sweeps was observed, showing that the modification of German silver indeed may be carried out in a controlled manner.

Comparative studies were carried on similarly sized glassy carbon rods having focus on surface coverage and electron transfer resistance determinations. Both were found to be smaller for German silver, suggesting that slightly less dense organic layers would be formed on this material. Also, it was noted that the films on German silver, in general, was less homogeneous than those on glassy carbon.



Figure 1. Homebuilt holder used in the electrografting of German silver.



P7: ELECTRODIALYTIC BIO-ASH TREATMENT – DETOXIFICATION AND USE OF TREATED ASH IN BRICKS

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Electrodialytic remediation (EDR) can be used to extract heavy metals and nutrients simultaneously from an ash body. In this study, EDR was applied to bio fly ash and bottom ash from straw and wood combustion. A set of experiments were carried out with fly ash as received, washed fly ash, bottom ash and washed bottom ash.

High cadmium contents (over 9 mg/kg based on dry mass) in the studied fly ashes make their direct return to agricultural land as fertilizer infeasible. On the other hand, high soluble salts content, mainly KCl, will cause a low, transference number for heavy metals during EDR. A 3-stage washing process was used to decrease the amount of soluble salts and a reduction of the chloride concentration to around 0.2% by dry mass in the ash was obtained. An X-ray diffraction study of the washed ash shows no KCl peaks.

By EDR the cadmium concentration was decreased to below the limiting value (5 mg/kg) set for straw ash reuse in Danish legislation. A removal efficiency of more than 80% was obtained. The bottom ash from the same boiler was non-toxic, and after remediation some heavy metal concentrations were higher than before, but still much lower than the limiting values.

The mineral compositions in the treated ashes were investigated by X-ray diffraction. SiO_2 is the main crystalline phase found in the ashes which suggests the possible reuse in the building materials, like brick. Therefore, the sintering behaviour was studied on small brick pellet specimens made from a mixture of 25 % fly ash and 75 % clay. The results show that the fly ash could be used to replace some part of the clay to produce low density and more porous clay bricks.



P8: ENHANCED ELECTROREMEDIATION OF PCB CONTAMINATED SOIL: PRELIMINARY RESULTS

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Polychlorinated biphenyls (PCB) are a group of 209 different congeners, classified as Persistent Organic Pollutants by the Stockholm Convention, and widely used in industrial applications between the 1930s and 1980s. Although the European Union restricted its use in 1985, given its chemical stability and toxicity, PCB continue to pose serious risks to both human health and ecosystems through bioaccumulation. It is necessary to find alternative remediation solutions for PCB contaminated soils and sediments, as incineration and disposal in an off site landfill are unsustainable.

Recent trends in soil remediation show that treatment trains (use of multiple technologies either sequentially or concurrently) can be more efficient for contaminants like PCB. In this work, we tested different substances to enhance the electroremediation of a PCB contaminated soil provided by a hazardous waste operator in Portugal. These substances targeted the PCB desorption, dechlorination and transport. The addition of surfactants (Tween 80 and biosurfactants), β -cyclodextrin, and the electro-Fenton process (with the addition of H_2O_2), were tested in conjunction with electrokinetics and zero valent iron nanoparticles (nZVI).

Preliminary results show that the addition of surfactants and β -cyclodextrin did not enhance the effectiveness of the electroremediation of the contaminated soil in the tested conditions. The transport of iron nanoparticles can be enhanced by the action of the electric current. However, there was rapid corrosion and aggregation of nZVI, limiting PCB effective dechlorination.

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P9: The initiation process as a crucial step in maximizing the efficiency of Microbial Fuel Cell Systems

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Microbial fuel cell systems (MFCS) have in the recent 10 years gained great interest for bioconversion of organic substrate into electricity and hydrogen due to the use of sustainable resources such as wastewater. MFCS are therefore considered as a potential technology for power generation by treating wastewater. The mechanism of power generation in MFCS has mainly been investigated with focus on the microbial community formation, effect of substrate on anode reaction and the cathode catalytic property.

To improve the performance of a MFCS, the initiation process requires more investigation because of its significant effect on the anodic biofilm formation. The key message is that optimal performance of MFCS requires the initial stage feeding with acetate, which favours the electrogenic bacterial biofilm formation followed by the use of target substrate. The reason is that some substrates such as glucose facilitate the growth of fermenting bacteria, which do not produce electricity since many electrogenic bacteria cannot metabolize glucose. Initiation of the MFCS using acetate is thereby a prerequisite for electricity production in a MFCS.



P10: IN SITU SCANNING PROBE MICROSCOPY

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The controlled atmosphere high temperature scanning probe microscopes (CAHT-SPMs) are versatile scanning probe microscopes working at temperatures up to 850 °C in an active atmosphere. A fine probe is used to scan the surface and techniques such as scanning surface conductance, Kelvin probe microscopy, conductive AFM and scanning tunneling microscopy can be used to acquire lateral information about the surface properties. Further, stationary measurements such as electrochemical impedance spectroscopy and scanning tunneling spectroscopy can be performed at selected locations. The microscopes specifications are presented and examples of the different modes and are demonstrated.



P11: Three-dimensional Nanofiber Cathode for Low Temperature and High Temperature Fuel Cells

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Electrochemical devices for clean energy conversion such as proton exchange membrane fuel cells (PEMFCs)¹⁻³ and solid oxide fuel cells (SOFCs)⁴⁻⁵ are currently and for the foreseeable future very much in the spotlight. Although these developing energy technologies have seen a rapid development, new break-through developments are needed to improve their durability, efficiency, power density and cost to make them commercial viable.

Electrospinning provides possibilities of generating composite networks from a rich variety of materials with the ability to control composition, morphology and secondary structure. Moreover, it is easy to scale up for industrial production. This simple and versatile method has been used in this research to address the sizable challenges facing those involved in materials research into energy conversion devices.

The objective of this poster is to show the potential of electrospinning in designing nanostructures of both organic and inorganic materials in electrochemical devices. Herein, we present results on 1) Nafion/ Pt-C composite cathodes for PEMFCs; 2) LSCF nanofiber cathode for SOFCs. Exceptionally high power densities and platinum mass activity are achieved when using the nanofiber mat as cathode in PEMFCs. The nanofiber cathode also exhibits outstanding stability in accelerated durability tests.⁶ In case of SOFCs, lanthanum strontium cobaltite ion perovskite nanofibers with controllable nanostructure were synthesized by combining sol-gel synthesis, electrospinning and sintering.

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P12: PERFORMANCE OF ELECTROLYTE SUPPORTED SOLID OXIDE FUEL CELLS WITH STN94 ANODES

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P. Holtappels¹ and T. Ramos¹**

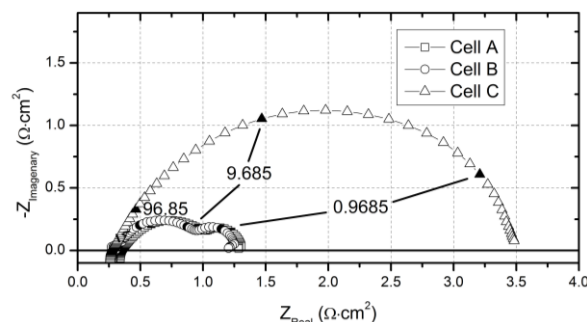
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In order to replace the state of the art Ni-cermet as SOFC anode, electrolyte supported cells comprising CGO/Ni infiltrated Nb-doped SrTiO₃ anodes, and LSM/YSZ cathodes have been developed and tested as single 5 x 5 cm² cells. The initial performance reached 0.4 W/cm² at 850 °C. Further tests under high fuel utilization and redox cycling have been performed to identify the performance limiting parameters in this new type of full ceramic SOFCs. Measured performances and stability have been further tentatively linked to modifications of the nano-sized infiltrates within the anode.

In the present work, electrolyte supported fuel cells (ESCs) with STN-based fuel electrodes (16 cm² area) were fabricated and infiltrated with CGO/Ni electrocatalysts, in order to evaluate their electrochemical performance under fuel cell operating conditions. An attempt is also made to correlate the performance of the fuel cell with the behavior of the electrocatalytic material. The microstructural features of the electrocatalytic material before and after test were compared, and possible reasons for the changes in electrochemical performance are discussed.

Electrocatalyst precursors CGO/Ni solution, in the form of aqueous nitrate solution, were infiltrated into the anodes and heat treated at 350°C for 2 h in air. Cells B and C were subsequently heat-treated in air at 1000°C, and cell C was heated to 1000°C, 2 h during the sealing period.



Nyquist-plots of the impedance spectra recorded for cells A, B and C at 850 °C, OCV, with 4% humidified H₂ at the anode and air at the cathode.



P13: ELECTRO-OXIDATION OF PULP AND PAPER MILL WATERS

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Interest in water treatment by electrochemical methods has grown in recent years. Electro-oxidation has been applied particularly successfully to degrade different organic pollutants and disinfect drinking water.

Electro-oxidation technique was used in inactivating different primary biofilm forming paper mill bacteria as well as sulphide and organic material in pulp and paper mill wastewater in laboratory scale batch experiments. Three different electrodes, boron-doped diamond (BDD), mixed metal oxide (MMO) and PbO₂, were employed as anodes. The impact on inactivation efficiency of parameters such as current density and initial pH or chloride concentration of synthetic paper machine water was studied. The electrochemical behaviour of the electrodes was investigated by cyclic voltammetry with MMO, BDD and PbO₂ electrodes in synthetic paper mill water as also with MMO and stainless steel electrodes with biocides.

Aerobic paper mill bacteria species (*Deinococcus geothermalis*, *Pseudoxanthomonas taiwanensis* and *Meiothermus silvanus*) were inactivated effectively (>2 log) at MMO electrodes by current density of 50 mA/cm² and the time taken three minutes. In real paper mill effluent treatment sulphide oxidation was effective with all the different initial concentrations (almost 100% reduction, current density 42.9 mA/cm²) and also anaerobic bacteria inactivation was observed (almost 90% reduction by chloride concentration of 164 mg/L and current density of 42.9 mA/cm² in five minutes). Organic material removal was not as effective when comparing with other tested techniques, probably due to the relatively low treatment times.

The results of the experiments showed that electrochemical oxidation could be used in paper mill waters for planktonic bacteria removal. Applying this technique together with some biocides can enhance the oxidation process, keeping the paper mill pipelines clean of slime formed by bacteria. Electrochemical oxidation is also a promising preliminary or tertiary treatment process in pulp and paper mill wastewater treatment, especially against refractory organic compounds which cannot be removed by biological processes.



P14 : An electrochemical cell for PXRD study on Li/Na ion battery at operando

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Li-ion batteries (LIB) have achieved a great success as portable power for consumer electronics in the last few decades, and it is now one of the most extensively studied energy storage devices.¹⁻³ The electrochemical performance of LIB is mainly limited by the structural evolution of the electrode materials during cycling. Hence, an in-depth understanding of the working mechanism and structure change of the electrode materials upon the LIB operation is crucial for further development of this technology. X-ray diffraction (XRD) is a powerful tool for probing structural information in atomically ordered materials. Especially the development of specialized batteries for *in situ* XRD measurement provides a real-time understanding of critical structural processes occurring at the electrodes during the battery operation. This technique is crucial for getting insight the reaction mechanisms and material stability of electrode materials under actual electrochemical processes. Most of the conventional *in situ* XRD cells are designed in a special shape that is different from the coin cells (for example they may use fragile glass capillary tubes⁴ or Swagelok-type⁵) and are targeted for use at synchrotrons, which are difficult to access. Moreover, beryllium is usually used as X-ray window.⁶ Since beryllium dissolves in a liquid electrolyte when raised above 3 V, plastic electrode need to be used for preventing the direct contact between the electrolyte saturated cathode and the beryllium window. This makes the cell structure complex and increases the absorption of the X-rays. In this work we have designed an easily assembled electrochemical cell allowing for *in situ* XRD on an ordinary laboratory X-ray diffractometer without the use of any beryllium components. This makes in situ studies easily accessible, cheap and safe. The cell is very well sealed, operates in reflective mode and allows fast data acquisition with good data quality. The key feature of our novel design is a very thin hemispherical graphite dome serving as the X-ray window and sealing component. We have also employed commercially available coin cell parts as the electrochemical cell body, which are easy to assemble and allow us to measure the electrode material in exactly the same condition as in a normal coin cells. Thus, the performance of the cells studied by in situ PXRD compare well with normal coin cells. The setup provides information about structural changes in the active material as the cell is repeatedly charged and discharged. Figure 1 shows the global picture of the *in situ* cell.

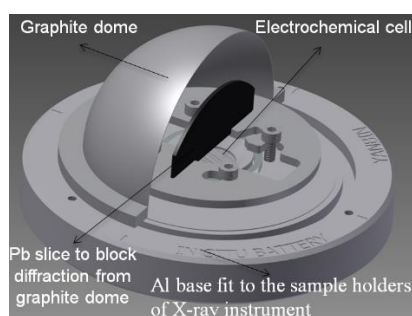


Figure 1. Global picture of the *in situ* battery

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P15: ELECTRODIALYTIC PHOSPHORUS RECOVERY DURING MUNICIPAL WASTEWATER TREATMENT FOR IMPROVED PLANT-AVAILABILITY IN SEWAGE SLUDGE (ASH)

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To sustain the global demand for agricultural products over the coming centuries, it is vital to maintain a constant supply of phosphorus (P). With current and predicted consumption rates, in the worst case scenario, the primary source of P reaches its production around 2033 and reserves will only last an estimated 50-100 years. Secondary sources, e.g. municipal wastewater and sewage sludges, become increasingly more important. However, P recovery from these sources is often restricted by both organic and inorganic contaminants as well as the applied wastewater treatment techniques. Most of these techniques focus on the production of clean water, not the recovery of nutrients. P removal from wastewater, in addition to biological processes, is often achieved by chemical coagulation, where iron or aluminium salts are used to bind P in the sludge. The formed coagulants are highly insoluble and their presence significantly reduces the plant-availability and recovery of P from the resulting sludge and if incinerated, sludge ash.

Phosphorus (P) in the form of ortho-phosphate ($H_mPO_4^{m-3}$) is extractable using electrodialysis (ED). ED is a form of electro kinetics where a current is used to transport charged complexes from a solution regulated by ion-exchange membranes. The main benefit of using ED to extract P during wastewater treatment is the reduced need for chemical coagulants, resulting in lower sludge production, increased plant-availability of P and the recovery of a pure fraction of P. In addition, ED can also be used to recovery heavy metals where concentrations exceed legislated limits. The efficiency of ED for the recovery of P or removal of heavy metals depends significantly on wastewater and sludge characteristics. In order to apply ED under the most optimal conditions, in combination with the most common wastewater treatment techniques, it is essential to identify these key characteristics and determine how they change through wastewater treatment. This study shows that ED can effectively be used to recover P and remove heavy metals from sewage sludge during several stages in wastewater treatment. It has also identified some of the key characteristics that influence ED efficiency, such as organic matter content and buffer capacity, but stresses the need for further investigation.