

Two day conference

Electrochemical Science and Technology

29th and 30th September 2011

at

University of Southern Denmark in Odense



Organized by:

Danish Electrochemical Society

In partnership with **ATV•SEMAPP**

Organizing committee:

Eivind Skou, University of Southern Denmark
Torben Lund, Associate Professor, Roskilde University

Sponsors:



Dansk Elektrokemisk Forening

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ATV•SEMAPP

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

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PROGRAMME:

Thursday the 29th September

- 14:30 – 15:00 **Arrival to SDU**
Auditorium 2, Niels Bohrs Allé 1, Odense M
- 15:00 – 16:00 **General Assembly in the Danish Electrochemical Society**
For members and guests.
- 16:00 – 16:05 **Welcome**
Eivind Skou, Department of Civil Engineering, SDU

Mini Symposium: Energy Storage for future demands

- 16:05 – 16:35 **Tejs Vegge**, DTU-Risø: Lithium-air batteries – potentials and challenges
- 16:35 – 17:05
Steen Yde-Andersen, IRD: Development of PEM and DMFC fuel cells and their application in private and professional setups
- 17:05 – 17:35
Jan H. Hales, DTI, Taastrup: Methanol driven Micro Fuel Cells for Hearing Aids
- 17:35 – 19:00 **Check-in at hotels**
- 19:00 **Conference Dinner**
Restaurant Kvægtorvet
Rugårdsvej 25
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Friday the 30th of September

- 09:00 – 09:05 **Opening of the conference**
Torben Lund, Department of Nature Systems and Models, Roskilde University, Chairman of the Danish Electrochemical Society
- 09:05 – 09:55 **Invited Talk:**
Leif Nyholm, Uppsala University: Electrochemistry in detection and energy storage

Oral presentations Session 1: Surface coatings

- 09:55 – 10:25 **Kim Daasbjerg et al**, AU: Using a Mediating Effect in the Electroreduction of Aryldiazonium Salts to Prepare Thick Conducting Organic Films
- 10:25 – 10:40 **Coffee break**
- 10:40 – 12:00 **Mogens Hinge et al**, Electrochemical assisted immobilization of mono functionalized β -cyclodextrins via phenyl diazonium grafting.
- Kristian Torbensen et al**, Scanning Electrochemical Microscopy (SECM)
- Martin Aggerbeck et al**, Corrosion protection and optical influence from Ti in aluminium based plasma coatings
- Svava Daviðsdóttir et al**, Investigation of photo-catalytic activity of titanium dioxide deposited on metallic substrates by plasma technique **Presentation by Rajan Ambat**
- 12:00 – 13:00 **Lunch**
- Oral presentations Session 2:
Environmental electrochemistry and Fuel cells**
- 13:00 – 14:20 **Jens Muff et al**, Application of electrochemical oxidation for degradation of aqueous organic pollutants
- Gregory Johnson et al**, Sulphur poisoning of SOFC's: Cell performance, electrochemical characterisation and impact of operating parameters
- Anders Harthøj**, Electroplating of Solid Oxide Fuel Cell Interconnects: Modelling of the current distribution
- Eivind M. Skou et al**, Durability of carbon nanofiber (CNF) & carbon nanotube (CNT) as catalyst support for proton exchange membrane fuel cells
- 14:20 – 15:20 **Poster Session and coffee**

Yuehua Wu et al, In-situ Investigation of Microelectrodes Using Controlled Atmosphere High Temperature SPM

Anders Thygesen et al, The effect on electricity production in MFC of the electrode area and substrate in the anode

Ane S. Christiansen et al, LiBH₄-LiI Mixtures as solid electrolytes for lithium Batteries

Daði Þ. Sveinbjörnsson et al, LiBH₄-LiI Solid Solutions as a Solid Electrolyte Material

Phuong Tuyet Nguyen et al, The performance of dye sensitized solar cells with 4-tert-butylpyridine and 1-methylbenzimidazole N719 substituted ruthenium dyes as sensitizers **Presentation by Torben Lund**

Daniel Risskov Sørensen et al, Development of highly efficient water electrolyzers

Sune Veltzé et al, Differences in oxygen reduction catalysis of platinised acid treated showa denko carbon nanofibres

Lisbeth Ottosen et al, Electrokinetic desalination – pilot scale tests

Curt Sander et al, Title to come - **expected to come (26th September)**

Oral presentations Session 3: Biosensors

15:20 – 16:00 **Jaime Casteillo et al**, Self assembled peptide nanostructures: A new option for the development of biosensors

Nicolaj Cruys-Bagger et al, Application of enzyme-modified electrodes based on cellobiose dehydrogenase in cellulose research

16:00 – 16:15 **Student Awards**

16:15 – 16:25 **Closing remarks**

Mini Symposium
Thursday 29th September
16:05 – 17:35



LITHIUM-AIR BATTERIES – POTENTIAL(S) AND CHALLENGES

**Tejs VEGGE¹, Jens S. HUMMELSHØJ², Jingzhe CHEN³, Jon S G. MYRDAL¹,
Kristian THYGESEN³, Alan C. LUNTZ², Jens K. NØRSKOV²**

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Secondary lithium-air batteries offer up to 10 times the gravimetric energy density of Li-ion batteries by use of air-electrodes, where the metal ions react with O₂ during discharge. The technology is known from primary Zn-air batteries and Li-air batteries have been shown to be rechargeable, but only at excessive overpotentials at charging and a poor cycle life [1]. The overpotential, i.e. the difference between the equilibrium potential ($U_0=2.96$ V for Li/Li₂O₂) and the voltage during current-flowing conditions, is found to depend explicitly on the current density.

Using density functional theory (DFT) calculations, we present a fundamental mechanism which captures the underlying physics of the charge/discharge processes. The calculations show that the kinetic overpotential for charging is significantly lower than the >1.0 V often reported for typical current densities around 0.1 mA/cm₂. The critical charging process is found to be limited by poor electron transport through the insulating Li₂O₂ discharge deposits in the cathode once it exceeds a few nanometers, leading to premature, sudden death of the discharge and cause significant overpotentials during charging. Both aspects imply important limitations for reversible battery performance, i.e. a poor power-capacity tradeoff in discharge and electrolyte degradation in charging, which must be solved for Li-air batteries to become commercially viable. We show that electronic conduction properties can be improved if defects like lithium vacancies are present in the Li₂O₂ layer.

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[2] J. S. Hummelshøj, J. Blomqvist, S. Datta, T. Vegge, J. Rossmeisl, K. Thygesen, A. C. Luntz, K. W. Jacobsen, J. K. Nørskov, Elementary oxygen electrode reactions in the aprotic Li-air battery, J. Chem. Phys. Communication 132, 071101 (2010).

[3] J. Chen, J.S. Hummelshøj, K. Thygesen, J.S.G. Myrdal, J.K. Nørskov and T. Vegge: The role of transition metals interfaces on the electronic transport in lithium-air batteries, Catalysis Today 165, 2 (2011).



DEVELOPMENT OF PEM AND DMFC FUEL CELLS AND THEIR APPLICATION IN PRIVATE AND PROFESSIONAL SETUPS.

Steen YDE-ANDERSEN, R&D Manager, IRD Fuel Cells A/S

The step from small-scale prototype manufacturing to real products for making fuel cells a commercial success is a major challenge.

Materials performance and their impact of the various operating conditions, study of components integrity is mandatory to tailor the right approach leading to further performance enhancement, reduced cost and enhanced durability.

The presentation will include discussion of the state-of-the art materials, their performance and latest results from the development aimed for commercial fuel cell applications.



METHANOL DRIVEN MICRO FUEL CELLS FOR HEARING AIDS

**Jan H. HALES¹, Torsten LUND-OLESEN, Christian KALLESØE, Yihua YU,
Drew ROSSKELLY, Leif H. CHRISTENSEN**

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One of the major challenges faced by hearing aid users is changing the small button cell batteries. The exchange frequency is currently one week on average but will increase as the functionality of the hearing aids increases, e.g., wireless streaming of music. The presented project aims at replacing the standard zinc-air batteries with methanol based fuel cells of the type *Direct Methanol Fuel Cells* (DMFC). The goal is to develop a highly efficient fuel cell, which will provide the required energy density for powering a hearing aid while featuring a volume that enables complete integration. Through a small docking station the integrated fuel cell can easily be replenished with methanol in less than 30 seconds. Existing rechargeable systems, based on NiMH batteries, requires several hours of recharging. In order to down-scale the fuel cell several elements have to be investigated. The catalytic efficiency has to increase, yet without increasing the catalyst loading to ensure low cost. This requires a research effort in developing new techniques and methods for synthesising and depositing catalyst particles. Furthermore, the proton conducting membrane has to be optimized, compared to the preferred NafionTM membrane, with respect to methanol permeability. Finally the encapsulation of the fuel cell has to be engineered to provide as much volume for fuel as possible, while retaining the required electrical, mechanical, and fluidic properties. Initial results from these main areas will be presented along with the project vision and goals.



Figure 1. Project components under development. From the left is shown the micro fuel cells, the cross-section of the fuel cell, a hearing aid with integrated fuel cell and on the right the docking station.

Acknowledgement

The authors would like to acknowledge both the Danish National Advanced Technology Foundation for partly funding the project and the associated project partners: Widex A/S, DTU Nanotech, and iNano/Chemical Institute at AU.

Invited talk
Friday the 30th September
09:05 – 09:55



ELECTROCHEMISTRY IN DETECTION AND ENERGY STORAGE

Leif NYHOLM

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This lecture will be focussed on the use of electrochemical methods and reactions for miniaturised detection and energy storage. The possibilities and drawbacks of on-line couplings of electrochemistry to electrospray mass spectrometry (EC/ESI-MS) [1,2] will be discussed as well as different approaches [3] for electrochemical detection in lab-on-a-chip devices.

Electrochemical deposition of nanostructured materials for Li-ion batteries [4,5] will likewise be discussed with particular emphasis of the design of materials for 3-dimensional Li-ion microbatteries.

In addition, it will be shown that porous conducting paper-based composites, based on cellulose and polypyrrole, can be used as an inexpensive and flexible material in energy storage [6,7] and biomolecular [8] applications.

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- 2 C. Zettersten, M. Co, S. Wende, C. Turner, L. Nyholm, P. J. R. Sjöberg, *Anal. Chem.*, 81 (2009) 8968.
- 3 O. Ordeig, N. Godino, J. del Campo, F. X. Munoz, F. Nikolajeff, L. Nyholm, *Anal. Chem.*, 80 (2008) 3622.
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- 5 K. Edström, D. Brandell, T. Gustafsson, L. Nyholm, *Electrochem. Soc. Interphase*, 20 (2011) 41.
- 6 G. Nyström, A. Razaq, M. Strømme, L. Nyholm, A. Mihranyan, *Nano Lett.* 9 (2009) 3635.
- 7 L. Nyholm, G. Nyström, A. Mihranyan, M. Strømme, *Adv. Mater.* (2011) DOI: 10.1002/adma.201004134.
- 8 A. Razaq, M. Strømme, L. Nyholm, A. Mihranyan, *ECS Trans.*, 35 (2011) 135.

Oral presentation Session 1: Surface coatings
09:55 – 12:00

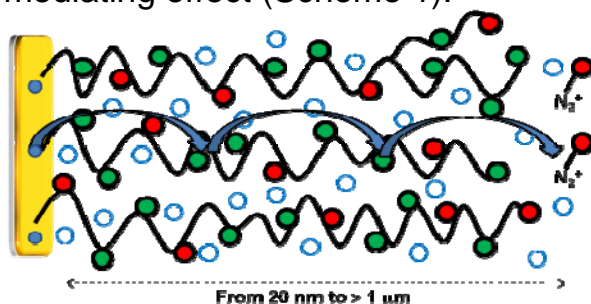


USING A MEDIATING EFFECT IN THE ELECTROREDUCTION OF ARYLDIAZONIUM SALTS TO PREPARE THICK CONDUCTING ORGANIC FILMS

Kim DAASBJERG, Antoine BOUSQUET, Marcel CECCATO, Mogens HINGE, and Steen U. PEDERSEN

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Extended cyclic voltammetric sweeping on aryldiazonium salts carrying an electroactive moiety (e.g., nitrobenzene, anthraquinone or benzophenone) allows the formation of thick conducting films, even in the micrometer size range, in a controlled manner in acetonitrile.¹ The method can successfully be carried out on various types of conducting materials such as carbon and metals. In many aspects, the electrochemical behavior resembles that of electroactive polymers but with the important notion that the films produced herein are covalently attached at the surfaces. The growth mechanism involves two concomitant phenomena, i.e., continuous layer opening through desorption of physisorbed species and the mediating effect (Scheme 1).



Scheme 1. Proposed Model Describing the Film Growth during Potential Sweeping on Aryldiazonium Salts Carrying an Electroactive Moiety.

In this respect, the use of the sweeping technique is essential for the diazonium salts studied herein, noticing that the film growth comes to a halt already at a thickness of a few nanometers, if the surface film is created by way of potentiostatic electrolysis. The redox moieties are the central units in the transport of electrons from the surface to aryldiazonium molecules at the outer layer. In particular, surface-immobilized nitrophenyl groups are found to be efficient, because of the fact that they, upon reduction, are able to reduce the corresponding diazonium salt with a high rate while, at the same time, having the required chemical stability against being irreversibly protonated by the residual water in acetonitrile.

In future studies, it would be interesting to investigate the prospect of using these thick films, which exhibit large electrochemical signals, as sensors.

References

- (1) Bousquet, A.; Ceccato, M.; Hinge, M.; Pedersen, S. U.; Daasbjerg, K. *Mater. Chem.* **2011**, 23, 1551–1557.



ELECTROCHEMICAL ASSISTED IMMOBILIZATION OF MONO FUNCTIONALIZED β -CYCLODEXTRINS VIA PHENYL DIAZONIUM GRAFTING.

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Surfaces modified with cyclodextrins (CD) have a large potential within many scientific and industrial applications (e.g. for liquid chromatography¹ and other separation processes²). Previous examples of surface immobilization of CD have been performed by thiol chemistry on gold surfaces (SAM)³, by silane chemistry on silicium surfaces⁴ and recently by an *in situ* diazotation route on glassy carbon⁵. The obvious reasons for pursuing the diazonium route are on one hand the vast amount of materials on which the diazonium grafting can occur and secondly the physical and chemical stability of the grafted layer.⁶

In the present approach a β -CD have been linked via Click-chemistry to meta or para phenyl diazonium salt (mDZ- β -CD and pDZ- β -CD, respectively). pDZ- β -CD and mDZ- β -CD were successfully prepared by Cu(I) catalyzed azide alkyne coupling of 6-monodeoxy-6-monoazido- β -cyclodextrin and 4-ethynylaniline and 3-ethynyl-aniline, respectively, followed by diazotization. The intermediates and final products were verified by ATR-FTIR, ¹H-NMR and HSQC. The synthesis route is illustrated in Fig. 1.

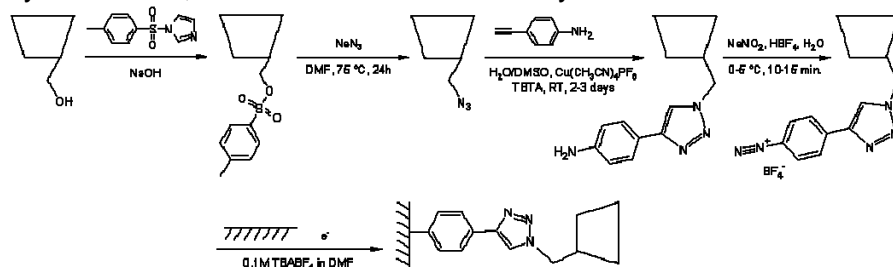


Fig. 1: Summary of the entire synthesis route illustrated for pDZ- β -CD

CD were electrografted onto glassy carbon and gold surfaces either via cyclic voltammetry (CV) or by potentiostatic electrolysis. The modified surfaces were investigated by CV using $K_3Fe(CN)_6$ as redox probe to analyse the extent of blocking of the surfaces. The ability of the CD to complex ferrocene was also studied with CV. Polarization Modulation Infrared Reflection Absorption Spectroscopy (gold only) was used to spectroscopically verify the surface modification. Results clearly showed that both pDZ- β -CD and mDZ- β -CD were efficiently grafted onto the surfaces and that the bound CD were indeed able to form inclusion complexes.

¹ Hattori, K.; Takahashi, K. *J. Chromatography A*, **1986**, 355, 383-391

² Xiao, Y.; Chung, T.-S. *J. Membrane Sci.*, **2007**, 290, 78-85.

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⁴ Wayner, D. D. M.; Wolkow, R. A. *J. Chem. Soc., Perkin Trans. 2*, **2002**, 1, 23-34

⁵ Wang, X.; Fan, H.; Zhang, F.; Qi, Y.; Qiu, W.; Yang, F.; Tang, J.; He, P. *Tetrahedron*, **2010**, 66, 7815-7820



SCANNING ELECTROCHEMICAL MICROSCOPY (SECM)

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Scanning Electrochemical Microscopy (SECM) is a powerful tool for studying structures and processes in micrometer -sized systems. It can probe electron, ion and molecule transfers,^{1,2} at solid-liquid, liquid-liquid and liquid-air interfaces.³⁻⁵ This versatility allows for the investigation of a wide variety of processes, from metal corrosion,⁶ adsorption phenomena and charge transfer⁷ to metabolism in single living cells.^{8,9} The precise positioning capabilities, which make high spatial resolution possible, give the SECM an important advantage over other electrochemical techniques. For example, the SECM can pattern the substrate surface, visualize its topography, and probe chemical reactivity on the micrometer scale. At the same time, SECM differs from other scanning probe techniques in its applicability to quantitative measurements through well-developed and rigorous electrochemical theory.

In this talk, a brief introduction to the technique will be given as well as some examples of the results obtained in our group (Organic Surface Chemistry Group, Aarhus University), e.g. surface patterning and studies of charge transport through organic films for the purpose of energy storage in super capacitors.

References:

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CORROSION PROTECTION AND OPTICAL INFLUENCE FROM TI IN ALUMINIUM BASED PLASMA COATINGS

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When using aluminium alloys, appearance of the anodizing layer is extremely important and demanding for many technological applications. However, the use of recycled aluminium can cause unpredictable optical appearance compromising product quality. Similarly, using cast aluminium as substrate provides enormous freedom and versatility when it comes to the product shape compared to machined components. Unfortunately cast aluminium is soft, has low corrosion resistance, and anodizing is not possible due to the high amount of silicon. Therefore it is not possible to produce optical surfaces using cast aluminium components alone.

Plasma coating processes can be used for producing aluminium based coatings on cast substrate components made by aluminium or plastics. The properties of the coating can be optimized by tuning the chemical composition and microstructure. In order to do this, it is required to obtain detailed knowledge on the effect of various alloying elements and secondary phases on the appearance of the anodized layer and corrosion properties. Investigations focus on two aspects, namely: (i) the effect of chemical composition and surface finish on the appearance of the anodized layer, and (ii) the effect of Ti as alloying element on optical appearance and corrosion resistance. The effect of heat treatment was also investigated to understand the role of nano- to micro-size second phase particles on the formation and appearance of the anodized layer. Optical properties were investigated using spectroscopic methods, and corrosion properties using micro electrochemical technique and flat cell. Surface morphology of the coating, anodized layer and corroded surfaces were investigated using SEM, EDS, and AFM. Results show that the optical properties of the anodized layer is a function of chemical composition of the alloy/coating and surface finish, while the alkaline corrosion resistance is largely improved with increase of Ti content in the coating.



INVESTIGATION OF PHOTO CATALYTIC ACTIVITY OF TITANIUM DIOXIDE DEPOSITED ON METALLIC SUBSTRATES BY PLASMA TECHNIQUE

Svava DAVIDSDÓTTIR¹, Juliano SOYAMA, Kai DIRSCHERL, Rajan AMBAT²

Titanium dioxide (TiO_2) in the anatase crystalline structure corresponds to one of the most powerful photo catalytic materials available today. Photons with the energy equal (UV region) to or higher than its band gap (~ 3.2 e.V) are able to initiate a photo activation process in TiO_2 , which creates hole/electrons pairs in the material. The hole/electron pair consists of high oxidizing and reduction power respectively which can split water into hydroxyl radicals and converting oxygen into superoxide. The hydroxyl and superoxide radicals can decompose various organic materials in contact with TiO_2 surface, maintain anti-bacterial surface.

Metallic material such as stainless steel and light weight aluminium alloys are widely used in several applications from household appliances, transportation, and hospitals to industrial environments. Therefore its combination with a functionalized self-cleaning and anti-microbial surface is extremely attractive for technological applications. However, the behaviour of TiO_2 film on metallic substrates is a little investigated.

In this investigation, TiO_2 coating were made on aluminium alloy (AA1050) and stainless steel (S316) substrate using pulsed DC reactive magnetron sputtering at varying thickness spanning from 100 nm to 2.5 μm . The photo catalytic activity was measured using three techniques namely: (i) electrochemical methods such as Open Circuit Potential (OCP) with and without UV light (ii) decomposition studies of an organic dye (methylene blue) using a flow cell (iii) Optical measurements using reflection. Microstructural investigation was carried out by Atomic force microscopy (AFM), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD).

The results of the decomposition and the electrochemistry indicated that the choice of the metallic substrate and the thickness of the coating had profound effects on the photo-catalytic properties. The optical measurements demonstrated the ability for coating to absorb light was depended on thickness of the coating. As the coating became thicker, the absorption increases until saturation limited was reached at certain thickness. The quantification of the AFM images showed that there is a linear relationship between the thickness of the coating and the cell size of the crystals.

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**Oral presentations Session 2: Environmental
electrochemistry and Fuel cells
13:00 – 14:20**



APPLICATIONS OF ELECTROCHEMICAL OXIDATION FOR DEGRADATION OF AQUEOUS ORGANIC POLLUTANTS

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The water resources as the rest of the natural environment on Earth are under pressure from increasing human activities all over the world. As the analytical capabilities improve, traces of these activities are intensively emerging in the form of harmful organic pollutants recalcitrant to natural degradation. This presentation will present research conducted on the use of electrochemical oxidation (EO) for degradation of organic pollutants in water. From an applied experimentally based approach, complex polluted water from sites contaminated with chemical waste and polluted sea water have been subject to studies in addition to model solution studies under controlled conditions. Several toxic organics as the organo-phosphoric pesticides parathion and malathion and the polycyclic aromatic hydrocarbons (PAHs) naphthalene and pyrene have been successfully degraded, COD has been removed in groundwater contaminated with pharmaceutical waste, and oxidative bleaching of dye have been demonstrated in addition to inactivation/disinfection of *E. coli* due to the strong oxidants produced in the cell.

Important differences in oxidation mechanisms and degradation power were found between two different reactors used with Ti/Pt-Ir and Si-BDD as the respective anode materials, and the mechanisms were further investigated by surface XPS studies. The major drawback of byproduct formation was investigated and showed that careful evaluation of reaction times is needed when treatment setups are designed. The presentation concludes that EO as a technique for degradation of organics in advanced water treatment definitely does possess a promising potential for industrial use and increase the competition with other advanced oxidation processes (AOPs), when facing problems with toxic, refractory, bio-incompatible organics. However, continuing efforts have to be invested in research aiming at providing a full understanding of the fate of by-products and scale-up challenges.



SULPHUR POISONING OF SOFCs: CELL PERFORMANCE, ELECTROCHEMICAL CHARACTERISATION AND IMPACT OF OPERATING PARAMETERS.

Gregory JOHNSON¹, Per HJALMARSSON¹, Anke HAGEN¹

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The impact of sulphur on SOFC anodes is known to be dependent on operating parameters such as temperature, current density, quantity of sulphur in fuel and anode material/micro-structure. There is however still a great deal of uncertainty in literature about the true influence of operating current density and in addition, the precise mechanistic details of anode poisoning/deactivation are not well known.

This research attempts to address the issue of operating current density on a Nickel/Scandia based SOFC with varying amounts of sulphur impurity, assessing the cell performance and degradation. The presentation discusses the result of sulphur poisoning tests on SOFC recently developed at Risø DTU. The anode supported cell consists of a Ni/Sc-YSZ anode, Sc-YSZ electrolyte and a composite LSCF:CGO cathode. The cell was operated at 850 °C on a fuel mixture of 29% CH₄, 58% H₂O and 13% H₂ with varying amounts of H₂S (0-100 ppm) and at current densities; 0.25, 0.5, 1.0 Acm⁻² and at OCV. In situ impedance spectroscopy measurements were also performed.

The discussion includes a presentation of cell voltage performance which typically showed a characteristic rapid initial voltage drop followed by a slower degradation over the remainder of the 24 h study period for each H₂S Concentration. The studied cell typically showed a higher voltage drop with increasing current density. However, analysis of relative change in cell resistance revealed a reverse trend where smaller increase in relative cell resistance was observed at higher current density. Analysis of the impedance measurements was also done in an attempt to deconvolute the impedance spectra into respective anode and cathode processes and to understand the sulphur poisoning and recovery behaviour of the studied SOFC. Using impedance analysis methods such as distribution of relaxation times (DRT) and analysis of difference in impedance spectra (ADIS), specific electrochemical processes were identified and subsequently quantified, giving an insight into mechanistic details of poisoning processes.

SEM was also used to analyse the micro-structure of the cell which had been operated for over 2200 hours to correlate micro-structural changes with observed loss in cell performance under sulphur poisoning.



ELECTROPLATING OF SOLID OXIDE FUEL CELL INTERCONNECTS: MODELLING OF THE CURRENT DISTRIBUTION

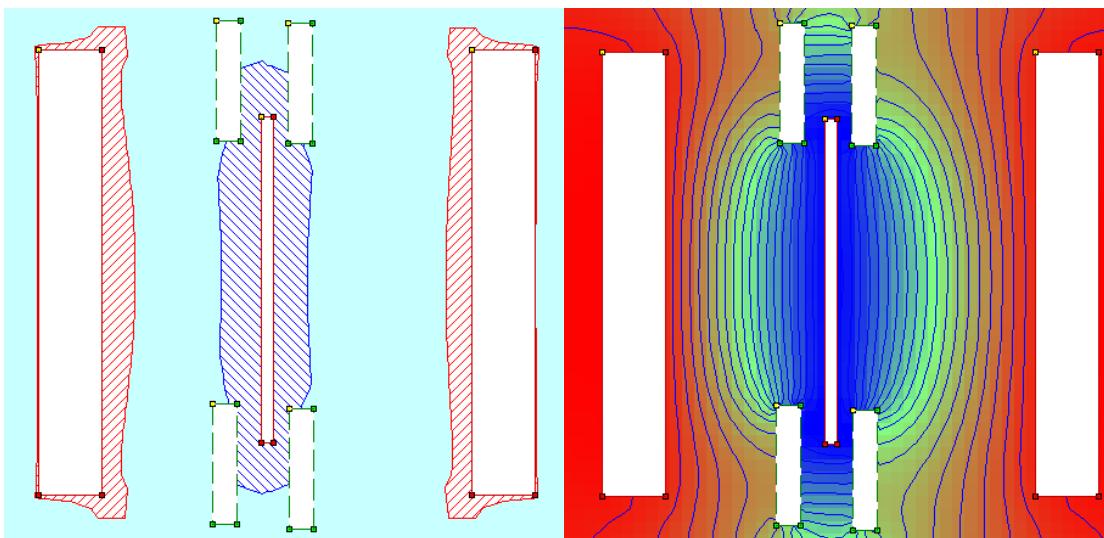
Anders HARTHOEJ¹

¹*Technical University of Denmark, Denmark, anhar@mek.dtu.dk*

A solid oxide fuel cell (SOFC) is an electrochemical device that can produce electricity when supplied with a fuel – such as hydrogen or methane – and oxygen. The solid oxide fuel cells are assembled in stacks where the individual cells are separated by interconnects. The development of a suitable interconnect material is needed before SOFC technology can become widespread. Chromia forming ferritic steel is a promising material but the high operating temperature around 800 °C and the presence of oxygen result in two unsolved issues: Volatile chromium species poisons the cathode and growth of a chromia scale decreases electrical conductivity.

The scope of the PhD project is to investigate the potential for using electrodeposition techniques to produce a coating on ferritic steel interconnects. The coating must prevent chromium evaporation and create a good electrical connection between the interconnect and the fuel cells anode and cathode.

This presentation will give an introduction to solid oxide fuel cells, and where electrodeposition can be used in the manufacturing of fuel cell systems. It will also be explained how electrodeposition can be simulated with the software Cell-Design.



Cell-Design simulation of current density and potential field in an electrochemical cell



DURABILITY OF CARBON NANOFIBER (CNF) & CARBON NAFIONTUBE (CNT) AS CATALYST SUPPORT FOR PROTON EXCHANGE MEMBRANE FUEL CELLS

Shuang Ma ANDERSEN¹, Maryam BORGHEI², Peter LUND³, Yli-Rantala ELINA⁴, Antti PASANEN⁴, Virginia RUIZ², Pertti KAURANEN⁴ and Eivind M. SKOU¹

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Durability issue is one of the most up-to-date topics among Proton Exchange Membrane Fuel Cell (PEMFC) researches. It gives fundamental definition for cell life time, capital cost, system stability and technique reliability. Lose of catalyst surface area due to corrosion of supporting material (normally carbon black) is one of the essential degradation mechanisms during cell operation. In this work, durability of Carbon Nanofiber (CNF) & Carbon Nanontube (CNT) as alternative platinum catalyst support for Proton Exchange Membrane Fuel Cells (PEMFCs) was assessed. Platinized CNF and CNT with a standard polyol method were prepared and fabricated as cathodes of Membrane Electrode Assembly (MEA) for PEMFC. Bothe the catalysts itself and the MEAs were evaluated regarding to thermal and electrochemical stability using traditional carbon black (Vulcan XC72) as a reference. Thermal gravimetric analysis (TGA), cyclic voltammetry (CV), polarization curve and impedance spectroscopy were applied on the samples under accelerated stress conditions. Carbon nano materials demonstrate outstanding stability as nano-sized platinum catalyst support in PEMFC related operating conditions. Electrode structure can still be optimized to improve overall cell performance.

Poster session
14:20 – 15:20



IN-SITU INVESTIGATION OF MICROELECTRODES USING CONTROLLED ATMOSPHERE HIGH TEMPERATURE SPM

Yuehua WU¹, Torben JACOBSEN², Karin Vels HANSEN¹, Mogens MOGENSEN¹

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The controlled atmosphere high temperature scanning probe microscope (CAHT-SPM) is capable of performing impedance spectroscopy on microelectrodes down to a size of a few microns at operating temperatures and atmospheres relevant for the study of solid oxide fuel cell electrodes. This is done by contacting the microelectrode with a very tiny probe and using this as the working electrode. The method allows the study of well defined electrodes and the possibility to study changes of specific electrodes. This is important in order to correlate electrode performance with chemical and microstructural changes.

Impedance measurements on Au microelectrodes deposited on polished yttria stabilized zirconia (YSZ) pellets is demonstrated at temperatures up to 700 °C in air. The influences of the tip-sample force and of the size of the microelectrodes on the electrical properties of the Au microelectrodes were also studied. The impedance spectra of circular Au microelectrodes down to 8 µm in diameter at different temperatures were successfully obtained.



THE EFFECT ON ELECTRICITY PRODUCTION IN MFC OF THE ELECTRODE AREA AND SUBSTRATE IN THE ANODE

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Due to increasing energy prices and concerns on long-term energy security, there is interest in bio-renewable energy generation technologies. Microbial fuel cells (MFC), if used for wastewater treatment, can provide clean energy for people, beside effective treatment of wastewater. The benefits of using MFC for wastewater treatment include clean, safe, quiet performance, low emissions, high efficiency, and direct electricity recovery. In this work, a H-shaped MFC with anode and cathode, separated with cation exchange membrane was used. Substrates, which were oxidized and used in the anode compartment, were sodium acetate and waste glycerol with a concentration of 2 g/l. In the cathode compartment, a solution of potassium ferrocyanide was used as electron acceptor. The power production was monitored with varied electrode area in the anode and electrodes placed parallel to each other. For electrochemical studies, a Keithley 2700 and a Gamry potentiostat were used.

The obtained voltage with acetate as substrate was more stable than using glycerol, especially when electrodes were covered with biofilm. The biggest value of current and power were obtained with four electrodes using acetate of 2.0 mW and 6.0 mA, respectively. Comparing waste and technical glycerol a more stabile system was gained using waste glycerol with quite constant voltage. In general, comparing anode electrode area, the best MFC reactor, with not to high electrical characteristic, was obtained using one or two electrodes due to increased resistance in the system with four electrodes.

It can be concluded that beside acetate, as a good source for producing electricity, relatively good substrate for MFC can also be waste glycerol, which is nowadays overproduced in the production of biodiesel.



LiBH₄-LiI MIXTURES AS SOLID ELECTROLYTES FOR LITHIUM BATTERIES

**Ane S. CHRISTIANSEN¹, Daði Þ. SVEINBJÖRNSSON², Poul NORBY³,
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All-solid-state lithium batteries are attracting more and more interest due to the increasing need for better batteries in e.g. transportation and microelectronics. It is, however, a challenge to find suitable solid materials with an ionic conductivity comparable to or exceeding that of commercially used liquid electrolytes.

LiBH₄ has been found to have a high temperature phase (above 110°C) with a very high ionic conductivity ^[1]. Furthermore, it has been shown that this highly conducting phase can be stabilized at room temperature by LiI addition ^[2,3]. This work demonstrates how such solid solutions of LiBH₄ and LiI can be used as a solid electrolyte in a lithium ion battery.

Li₄Ti₅O₁₂ and Li-metal were used as cathode and anode respectively. Li₄Ti₅O₁₂/LiBH₄-LiI/Li cells with a thickness of approx. 2 mm and a diameter of 13 mm were pressed with 1 ton/m² and subsequently sealed in a 'coffee bag' under an Ar atmosphere. Charge-discharge cycling of the cells was performed using galvanostatic cycling with potential limits (GCPL) between 1.2 and 1.9 V. Up to 120 cycles have been performed with a current density at 1-2 μA/cm². The discharge plateau was relatively flat at 1.35 V vs. Li/Li⁺, and no decrease in the energy capacity of the cell was observed after the cycling.

Electrochemical impedance spectroscopy (EIS) was used to examine the impedance of the cells before and after the cycling. The results showed an increased resistance in the cell after the cycling. Furthermore, synchrotron radiation was used to perform XRD area scans of the cells before and after discharging in order to observe the structural changes caused by the discharging process. Although the discharge potential of the tested battery is low, the results reveal the possibility of using LiBH₄-LiI as a solid electrolyte.

[1] S. Orimo et al., Appl. Phys. Lett. 91, 224103 (2007)

[2] S. Orimo et al., J. Am. Chem. Soc. 131, 894-895 (2009)

[3] T. Vegge, S. Orimo et al., Appl. Phys. Lett. 94, 141912 (2009)



LiBH₄-LiI SOLID SOLUTIONS AS A SOLID ELECTROLYTE MATERIAL

Daði Þ. SVEINBJÖRNSSON¹, Didier BLANCHARD², Jón Steinar Garðarsson MÝRDAL³, Mogens Bjerg MOGENSEN⁴, Poul NORBY⁵, Tejs VEGGE⁶,

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The need for better methods of electrical energy storage is growing fast, especially in the energy and the transportation sectors. Here, batteries could be a convenient solution. However, for large-scale usage in high power applications, such as automobiles, today's battery technologies must be substantially improved to reach satisfactory levels of energy and power densities, charge-discharge rates, cycle life, safety, etc.

Typical lithium-ion batteries use liquid electrolytes. This can result in degradation of the battery due to dendrite formation at the electrodes, which in turn leads to a limited charge-discharge cycle life, as well as decreased safety due to an increased risk of internal short circuiting. A possible solution to this is to use crystalline materials as electrolytes. Such solid electrolyte materials with sufficient stability and high lithium ion conduction still have to be developed.

New solid electrolytes based on mixed (1-x)LiBH₄+xLiI systems with a Li⁺ conduction close to that of commercial liquid Li-ion electrolytes have been discovered^[1], but the conduction mechanisms and stability still need to be understood. Here, these systems are characterized using powder x-ray diffraction, impedance spectroscopy and density functional theory calculations.

Lithium borohydride has a poorly conducting orthorhombic structure at room temperature, but changes to a highly Li⁺ conducting hexagonal structure at 110°C^[2]. The hexagonal phase exhibits excellent Li⁺ conduction (10⁻³ S/cm at 120°C). We show that the hexagonal phase can be stabilized at room temperature by adding LiI in ratios of x=12.5 or higher. Powder diffraction data have revealed that the I⁻ partially substitute into the hexagonal structure at the sites of the BH₄⁻ groups to form a solid solution. We show that the microstructure of the samples greatly affects the Li⁺ conductivity. Results on the conduction mechanism will also be presented.

[1] S. Orimo *et al.*, J.Am.Chem.Soc. 131, 894-895 (2009)

[2] S. Orimo *et al.*, Appl. Phys. Lett. 91, 224103 (2007)



THE PERFORMANCE OF DYE SENSITIZED SOLAR CELLS WITH 4-*TERT*-BUTYLPYRIDINE AND 1-METHYLBENZIMIDAZOLE N719 SUBSTITUTED RUTHENIUM DYES AS SENSITIZERS

Phuong Tuyet NGUYEN^a, Binh Xuan Thi LAM^a, Anders Rand ANDERSEN^b, Poul Erik HANSEN^a, Torben LUND^a.

a) Department of Science, Roskilde University, Denmark]

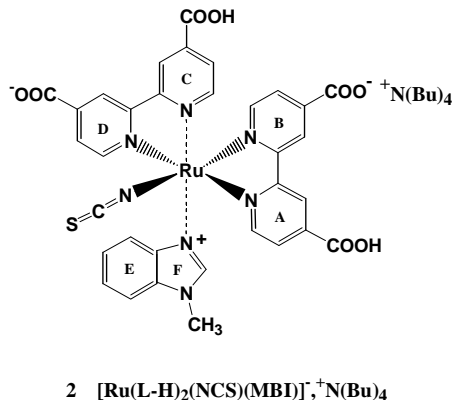
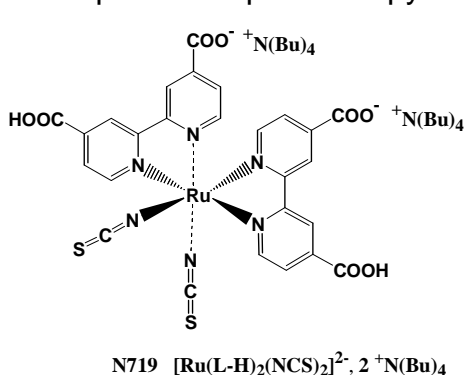
b) University of Southern Denmark,

[†]Danish Technological Institute, Denmark

While the 4-*tert*-butylpyridine (4-TBP) and 1-methylbenzimidazole (MBI) additives have a very positive effect on the efficiency of the dye sensitized solar cell (DSC), the additive causes problems in terms of thiocyanate substitution reactions with the ruthenium dyes at elevated temperatures. We have recently shown that ruthenium dyes containing thiocyanate ligands such as N719 and Z907 may undergo ligand substitution reactions with the DSC additive 4-TBP at elevated temperature (> 80 °C).



The thermal degradation products of N719, $[\text{RuL}_2(\text{NCS})(4\text{-TBP})]^+$ and $[\text{RuL}_2(\text{NCS})(\text{MBI})]^+$ are themselves sensitizers. In this work we synthesized, characterized and applied the substitution products as dyes in DSC and their sensitizer efficiencies were evaluated from the current to voltage (IV), incident photon to current efficiency (IPCE) and AC-impedance spectroscopy measurements of the DSC.





DEVELOPMENT OF HIGHLY EFFICIENT WATER ELECTROLYSERS

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In order to realize the hydrogen economy, highly efficient fuel cells and water electrolyzers are required. Numerous materials for such devices have been investigated, all with their individual advantages and disadvantages. A relatively new group of materials for the solid electrolyte is the so-called solid acids, bearing properties similar to both solid salts and liquid acids. One such compound, CsH_2PO_4 , is the focus of this project. The interesting feature of CsH_2PO_4 is an apparent increase in the protonic conductivity of several orders of magnitude as the temperature is increased to around 230 °C [1]. This makes it very suitable for use in medium temperature fuel cells. The disadvantages include the very high water solubility of CsH_2PO_4 which makes water condensation during cell shutdown very problematic. CsH_2PO_4 is also quite plastic which can result in delamination from the electrode material. In this project an attempt will be made to address these problems as well as to further the overall understanding of the properties of CsH_2PO_4 .

[1] Sossina M. Haile et al., *Faraday Discuss.*, 2007, 134, 17-39



DIFFERENCES IN OXYGEN REDUCTION CATALYSIS OF PLATINISED ACID TREATED SHOWA DENKO CARBON NANOFIBRES

Sune VELTZÉ¹, Elina YLI-RANTALA², Maryam BORGHEI³, Pertti KAURENAN², Eivind M. SKOU¹

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The use of carbon as support material for platinum nano-crystallites in polymer electrolyte fuel cells (PEFC) is a common method for increasing the electrochemical specific surface area (ECSA) of platinum. During fuel cell operation, the conditions that catalysts are subjected to lead to various forms of the ECSA degradation: By agglomeration of the platinum crystallites, Rietveld ripening or indirectly by corrosion of the carbon support. Graphitised carbon nanostructures like carbon nanotubes (CNTs), carbon nanofibres (CNFs), etc. are proposed as carbon support substitutes to avoid carbon corrosion, as the nanostructures are thermally and chemically more durable.

The presented work describes the effects on surface defect of acid treated Showa Denko vapour grown carbon fibres (VGCF[®]/VGCF-H[®]). A selection of carbon fibres have been platinised and the differences of the oxygen reduction currents without mass transport effects are determined by Koutecký-Levich plots at 900 mV and 850 mV vs. RHE. The normalised kinetic currents of the differently pre-treated fibres are presented from room temperature measurements and elevated temperature measurements.

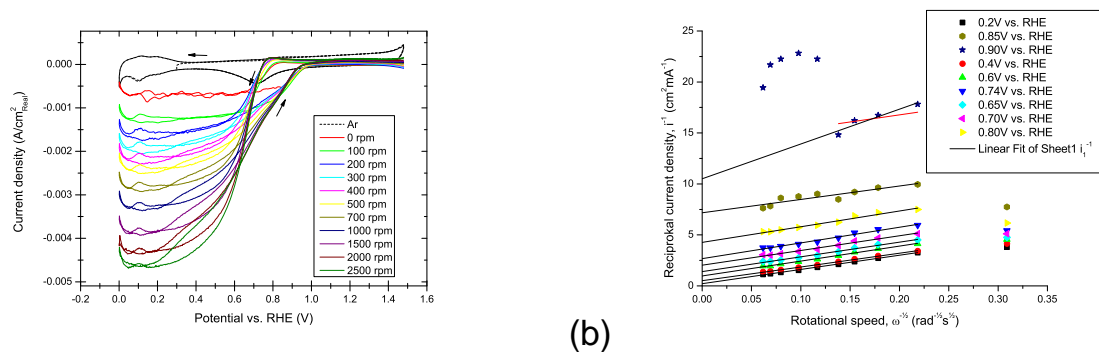


Figure 1 : (a) Oxygen reduction curves for 20 wt.% Pt on Vulcan[®] (BASF) at r.t. (25° C) in 0.1 M HClO₄ (aq.). (b) Koutecký-Levich plots for 20 wt.% Pt on Vulcan[®] (BASF) at r.t. (25° C) in 0.1 M HClO₄ (aq.) at different potentials.



ELECTROKINETIC DESALINATION – PILOT SCALE TESTS

Lisbeth M. OTTOSEN*, Gry SKIBSTED, Juan M PAZ-GARCIA

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Many masonry buildings worldwide are suffering from salt decay. Chlorides are a group of damaging salts and they often enter the building stone by advection in the capillary rising groundwater. The damaging effect of the salts is not due to a chemical reaction between stone and salt, but due to crystallization/dissolution cycles caused by changes in relative humidity.

A new method for electrokinetic desalination of brick masonry is under development at DTU Byg. The method has shown a very efficient desalination when dealing with single bricks in the laboratory and the next step was to make pilot scale tests at salt infected masonry. Electrode units were developed and three pilot scale tests have been conducted (one of them is seen in figure 1).



Figure 1: Pilot scale experiment for electrokinetic desalination of masonry

The initial concentration of chloride differed significantly in the different cases (from an average of 580 mg/kg to 27 g/kg). The transport numbers for chloride were high in all cases (0.33 to 0.48), showing an efficient removal. The duration was however too short (5 month) for the two most contaminated masonries to be desalinated sufficiently. The experiment with the least contaminated masonry, however, showed that very low concentrations can be reached.

Curt SANDER et al, Title to come

– **presentation expected to come** (26th September)

Oral presentations Session 3: Biosensors
15:20 – 16:00



SELF-ASSEMBLED PEPTIDE NANOSTRUCTURES A NEW OPTION FOR THE DEVELOPMENT OF BIOSENSORS

Jaime CASTILLO-LEÓN¹, Luigi SASSO¹, Kinga ZOR², Winnie E. SVENDSEN¹

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Biological building blocks such as peptides or proteins are able to self-organize into 3D nanostructures with particular properties that open several possibilities for their use in applications such as drug delivery, biosensing and tissue engineering (figure 1). Recently the use of these biological nanostructures in bionanotechnology has been reported due to their easy and low-cost fabrication, their stability and their facile functionalization. These features suggest the use of self-assembled peptide nanostructures as candidates for the integration with transducers and biorecognition elements for the development of biosensing platforms. In this presentation the use of these self-assembled biological nanostructures for biosensing purposes is reviewed. The different immobilization strategies, mechanisms and detected substrates are described. Additionally different possibilities to functionalize and modify their structure towards their use in sensing applications are also discussed in a critical way. Finally our latest results using biological self-assembled nanostructures for the development of electrochemical biosensors for biomedical applications will be presented.

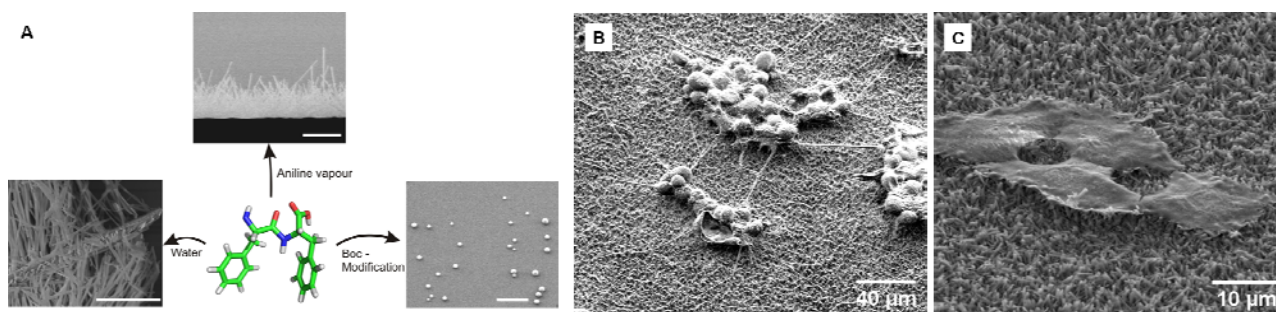


Figure 1. A) SEM Image of self-assembled peptide nanostructures formed using the diphenylalanine peptide; the scale bar in the images corresponds to 1 µm. B) SEM image of PC12 cells and C) HeLA cells grown onto top of functionalized self-assembled peptide nanofibers for the development of a combined cell culture/biosensing platform.



APPLICATION OF ENZYME-MODIFIED ELECTRODES BASED ON CELLOBIOSE DEHYDROGENASE IN CELLULASE RESEARCH

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Production of carbon neutral second-generation ethanol from renewable lignocellulosic biomass is a promising sustainable alternative for fossil fuels in the transport sector. The primary challenge for this application is the breakdown of cellulose to fermentable sugars. This can be done by enzymatic treatment with cellulolytic enzymes. However, it was recently stated that one of the key challenges in biomass research lies in the limited selection of simple, fast and quantitative cellulase activity assays [1]. Here we present a cellulase assay based on mediator-modified carbon paste electrodes with the enzyme cellobiose dehydrogenase as the sensing element. Our result shows that this enzyme-modified electrode can be utilized for continuous monitoring cellulase action on both cellulose substrates and lignocellulosic biomass. In comparison with conventional assay methods the electrochemical measurements have the advantage of being free from the influence of optical properties of the reaction mixture and monitoring in real-time. The assay has potential in both fundamental cellulase research to probe the basic mechanism behind enzymatic cellulose degradation.

[1] Zhang et al. "Outlook for cellulase improvement: Screening and selection strategies" *Biotechnology Advances* 24 (2006)

For personal notes: