

# Two day conference

## Electrochemical Science and Technology

30<sup>th</sup> September and 1<sup>st</sup> October 2010

at

the Technical University of Denmark



**Organized by:**

**Danish Electrochemical Society**

In partnership with **ATV•SEMAPP**

**Organizing committee:**

Torben Lund, Associate Professor, Roskilde University

Henrik Jensen, Associate Professor, Copenhagen University

Lisbeth M. Ottosen, Associate Professor, Technical University of Denmark



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PROGRAMME:

**Thursday the 30<sup>th</sup> September**

- 14:30 – 15:00     **Arrival to Danish Technical University**  
Mødelokale 1, Bygning 101 A, DTU, Anker Engелunds Vej, DK-2800 Kgs. Lyngby
- 15:00 – 16:00     **General Assembly in the Danish Electrochemical Society**  
For members and guests.
- 16:00 – 16:05     **Welcome**  
*Lisbeth M. Ottosen, Department of Civil Engineering, DTU*
- 16:05 – 17:35     **Mini symposium on applied electrochemistry for conservation of ancient and modern buildings and cultural treasures**
- **Corrosion monitoring and cathodic protection of civil structures, bridges, tunnels and marine structures**  
*Birit Buhr, COWI A/S*
  - **The use of electrokinetics in conservation and treatment of cultural heritage**  
*Iben V. Christensen, DTU BYG*
- 17:35 – 19:00     **Check-in at hotels**
- 19:00                **Conference Dinner**  
***Brede Spisehus***  
I.C. Modewegs Vej  
DK-2800 Kongens Lyngby  
Phone: +45 4585 5457

**Friday the 1st October**

- 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 – 09:35     **High temperature fuel cells – from research to industrial technology**  
*Niels Christensen Haldor Topsø A/S*
- 09:35 – 10:05     **In-Situ Electron Microscopy of Electrochemical Processes**  
*Kristian Mølhave, DTU Nanotech*
- 10:05 – 10:25     **Coffee break**

## ORAL PRESENTATIONS

10:25 – 12:05     **Sensors and electrode modifications**

**Electrochemical characterization of self-assembled peptide nanofibres and their application in the development of metal ion biosensors**

*Kinga Zor, Bruno Viguier, Jaime Castillo-Leon, Emmanouil Kasotakis, Anna Mitraki, Winnie E. Svendsen, DTU, Nanotech*

**Diphenylalanine Peptide Nanowires for Sensing Applications**

*Luggi Sasso, Indumathi Vedarethinam, Jaime Castillo, Jenny Emneus, Winnie E. Svendsen, DTU Nanotech*

**Polypyrrole coating to enhance three dimensional electrodes for neurological studies**

*Patricia Vasquez, Luggi Sasso, Maria Dimaki, Winnie E. Svendsen, DTU Nanotech*

**Introducing electrochemical readout to mechanical sensors**

*Maria Tenje, Lee M. Fisher, Xueling Quan, Anja Boisen, DTU Nanotech.*

**Functionalization of Surfaces using Aryltriazene Chemistry**

*Jesper Vinther, Mikkel S. Kongsfelt, Kristoffer Malmos, Cindy S. Knudsen, Steen U. Petersen, Kurt V. Gothelf, and Kim Daasbjerg, Department of Chemistry, Aarhus University*

12:05 – 13:00     **Lunch**

## POSTER PRESENTATIONS

13:00 – 14:00

- **Covalent attachment of polymer brush on metal substrates**  
*Mie Lillethorup, Joseph Iruthayaraj, Marcel Ceccato, Peter Kingshott, Flemming Besenbacher<sup>2</sup>, Steen Uttrup Pedersen, Kim Daasbjerg, Department of Chemistry, Aarhus University, <sup>2</sup>iNano Institute of Physics and Astronomy*
- **Carbon Nanotubes and Other Nanostructures as Support Material for Nanoparticulate Noble-Metal Catalysts in Fuel Cells**  
*Mikkel J. Larsen, Sune Veltze, Eivind M. Skou, Institute of Chemical Engineering, University of Southern Denmark*
- **Degradation and contamination of perfluorinated sulfonic acid membrane due to swelling-dehydration cycles**  
*Shuang Ma Andersen, Eivind M. Skou, Institute of Chemical Engineering, SDU*

- Novel – and yet still “squared” – electrocatalytic materials**  
*Pia Nielsen, Hans Toftlund Nielsen, Eivind M. Skou. Department of Physics and Chemistry, University of Southern Denmark*
- Electrochemical losses in microbial fuel cells**  
*Anders Thygesen\*<sup>1</sup>, Booki Min<sup>2</sup>, Finn Willy Poulsen<sup>1</sup>*  
<sup>1</sup> *Risø National Laboratory for Sustainable Energy, Technical University of Denmark*  
<sup>2</sup> *Department of Environmental Science and Engineering, Kyung Hee University, Yongin-Si, Gyeonggi-Do 446-701, South Korea.*
- In situ investigation of microelectrodes using Controlled Atmosphere High Temperature SPM**  
*Suresh Kannan Balasingam, Yuehua Wu, Karin Vels Hansen, Fuel Cells and Solid State Chemistry Department, Risø*
- ABL90 Flex-Radiometers New Blood-Gas Analyser with Miniaturized Sensors**  
*M. Taagaard, B. Zachau-Christiansen, Radiometer Medical Aps*
- Numerical Simulations of Electrokinetic Processes Comparing the Use of a Constant Voltage Difference or a Constant Current as Driving Force**  
*Juan Manuel Paz-Harcia, Björn Johannesson, Lisbeth M. Ottosen, Departement of Civil Engineering, DTU*
- Application of an electric DC field for sodium chloride removal from rendered briks**  
*Ana Fragata<sup>1</sup>, Rosário Veiga<sup>1</sup>, Ana Veiosa<sup>2</sup>, Lisbeth Ottosen<sup>3</sup>*  
<sup>1</sup> *National Laboratory of Civil Engineering, Building Department, Lisboa, Portugal*  
<sup>2</sup> *University of Aveiro, Department of Civil Engineering, Aveiro Portugal*  
<sup>3</sup> *Department of Civil Engineering, DTU*
- Polyaniline Micro-Electrodes for Sensor Applications**  
*Mohammed Al-Abaddi, Luigi Sasso, Winnie E. Svendsen, DTU Nanotech.*
- Polymer planar electrodes for cellular sensing**  
*Francesco Diazzì, Luigi Sasso, Artho Heiskanen, Maria Dimaki, Jenny Emeus, Winnie E. Svendsen, DTU Nanotech.*
- Characterization of nanoporous gold electrodes by electrochemical methods**  
*Xueling Quan, Erol Zekovic, Lee M. Fischer, Anja Boisen, Maria Tenje, DTU Nanotech*

- **Stability of Au and Pt working electrodes and Ag/AgCl reference electrodes in Gamble's solution for engineered nanoparticles toxicity characterization**  
*Shoko Yamada, Silvan Schmid, Anja Boisen, Department of Micro-and Nanotechnology, DTU*
- **Galvanic series for metals and alloys used in electronic circuit board assemblies**  
*Umadevi Rathinavelu, Morten S. Jellesen, Per Møller, Rajan Ambat, DTU Mekanik*
- **Relation between alloy composition, surface finishing and optical properties when anodising aluminium**  
*Martin Aggerbeck, Rajan Ambat, DTU Mekanik*
- **Novel electrochemical microfluidic device for drug compounds characterisation**  
*Aleksandra Glosnicka<sup>1</sup>, Jaime Castillo-Leon<sup>1</sup>, Jacob Neresco Lange<sup>1</sup>, Maria Deryabina<sup>1</sup>, David Sabourin<sup>1</sup>, Henrik Jensen<sup>2</sup>, Winnie E. Svendsen<sup>1</sup>, DTU Nanotech*  
<sup>1</sup>Technical University of Denmark,  
<sup>2</sup>Copenhagen University, Denmark
- **Preparation of Nafion 117TM-SnO2 Composite Membranes using an Ion-Exchange Method**  
*C. F. Nørgaard<sup>1</sup>, U. G. Nielsen<sup>2</sup>, E. M. Skou<sup>1</sup>*  
<sup>1</sup> Institute of Chemical Engineering, Biotechnology and Environmental Technology, Faculty of Engineering, University of Southern Denmark  
<sup>2</sup> Department of Physics and Chemistry, Faculty of Science, University of Southern Denmark
- **The impact of calcium ions on the electrokinetic desalination of sulfate from stone: Preliminary results**  
*Gry Skibsted\*, Lisbeth M. Ottosen, Pernille E. Jensen, Department of Civil Engineering, Technical University of Denmark*

#### ORAL PRESENTATIONS (continued)

14:00 – 15:00      **Solar cells, Photocatalysis and Fuel cells**

##### **Thermal stability of Dye-sensitized Solar Cells**

*Anders Rand Andersen<sup>1</sup>, Jens Christianesen<sup>2</sup>, Torben Lund<sup>3</sup>, Phuong Tuyet Nguyen<sup>3</sup>*

<sup>1</sup>Sense Institute SDU, <sup>2</sup>DTI Plastics Technology, <sup>3</sup>RUC



**Investigation of photocatalytic activity of titanium dioxid coating with varying thickness on metallic substrates**

*Juliano Soyama, Rajan Ambat, DTU Mekanik*

**Effect of chloride impurities on the performance and durability of polybenzimidazole -based high temperature proton exchange membrane fuel cell**

*Syed Talat Ali, Qingfeng Li, Chao Pan, Jens Oluf Jensen, Lars Pleth Nielsen, Per Møller, Department of Mechanical Engineering, DTU*

15:00 – 15:15      **Coffee break**

**ORAL PRESENTATIONS (continued)**

15:15 – 15:55      **Corrosion and remediation**

**Evaluation of environmental corrosivity by cathodic reduction analysis**

*Marie Louise Petersen, Danfoss A/S*

**Energy saving in electrochemical remediation of contaminated soil by pulse current**

*Tian R. Sun, Lisbeth M. Ottosen, Department of Civil Engineering, DTU*

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

16:10 – 16:20      **Closing remarks**



## ORAL PRESENTATIONS

## Corrosion monitoring and cathodic protection of civil structures,

Birit Buhr Jensen, COWI

For civil structures design has for many years had the objective to design to fulfil a load carrying capacity. However experience has shown that structures deteriorate due to material degradation, be it the concrete and its composition or the reinforcement. This in many cases jeopardised the durability and thereby also the service life. In 1986 the first code for concrete composition saw the light in Denmark, BBB the so-called "basis-beton-beskrivelsen". With that many durability issues were addressed especially on alkali-silika reactions. Today the codes and standards address the majority of deterioration mechanisms including reinforcement corrosion taking a 50 year service life into account. Where a longer service life is required, like the Copenhagen cityring project where 120 years of service life is required or the Messina Strait where 200 years of service life is required, we operate outside the codes and standards. Durability strategies need to be considered, and where carbon steel reinforcement is chosen as strategy, the concrete cover and quality needs to be designed. And as importantly we need to verify and update the service life during service life of a structure. This is done using corrosion monitoring. The presentation will give examples on corrosion monitoring on large civil structures and the experience from these. For new and existing structures especially in a marine environment cathodic protection is often considered technical and economical cost optimum as durability or repair strategy. The presentation will give examples on types of cathodic protection and examples on civil structures where cathodic protection has been applied, e.g. the Faro Bridges, the Øland bridge, Busan-Geoje tunnel etc.

## **The use of electrokinetics in conservation and treatment of cultural heritage**

Iben V. Christensen, DTU BYG

Valuable cultural heritage is lost in many parts of the world due to problems in conservation and treatment of the objects worthy of preservation. The problems include salt decay of historic masonry and sandstone monuments, degradation of archeological wood that has been preserved with alum and also biological decay of wood in structures.

At present there are no efficient implemented methods to hinder the decay and there is an urgent need for the development of such methods.

At DTU Byg, methods based on electrokinetic principles applied to porous materials are being developed to both remove salts and impregnate wood in-situ. Here the problems and proposed electrokinetic methods are presented in brief.

Damage caused by soluble salts is a frequently encountered problem in the field of conservation of historic sandstone and brick monuments. The damage is caused by soluble salts (most often chlorides, nitrates and sulphates) and is generally due to their accumulation and phase transmission at or near to the surface of the object, as a result of moisture transfer processes.

Precipitation of salt near the surface will lead to decay of the material itself. In cases where the precipitation takes place on the surface of a brick or a stone, the damage will often be of an aesthetic character. However, if the brick is e.g. placed in a church vault and covered with murals from the Middle Ages or if it is a ceramic glazed tile placed in an important Portuguese tile panel the implications are more severe. Precipitation on the surface would imply precipitation between the brick and a valuable covering. The result is murals or glazing being pushed off in small pieces and valuable cultural heritage lost forever.

Archaeological wood may also be subjected to salt decay. Waterlogged wood from archeological excavations, may appear to be in good condition with the original shape and ornamentations intact. However when such finds are more than 2000 years old, like the wood in the Iron age Hjortspring find dated 350 BC the wood may be severely decayed and only the presence of water keeps the wood from collapse.

The conservators in the museums therefore have to treat the wood before it is dried and ready to present on display in the museums. From 1850-1960 a hot solution of alum ( $\text{KAlSO}_4$ ) was the preferred treatment and many important finds have been treated with alum. However we now know that the alum treatment does not provide adequate protection of the wooden objects and there is an urgent need for re-conservation of the valuable objects. The first step in the re-conservation process is the removal of alum. At the Danish National Museum today, alum is removed by extraction in water. The process is slow and may not be suited for larger objects or especially fragile objects, since complete immersion in water is needed for this method.

At DTU Byg we have developed a method where a low voltage DC field is used to remove salt ions from porous materials. The method was originally used for decontamination of soil, but the

principles can be transferred to other porous materials with unwanted ions, like salt decayed masonry and sandstone, and alum treated archeological wood. A low voltage DC field is applied across the porous material and the soluble salts are transported as charged ions by the electric field out of the masonry/sandstone/wood. The electrodes are placed in a clay poultice. The poultice serves multiple purposes: As a reservoir for the removed ions, it ensures good electric contact between the electrode and porous material to be treated, without damaging the object and it contains a buffering system to avoid acid produced at the anode from leaving the clay.

The electrokinetic principles are also used for the opposite, i.e. transport of ions *into* wood. When wood in structure starts to decay, surface treatment with a suitable wood preservative (often boron or copper based) or replacement of the wood are the only alternatives. In surface treatment the ingress of the fungicides is based on diffusion. Passive diffusion is a relatively slow process and with starting decay in the wood, this may be too slow a process and replacement of (part of) the wood unavoidable. If the wood is part of our cultural heritage – e.g. carved ornaments or painting on wooden panels, replacement of the wood is an undesirable solution. In this situation electrokinetics may be used to accelerate the transport of fungicides into the wood. The electrodes may be placed outside the wood, in a similar setup as with removal of salts. However using copper nails as anodes provides a solution where the wood is treated in depth from the start. Cu ions are released from the copper nail and acts as fungicide being transported towards the cathode.

The presentation will include a presentation of the method and the materials we have worked with, as well as the results so far.

## Microfabricated systems for electron microscopy of nanoscale processes: Towards in-situ TEM & SEM electrochemistry

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<sup>1</sup> DTU-Nanotech, Dept. of Micro and Nanotechnology, Technical University of Denmark, Denmark.

<sup>2</sup> School of Materials Engineering & Birck Nano technology Center, Purdue University, West Lafayette, Indiana, USA,

<sup>3</sup> IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York, USA

<sup>4</sup> Dept. of chemistry, Technical University of Denmark, Denmark.

<sup>5</sup> DTU CEN, Center for Electron Nanoscopy, Technical University of Denmark, Denmark.

We are developing novel methods for imaging of complex processes based on microfabricated chip systems, where a wide range of functionality to be incorporated into small systems that can be used inside TEM and SEM.

A range of novel systems are under development for imaging fluid samples, such as commercially available polymer membrane SEM capsules for liquids [1], and TEM devices for gasses and liquids, used in a variety of studies, such as high temperature CVD[2], nanoscale chemical processes in liquids [3][4], or biological samples [5]. We have for instance used microcantilever systems to create and characterize processes nanocircuits in environmental TEM [6] [7].

We here report on our work on incorporating a complete set of environmental sensors into such liquid cell systems to perform in-situ studies under controlled physical and chemical conditions. To study processes in liquids at ambient conditions, we are developing microchips with silicon nitride membrane windows transparent to the electron beam, where we can integrate microelectrodes, temperature sensors, and pressure sensors in the chip system. The system enables us to follow electrochemical processes, such as electrodeposition (Fig 1). The thin membrane with temperature sensors also make it possible to characterize ultrafast cryo fixation of the sample when plunged into a cryogen, thereby opening for the possibility of high time resolution of fast processes and subsequent 3D nanoscale imaging by Focused ion beam milling combined with SEM (FIB-SEM). The FIB-SEM imaging is also highly useful for imaging complex structures such as biological cells' interactions with nanostructured surfaces with ~10 nm resolution in 3D.

### References

- [1] S. Thiberge et al., *Proceedings of the National Academy of Sciences*, vol. 101, 2004, pp. 3346-3351.
- [2] J. Creemer et al., *Ultramicroscopy*, vol. 108, Aug. 2008, pp. 993-998.
- [3] M.J. Williamson et al., *Nature Materials*, vol. 2, 2003, pp. 532-536.
- [4] H. Zheng et al., *Science*, vol. 324, 2009, pp. 1309-1312.
- [5] D.B. Peckys et al., *PLoS One*, vol. 4, 2009, p. e8214.
- [6] K. Molhave et al., *Nano Letters*, vol. 6, 2006, pp. 1663-1668.
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\*Part of this study is supported financially through FP7 CP-FP 214566-2 "Nanoscale".

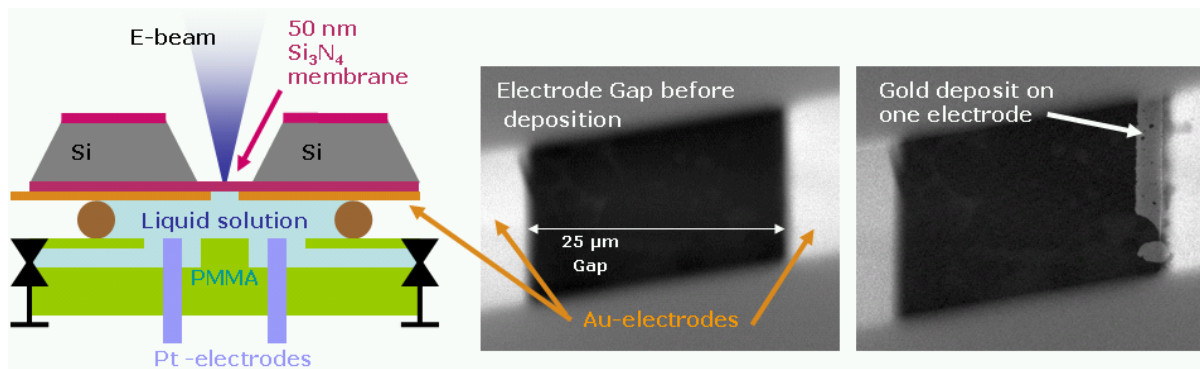


Fig 1: The microchip system for imaging liquid processes in-situ SEM. Here gold is deposited from solution onto one of two gold thin film electrodes on a 50nm electron transparent  $\text{Si}_3\text{N}_4$  membrane.



# Electrochemical characterization of self-assembled peptide nanofibres and their application in the development of metal ion biosensors

Kinga Zor<sup>1\*</sup> (Kinga.Zor@biotek.lu.se), Bruno Viguiet<sup>1</sup> (Bruno.Viguiet@biotek.lu.se), Jaime Castillo-León<sup>2</sup> (Jaime.Castillo@nanotech.dtu.dk), Emmanouil Kasotakis<sup>3</sup> (mkasotakis@materials.uoc.gr), Anna Mitraki<sup>3</sup> (mitraki@materials.uoc.gr), Winnie E.Svendsen<sup>2</sup> (winnie.svendsen@nanotech.dtu.dk)

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Biomolecules able to spontaneously form nanoscale structures are promising materials for their integration in future generations of micro and nano devices with possible bionanotechnological applications<sup>1</sup>.

Self-assembled peptide nanofibers (PNFs) are water soluble materials that can be formed under mild, physiological conditions<sup>2</sup> outside of the clean room. These type of biological nanostructures display features such as functional flexibility, exceptional resistance to thermal and chemical extreme conditions<sup>3</sup>. These characteristics make them attractive candidates for applications in bionanotechnological applications such as development of biosensing devices (Bio-FET, biosensors).

The aims of the study were the electrochemical characterization of immobilized self assembled PNFs on different electrode materials (Au, Pt and C) and the investigation of their possible application in the development of a biosensor for the detection of metals.

Some of the nanofibers displayed a high affinity towards Au due to the presence of cysteine residues in the self-assembled fibril structure. Based on the electrochemical behaviour and stability of immobilized layer the optimum electrode material and PNF was chosen. From the available literature concerning the ability of amino acid and peptides to bind metal ions<sup>4, 5</sup>, and knowing that the used PNFs have functional groups which have the potential of Cu<sup>2+</sup> complexation our target in the biosensor development was the copper ion, an essential metal which can be toxic at high concentration levels leading to gastrointestinal symptoms<sup>5</sup>.

The developed sensor could be regenerated, without affecting its binding properties as it is shown on Figure 1.

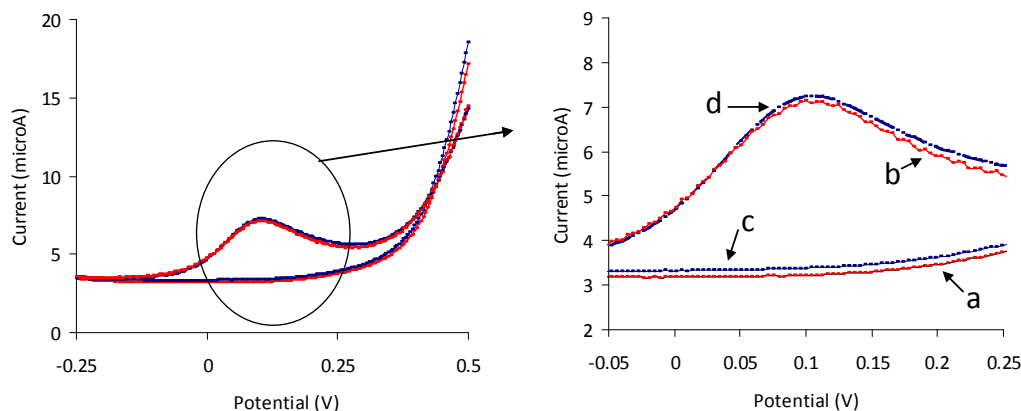


Figure 1. Square wave voltammogram of an Au-NC electrode before preconcentration in  $\text{Cu}^{2+}$  (a) , after preconcentration in  $60\mu\text{M}$  (b) , then regenerated (c) and finally reincubated with  $60\mu\text{M}$  of  $\text{Cu}^{2+}$  (d)

The biosensor using NC type PNFs as the biorecognition element was capable to detect copper and presented a linear range up to  $50\mu\text{M}$  with a sensitivity of  $0.68\mu\text{A cm}^{-2}\mu\text{M}^{-1}$ (Figure 2).

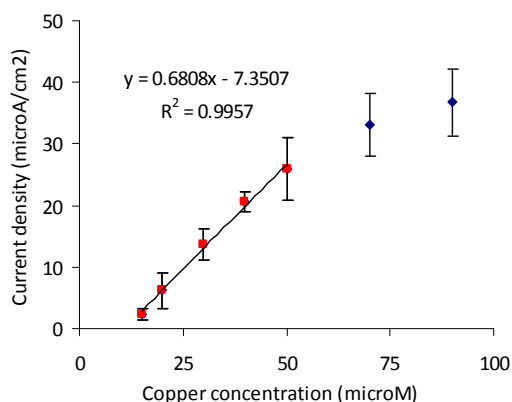


Figure 2. Calibration curve obtained for  $\text{Cu}^{2+}$  complexation NC type PNF modified Au electrodes.

Since is known that the maximum amount of copper allowed in drinking water being around  $30\mu\text{M}$ <sup>6</sup> the linear range of the sensor is suitable for  $\text{Cu}^{2+}$  monitoring in the drinking water samples.

## References:

1. Scanlon, S. et al., NanoToday, 2008, 3 (3-4), 22-30
2. Dinca, V. et al., Nano Letters, 2008, 8 (2), 538-543
3. Ryu, J. et al., Biotechnology and Bioengineering, 2010, 105 (2), 221-230
4. Yang, W. et al., Journal of Electroanalytical Chemistry, 2001, 516, 10-16
5. Chow, E. et al., Electroanalysis, 2006, 18 (15), 143-1448
6. <http://www.lenntech.com/applications/drinking/standards/drinking-water-standards.htm>

# Diphenylalanine Peptide Nanowires for Sensing Applications

Luigi Sasso, Indumathi Vedarethinam, Jaime Castillo, Jenny Emnéus, Winnie E. Svendsen

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*Preferred form of presentation: ORAL*

The EU project EXCELL [1] aims at exploring and understanding how the insertion of nanostructures inside cells and the exposure of cells/tissues to nano-structured surfaces affect cell function dynamics. This investigation is carried out by developing sensors for intra- and extra cellular monitoring. This would give deeper insights into some biological dynamic processes such as gene and protein expression, metabolism, signalling, and physiological responses.

Peptide based nanostructures are a candidate for the fabrication of 3-dimensional intra-cellular electrodes. This bio-material self-assembles into stiff tubular structures under mild conditions (aqueous solution at room temperature). Aside from their simple high-yield fabrication method, these peptide nanostructures are not toxic to cells, are mechanically and chemically stable, are resistant to some organic solvents, can be easily functionalized and can be used in various biological and non-biological applications [2].

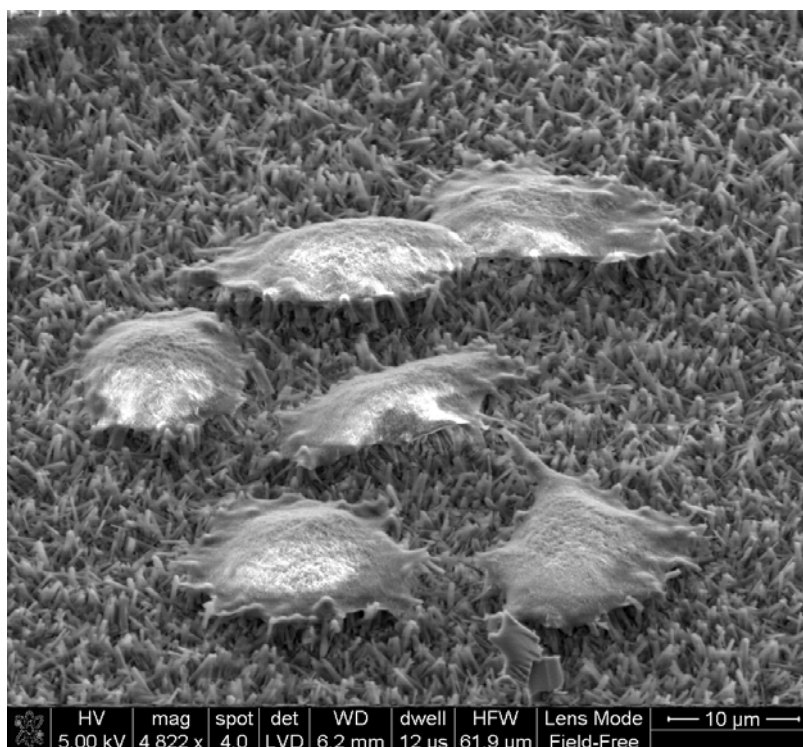
Vertically organized self-assembled peptide nanowires (PNWs) can be synthesized from an amorphous  $\beta$ -amyloid diphenylalanine peptide film by a high-temperature aniline vapor treatment [3]. The obtained structures are about 150-300 nm in diameter and 6-10  $\mu$ m in length. These structures have been found to have excellent chemical and thermal stability and to be resistant to proteolytic attacks [4]. We show here how these self-assembled diphenylalanine nanowires can be used for sensor applications.

The nanostructures' surface was modified and coated with conductive polymer materials such as polyaniline and polypyrrole. Polymer films were formed onto the peptide nanowires by a chemical electroless synthesis method, therefore creating peptide/conducting polymer nanowire structures vertically attached to a metal surface. The electrochemical behaviour of the modified metal electrode surfaces was studied with several electrochemical techniques such as cyclic voltammetry, chronoamperometry and impedance spectroscopy.

A functionalization of the PNW surface has been achieved via a Biotin-Streptavidin coupling. Biotin, linked to the free amino groups at the nanowires' surfaces, has been used as an anchoring base for various conjugated streptavidin complexes.

HeLa and PC12 cells have additionally been cultured on a PNW modified surface as an initial proof for the nanostructures' biocompatibility (figure 1).

The results obtained show the functionalization capability and biocompatibility of the PNWs, reflecting the structures' potential for the development of sensor devices



**Figure 1:** *Scanning Electron Microscopy image of HeLa cells cultured on a peptide nanowire surface*

### References

- [1] EXCELL: EU Project within the FP NMP program, <http://www.excell.nu/>
- [2] J. Castillo, S. Tanzi, M. Dimaki and W. Svendsen, *Electrophoresis*, 29, 5026 (2009).
- [3] J. Ryu, and C.B. Park: High-Temperature Self-Assembly of Peptides into Vertically Well-Aligned Nanowires by Aniline Vapor. *Adv. Mater.* 20, 3754 (2008).
- [4] J. Ryu, and C.B. Park: High Stability of Self-Assembled Peptide Nanowires Against Thermal, Chemical, and Proteolytic Attacks. *Biotechnol. Bioeng.* 105, 221 (2010).

# POLYPYRROLE COATING TO ENHANCE THREE DIMENSIONAL ELECTRODES FOR NEUROLOGICAL STUDIES

Patricia Vazquez, Luigi Sasso, Maria Dimaki and Winnie E. Svendsen

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*Submitted for oral presentation*

This work outlines an innovative approach to metallization of high aspect ratio electrodes for neurological studies. It ~~is~~ has been proved that out-of-plane electrodes enhance the sensitivity of the system in terms of measuring electrical signals in cell cultures [1]. Despite this advantage, their metallization is a challenge and a common obstacle in the development of microelectromechanical system (MEMS) devices of high aspect ratio and vertical walls [2].

In this work, electrode-pillars fabricated in silicon, with heights of about 70  $\mu\text{m}$  and very straight walls, are made conductive with this novel method, and their electrochemical sensitivity is greatly enhanced with the addition of the conductive polymer.

Polypyrrole (PPy) is a polymeric conductive material, used here as a coating of the electrode surfaces and patterned by standard photolithographic methods. The simplicity of this method resides in the synthesis of polypyrrole by chemical oxidation, in opposition to electropolymerization deposition [3], where a conducting substrate is needed.

The process guaranties perfect step coverage and thus electrical activity in the tall structures, unlike standard methods like sputtering or metal evaporation, that don't manage to cover all areas.

A first characterization of the electrodes by energy dispersive X-ray analysis (EDX) proved the viability of PPy on the walls, even after the lift-off process used for patterning. Also, a two point measurement of the resistivity of the material deposited on the silicon wafer gave a result of 32 kOhms over a distance of 1 cm, which demonstrates the conductivity of the system.

Moreover, electrodes in combination of metal/conducting polymer materials have been characterized by cyclic voltammetry; the presence of the conducting polymer film has shown to increase the electrochemical activity by over a factor of 10 when compared with electrodes coated only with metal. An electrochemical characterization of gold/polypyrrole electrodes showed exceptional electrochemical behaviour and activity, making the structures suitable for future in-vitro neurological measurements.

Furthermore, preliminary studies of cell biocompatibility encourage high expectations for neuronal recordings with this material; this will be the ultimate goal of our experiments.

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# Introducing electrochemical readout to mechanical sensors

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We present a micro-meter sized chemical sensor that combines mechanical and electrochemical readout principles. The sensor is structured as a cantilever (mechanical part) with an Au coating on top for the electrochemical readout.

A cantilever is a beam that is clamped at one end and free to move at the other. When a binding event occurs on one of the two surfaces the cantilever deflects, as a result of the generated surface stress<sup>1</sup>. The surface stress can either be compressive (downward deflection) or tensile (upward deflection) depending on how the molecules re-arrange themselves during the event. One therefore does not only obtain information on the *presence* of the molecules but also important information on the binding event itself<sup>2</sup>.

Cantilever sensors have found several applications ranging from detection of single DNA base-pair mis-matches to pesticide and explosives detection<sup>3, 4</sup>. The downside of cantilever sensing is that a target specific receptor layer needs to be immobilised onto the cantilever before it can specifically recognise a molecule or compound. This process can be rather time-consuming and limits the areas where this type of sensor can be applied.

In our work we present a method to increase the reliability of cantilever-based sensors by introducing electrodes on the cantilevers. In this way e.g. voltammetric techniques can be used for fingerprinting of the bound receptors. The combination of these two sensing principles are highly beneficial since also voltammetric techniques have its limitations. A CV does for example not provide any direct information on the conformational changes that might take place.

We therefore strongly believe in our novel sensing platform and are looking for collaborators within the electrochemistry community who are interested in understanding chemical binding events at the molecular scale.

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# Functionalization of Surfaces using Aryltriazene Chemistry

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One of the most versatile methodologies for carrying out covalent functionalization of surfaces is based on the reduction of aryldiazonium ions.<sup>1</sup> One of the few limitations of using aryldiazonium ions is associated with their high reactivity, which excludes the simultaneous presence of nucleophiles or strong reductants in the grafting solution. In addition, a controlled structuring of the modified layers becomes exceedingly difficult.<sup>2</sup>

Both these problems can be overcome by masking the aryldiazonium salt as an aryltriazene (through a reaction with a secondary amine). In a one-pot reaction the aryltriazene functionality can at any time be chemically cleaved (e.g. by adding an acid) to liberate the aryldiazonium once again as grafting agent. So far this approach has been employed successfully to carry out spontaneous grafting of a ferrocene functionality<sup>3</sup> and cathodic grafting of deoxyribonucleic acid (DNA);<sup>4</sup> two chemical systems which under ordinary conditions would be incompatible with aryldiazonium ions.

In this study, methods for using aryltriazene functionalities in acetonitrile as precursors for aryldiazonium ions for doing surface functionalization have been investigated to obtain a deeper understanding of the mechanism of the grafting process. Two main results will be presented: (i) A distinct linearity exists between the ratio of acid to aryltriazene concentration and the concentration of aryldiazonium ions in solution. (ii) Aryltriazenes can be anodically oxidized to liberate the corresponding aryldiazonium ions,<sup>5</sup> which upon a switching of the polarity of the electrodes may be used in a reductive electrografting of the surface. This approach has been further developed in an indirect version, in which the anodic potential may be lowered by as much as 1 V.

The method offers new ways of controlling the surface concentration of the grafting agent and hence ultimately the morphology of the resulting modified film formed. Because the grafting agent is only generated at the electrode surface and not in the bulk of the solution specialized and costly functionalities such as synthetic DNA for biosensor applications can be assembled at the surface. Finally, the procedure may be exploited in a scanning electrochemical microscopy (SECM) setup for decorating a surface with functional groups in a predesigned pattern.

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## Thermal stability of Dye-sensitized Solar Cells

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Currently photovoltaics (PV) account for 0.04% of the terrestrial energy sources, but this figure will grow to 1% in the year 2030. Even though different solar cell technologies will have different applications, the competition will presumably be fierce and the most effective and robust technologies will win the market. Conventional silicon (Si) PV can only sustain itself if the electronic Si industry will grow at the same rate as PV industry, but this seems unlikely, and hence the future PV market will probably be dominated by thin film PV and new concepts.

A newer thin film PV technology called Dye-sensitized Solar Cell (DSC) has shown very promising results. The DSC is thus close to market introduction and there remain only few obstacles to overcome in order to make this technology able to compete with more conventional thin film PV. [1]

In this work the high temperature stability of the DSC is examined.

Specifically it is shown that ruthenium based DSC dyes containing thiocyanate ligands such as N719 and Z907, may undergo ligand substitution reactions with electrolyte contained species such as 3-methoxypropionitrile (3-MPN) and 4-*tert*-butylpyridine (4-TBP) at temperatures above 80° Celsius.

Laboratory scale DSC based on ruthenium dyes containing thiocyanate ligands and cells based on synthetic degradation products, have been investigated using standard performance characterization, Liquid Chromatography-Mass Spectrometry (LC-MS) and Electrochemical Impedance Spectroscopy (EIS).

[1] Energy Environ. Sci., 2008, 1, 655-667

# Investigation of photocatalytic activity of titanium dioxide coating with varying thickness on metallic substrates

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Titanium dioxide ( $\text{TiO}_2$ ) in the anatase crystalline structure has been widely researched due to its photocatalytic nature. When photons with the energy equal to or higher than its band gap ( $\sim 3.2$  eV) are absorbed, a photo activation process produces holes and electrons. These electrons and holes generated can interact with the environment to produce redox reactions leading to the decomposition of organic molecules that come into contact with the surface. One of the most important species is the hydroxyl radical, which has a high oxidative power. In presence of suitable irradiation sources (such as UV light or visible light in the case of doped  $\text{TiO}_2$ ),  $\text{TiO}_2$  coating could be super-hydrophilic, self cleaning, anti-bacterial, etc. as anything that comes into contact with the surface can be decomposed due to its redox power. This has led to its interest as a technologically important material for various applications.

Photocatalytic titanium dioxide coatings on metallic substrate such as aluminium are of great interest as a self-cleaning and anti-microbial surface for various applications such as in the health and hygienic applications. In this case, the lightness of aluminium is combined with the functionality of  $\text{TiO}_2$  coating making it energy efficient and environmental friendly. However, since the photocatalytic effect is greatly dependent on the structure and properties of the  $\text{TiO}_2$  film, its characterization and proper deposition are essential for maximizing the efficiency according to each application. In this research work,  $\text{TiO}_2$  coatings on aluminium substrate (and on glass substrate as control samples) were fabricated by pulsed DC reactive magnetron sputtering with varying thicknesses (100 and 500 nm, 1 and 2  $\mu\text{m}$ ) in order to evaluate the relationship between thickness and the photocatalytic effect. The photocatalytic activity was measured using two techniques namely: (i) electrochemical methods such as Open Circuit Potential (OCP) measurements using a specially designed cell, and (ii) decomposition studies of an organic dye (methylene blue) using a flow cell followed by analysis of the reacted solution using UV spectrophotometer. Microstructure, phase distribution, and composition of the coatings were investigated using Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), and Glow Discharge Optical Emission Spectroscopy (GDOES). The results indicate a clear relationship between thickness and structure of the coating to the photocatalytic activity. Thicker coatings showed a higher degree of decomposition of methylene blue, while the thinner coatings were more transparent and induced less change in the visual aspects compared to the uncoated substrates.

**Keywords:**  $\text{TiO}_2$  coatings, magnetron sputtering, photocatalytic effect, methylene blue

# Effect of chloride impurities on the performance and durability of polybenzimidazole -based high temperature proton exchange membrane fuel cell

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## Abstract

The effect of chloride as an air impurity and as a catalyst contaminant on the performance and durability of polybenzimidazole (PBI) - based high temperature proton exchange membrane fuel cell (HT-PEMFC) was studied. The ion chromatographic analysis reveals the existence of chloride contaminations in the Pt/C catalysts. Linear sweep voltammetry was employed to study the redox behavior of platinum in 85% phosphoric acid containing chloride ions, showing increase in both oxidation and reduction current densities during the potential scans. The fuel cell performance, i.e. the current density at a constant voltage of 0.4 V and 0.5 V was found to be degraded as soon as HCl was introduced in the air humidifier. The performance loss was recovered when switching from the HCl solution back to pure water in the air humidifier. Under an accelerated aging performance test conducted through potential cycling between 0.9 V and 1.2 V, the PBI - based fuel cell initially containing  $0.5 \text{ mg.cm}^{-2}$  NaCl on the cathode catalyst layer exhibited a drastic degradation in the performance as compared to the chloride free MEAs. The mechanisms of the chloride effect on the fuel cell performance and durability were further discussed.

**Keywords:** Chloride impurities, acid doped poly benzimidazole, proton exchange membrane fuel cell, durability, catalyst.

## **Evaluation of environmental corrosivity by cathodic reduction analysis**

Marie Louise Petersen (Danfoss A/S)

### **Abstract:**

Electrochemical analysis techniques can also be used in Industry with great success. In Danfoss we use electrochemistry to evaluate the corrosivity level of the environment at our customers. This helps us to design more reliable electronic products and to develop more accurate life time tests. Simple corrosivity data about the external environment can be found in literature but often large variations can occur in the specific user environment.

One way to determine the corrosivity of the user environment is to place metal coupons (usually silver and copper coupons) at the customer site and expose them for approx. 30 days. After exposure the metal coupons are returned to the laboratory for analysis.

Cathodic reduction analysis is performed on the metal coupons. In this electrochemical process the corrosion products formed on the metal surface is reduced to pure metal. The reduction time will be proportional to the layer thickness of the corrosion products and thus the corrosivity of the environment.

The measured layer thickness of corrosion products on copper is compared to the layer thickness limits stated in ISA-S71.04-1985. This standard classifies four different corrosivity levels – G1, G2, G3 and GX – where GX is the most severe environment.

In the presentation the principle behind the analysis will be presented and various examples of user environments and their corrosivity level are shown.

# **Energy saving in electrodialytic remediation of contaminated soil by pulse current**

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## **Abstract**

The aim of this study was to investigate the possibility for energy saving in electrodialytic remediation of contaminated soil by pulse current. The experimental soil was contaminated by Cu with concentration of 1500 mg/kg. After four experiments, the results showed the total energy consumption was saved with 25% and 67%, and the energy consumption per removed Cu was saved with 25% and 94% respectively in 5mA and 10mA pulse current experiments. The highest Cu removal efficiency was obtained in pulsed current experiment with 10mA. Moreover, the application of pulsed current could intensify the acidification of soil samples, which benefits the removal of heavy metals.

**Key words:** Electrodialysis, Soil remediation, Pulse current, Energy saving



## **POSTER PRESENTATIONS**

## Covalent Attachment of Polymer Brush on Metal Substrates

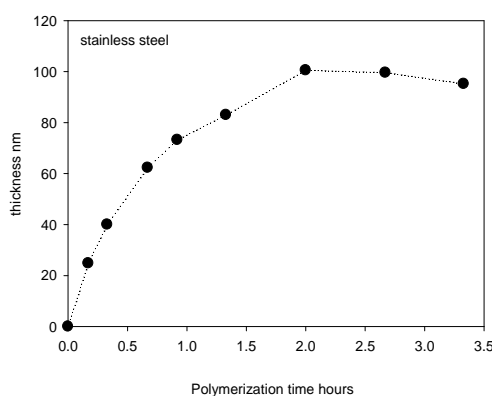
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Many technological applications such as retort pouches, food packaging, corrosion protection and prosthetic devices rely on strong integrity of metal-polymer laminates. In many such applications it would be highly desirable to covalently attach polymers on metal substrates to enhance metal-polymer interactions. Amongst other *grafting from* techniques SI-ATRP (surface initiated atom transfer radical polymerization) technique has gained much research impetus for providing simple and robust routes to form well-defined brush layers. The SI-ATRP technique offers better control over graft density, thickness of the grafted polymer layer and it is also easily adaptable to different functional monomers.

In this work we show that it is feasible to obtain polymer layers of PMMA [poly(methylmethacrylate)] of different thicknesses in a controlled manner on stainless steel using diazonium based chemistry<sup>1</sup> to form a precursor layer. Specifically, the stainless steel substrate was electrografted using  ${}^+\text{N}_2\text{-C}_6\text{H}_4\text{-(CH}_2\text{)}_2\text{-OH}$ , and after a subsequent reaction involving isobutyrylbromide a covalently bound ATRP initiator could be formed. The initiator layer structure, thickness, and bromine content were characterized using ellipsometry, XPS and PM-IRRAS. The surface-bound initiator has been successfully utilized to initiate ATRP of methylmethacrylate monomer in toluene at 75°C. The polymer thickness of PMMA has been measured as a function of polymerization time to show the overall controllability of the surface initiation process.



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# Carbon Nanotubes and Other Nanostructures as Support Material for Nanoparticulate Noble-Metal Catalysts in Fuel Cells

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## Abstract

In polymer electrolyte membrane fuel cells (PEMFC) a fuel – usually hydrogen – and oxygen are combined to produce electricity and water in an electrochemical process, which is commonly carried out at 60 – 80°C. For oxygen reduction and fuel oxidation to occur at such low temperatures platinum or platinum-alloy catalysts in the electrodes are required. To maximize the utilization of the noble metal it is frequently deposited as nanoparticles (1-5 nm) on a stabilizing support of carbon black. Carbon black provides good anchoring of the catalyst particles, but is prone to severe destructive oxidation at high electrical potentials encountered occasionally in fuel cells. Other nanostructures of carbon are being investigated as alternatives to carbon black as they have several beneficial properties. Multi-walled carbon nanotubes (MW-CNT) are an example of one type of these promising materials. Like carbon black they can conduct electrons to and from the reaction sites, and in addition their resistance to electrochemical degradation is better than that of carbon black due to their much higher structural perfection. This latter feature is indeed highly desired with a view to the durability of the fuel-cell electrodes. However, the low concentration of structural defects also poses challenges with regard to anchoring of the catalyst particles on the CNT surface. Thus, activation treatments introducing surface functional groups may be necessary. Also, the surface properties are responsible for difficulties in contacting the nanotubes with other substances in the electrode or electrode preparation. Other promising candidate structures for catalyst support include carbon nanofibres (CNF) and various modifications of CNTs. We present some of our work with the investigation of surface properties that are relevant for the preparation of fuel-cell electrodes with increased durability. This includes adsorption studies and studies of the role of the surface structure in the generation of materials-deteriorating reaction intermediates during the electrocatalytic processes.

## **Poster Presentation**

### **Degradation and contamination of perfluorinated sulfonic acid membrane due to swelling-dehydration cycles**

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#### **Abstract**

The property changes of commercially available perfluorinated sulfonic acid membrane – Nafion<sup>®</sup> 212 were continuously monitored during over 60 times swelling (distilled water boil at 1. atm.) – dehydration (vacuum dry, 80 °C,  $8 \times 10^{-2}$  mBar) cycles. A combination of weight loss, conductivity, ion exchange capacity, fluoride release and different types of microcopies and spectroscopies were applied in the study. The degradation behaviors include decreased conductivity, lower water content, release of fluoride, almost complete loss of ion exchange capacity etc. Despite only distilled water was used during the treatment, contamination from calcium was confirmed from both EDX element mapping and Raman spectroscopy. Calcium was found forming stable product with sulfonic group, which explains the enhanced membrane thermal property, and also lower water content and consequently lower protonic conductivity.

**Titel:**

Novel – and yet still “squared” – electrocatalytic materials

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**Abstract:**

An array of new Metal Organic Frameworks (MOFs) has been synthesized. All compounds are centred around the anion  $[\text{Pt}_2(\text{squa})_4]^{x-}$ , a partially oxidised bis-platinum complex in which two platinum ions are coordinated to four  $\mu$ -squarato (3,4-dioxocyclobut-1-ene-1,2-diolate,  $\text{squa}^{2-}$ ) ligands forming a windmill-like structure [1]. The cations in these MOFs are of the form  $[\text{X}(\text{NH}_3)_{4/6}]^{2+/3+}$  where X is a wide variety of metals from the fourth and fifth row.

One of these materials in particular, the Pt-Pt MOF, has been found to possess good catalytic properties. The initial catalytic experiments reveal a compound with catalytic properties comparable to those of the well-known commercially available HighSpec1000. It is especially note-worthy that the initial results show that the Pt-Pt MOF is capable of catalysing the oxidation of methanol at a significantly lower potential than HighSpec1000.

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## Electrochemical losses in microbial fuel cells

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A microbial fuel cell (MFC) is a bioreactor which uses bacteria to oxidize sugars and fatty acids in waste water resulting in electricity generation. Oxygen from the air is reduced at a platinum catalyst on the carbon cathode. Protons formed in the anode compartment transfer through a PEM membrane to the cathode. The bacteria grow in the carbon-paper anode and form a biofilm after some days.

The aim of this study was to demonstrate the advantages of a submersible MFC compared to a conventional two chamber H-shaped cell. DC I/V polarisation and Electrochemical Impedance Spectroscopy (EIS) was used to investigate the electrochemical losses in microbial fuel cells: anode/PEM/cathode. Symmetrical combinations anode/PEM/anode and cathode/PEM/cathode were used to resolve the AC response of anode, respectively cathode.

According to the EIS study the anodic resistance was lowest in the submersible MFC compared to an H shaped MFC due to the short electrode distance. This resulted in a 2-3 times higher power generation due to smaller ohmic losses. The biofilm on the anode reveals itself as semicircle in Nyquist-diagrammes. The anode behaved ohmic, whereas the oxygen electrode behaved Tafel-like.

As cathode, oxygen reduction and platinum catalyst worked well. Still, in laboratory setups one can benefit from using reduction of  $\text{Fe}(\text{CN})_6^{3-}$  in the cathode.

# **In situ investigation of microelectrodes using Controlled Atmosphere High Temperature SPM**

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Controlled atmosphere high temperature scanning probe microscopy is a unique instrument used to study the in situ investigation of microstructures of solid oxide fuel cell materials. The CAHT-SPM is designed for the purpose of not only obtaining the topography but also to get the conductivity images of the surface at high temperature (up to 650°C) with controlled atmosphere (air / hydrogen / oxygen). Topographical information is obtained like in a normal AFM in contact mode. In situ electrochemical impedance spectroscopy measurements can be obtained using the probe as working electrode. For this purpose thermally stable, highly conductive platinum-iridium alloy tips are used. In this investigation, metal microelectrodes on yttria stabilised zirconia were fabricated using sputtering deposition followed by photolithographic etching method. The electrochemical oxygen exchange reaction on yttria stabilised zirconia (YSZ) was investigated by means of metal microelectrodes. Surface topography and impedance images were obtained at 600°C using Pt-Ir tips that can be positioned at the desired surface locations for electrochemical measurements.

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## ABL90 Flex – Radiometers New Blood-Gas Analyser with Miniaturized Sensors

**M. Taagaard & B. Zachau-Christiansen**  
**Radiometer Medical Aps**

### Abstract

The keywords from the market needs for introducing a new blood-gas analyzer is *simpler, faster, better*. The instrument is intended for analyzing blood samples "Point of Care" i.e. near the patient on an intensive care unit.

ABL90 – Flex meets these requirement by introducing miniaturized sensors based on thick-film, screen-printed, solid state sensors combined on a ceramic alumina substrate. The analyzer contains mostly electrochemical sensors, but also some optical sensors are included. The electrochemical sensors are ion-selective electrodes for pH,  $cNa^+$ ,  $cK^+$ ,  $cCa^{2+}$ , and  $cCl^-$ . The  $pCO_2$  sensor is a Severinghaus type based on measuring the pH-change in an  $HCO_3^-$ -electrolyte after the  $CO_2$  has diffused through a silicone membrane. The metabolites are quantified by conventional biosensors measuring the current used for oxidation of  $H_2O_2$  after reaction of the substrate and oxygen – catalyzed by lactate and glucose oxidase, respectively. The oxygen sensor and the hemoglobin derivatives are all measured optically.

The simplicity is implemented by allowing only 2 accessories for operating the instrument. These are the Sensor Cassette and the Solution Pack. Also the inlet for aspiration of the sample is optimized for easy operation.

The Solution Pack contains calibrating solutions, quality control solutions and rinse-solutions.

The fast performance has been the largest challenge. The first step is implementation of a very compact flow channel allowing the measurement of 17 parameters in a very small sample volume (65  $\mu$ l). Further introduction of a one-point calibration point to be taken before the sample has been introduced – the back-log signal treatment – has allowed a very short analysis time of 35 s. Here it has been not trivial to ensure that the one-point calibration solution maintains all concentration values in the time from one sample introduction/calibration to the next. This means that the concentration shall remain constant during up to 4 h and the sensors have to be generated within the cycle time of 60 s. Furthermore it is necessary that the temperature equilibration of the sample is fast (/5s) and the sensors are fast enough to allow measurement within 17 s after aspiration. In this compact instrument the measuring performance is comparable to the specifications of our traditional bench top analyzers, e.g. ABL 800 – or better.



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**Title:**

**Numerical Simulations of Electrokinetic Processes Comparing the Use of a  
Constant Voltage Difference or a Constant Current as Driving Force**

**Abstract:**

Electrokinetic techniques are characterized by the use of a DC current for the removal of contaminants from porous materials. The method can be applied for several purposes, such as the recuperation of soil contaminated by heavy metals or organic compounds, the desalination of construction materials and the prevention of the reinforced concrete corrosion.

The electrical energy applied in an electrokinetic process produces electrochemical reactions at the electrodes. Different electrode processes can occur. When considering inert electrodes in aqueous solutions, the reduction of water at the cathode is usually the dominant in the process. On the other hand, the electrode processes at the anode depend on the ions present in its vicinity. Oxidation of water and chloride are typically assumed to be the most common processes taking place. Electrons produced in the electrode processes are transported from the anode to the cathode through the closed electrical circuit of the cell. In the solution, the electrical current is carried by the ions, which move towards the electrode with different charge. Therefore, different authors have studied the system using the circuit theory. Assuming that it is possible to study the region limited by the electrodes as a one-dimensional problem, the system consisting of electrolyte, electrodes, conductors and power supply can be considered as an electrical circuit connected in series. According to the Ohm's law, the voltage and the electrical current would be related to the conductivity of the media. This conductivity will vary as the electrokinetic process proceeds.

For a better control of the electrokinetic process, a constant difference of voltage or a constant current density between the electrodes is typically used. Most authors argued that fixing the current density results in more efficient electrokinetic experiments with less operative problems. Nevertheless, in long term treatments, maintaining a constant current density can be difficult due to limitations of the power supply.

In the present study, a theoretical comparison between these two working conditions, constant voltage or constant current, is discussed. A finite elements method was implemented and used for the modeling of electrokinetic processes. Results are consistent with the simplified circuit analysis, but the model offers a detailed theoretical description based in the integration of the more general continuity equations. Electrical potential distribution is calculated using the Poisson equation of electrostatics and current density is calculated from the flux term in the mass balance equation.

Numerical simulations of simple cases of desalination are shown. Results coincide with the experimental conclusion, being a constant current density more efficient in most cases. The relative importance between the electromigration transport term and other transport contributors, such as the diffusion term, is considered to be responsible of the differences observed.



## APPLICATION OF AN ELECTRIC DC FIELD FOR SODIUM CHLORIDE REMOVAL FROM RENDERED BRICKS

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### ABSTRACT

Renders are used as decorative and protective coats, acting as sacrificial layers and becoming the most vulnerable constituents of historical buildings. Repair render solutions incompatible with the background, pre-existing materials and inappropriate for the specific situation are still specified, producing new pathology [1, 2]. Salt damage is one of the major causes of renders decay. The salt transport behaviour of the substrate/render and the unfavourable environmental conditions may cause repeated cycles of dissolution-crystallization, which lead to the crystal growth and decay of building materials [3]. Sodium chloride is among the most abundant and common salts present in walls. They may have been originally present in materials (mortars prepared using unwashed beach sand) or may have penetrated later into walls from external sources (rising ground water, sea-salt spray, etc) [4]. Salt damage may occur at the surface or within the render layer (crypto-florescence), this last one usually causes more serious damage [5].

The present work is focused on the electrokinetic removal of chlorides from rendered bricks, as a step towards developing a desalination method for brick masonry, taking into consideration the interface between brick and mortar. Although there are studies concerning the sodium chloride removal with the application of an electric field DC on bricks and tiles [6, 7, 8], the influence of the whole system (brick + render) still need to be deeply studied.

The experiments were conducted at laboratorial scale on one type of bricks (80 mm × 60 mm × 34 mm) rendered in both sides using four different renders: two permeable lime mortars (L – slaked lime putty and LMet – slaked lime putty with metakaolin) and two high hydraulic, low permeability mortars (C – cement and CRes – Ready-to-use cement mortar with acrylic addition). All mortars were prepared according to standard procedures – EN1015-2 and cured in conditioned environment (20°C and 65%HR). After curing the specimens were contaminated with NaCl (79,61 g/L) through total submersion in the salt solution to prior application of current.

After treatment the chlorides were transported towards the anode (positive electrode). The results obtained until now, show that electrokinetic desalination could be efficiently used for desalination of the rendered bricks and reduce the risk of decay: by applying 10 mA during 5 days there was possible to obtain a reduction in chloride concentration in brick from 7457 mg/Kg to 2427 mg/kg and in the mortar near the cathode from 5230 mg/kg to 631 mg/kg. The removal % of chlorides strongly depends on render formulation as was confirmed by the different results obtained for the several specimens. Comparing the results obtained with the Austrian Norm ONORM B 3355-1, 5 days of treatment were not enough for chloride removal, and active salt removal is still advised.

The results found in the laboratory are encouraging for the efficiency of electrokinetic desalination, although further experimental work is being carried out to better quantify the time required for sodium

chloride removal in laboratory and to establish a possible correlation between the efficiency of this method in laboratory and in-situ scale.

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# Polyaniline Micro-Electrodes for Sensor Applications

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## Abstract

This work involves the use of co-doped polyaniline coated electrodes as pH sensors. Fabrication of the electrodes is achieved by defining and transferring the shapes/patterns of the electrodes by standard microfabrication techniques such as photolithography and metal lift-off. Doped and non doped polyaniline were investigated as sensing material, and characterized by Cyclic Voltammetry and Square Wave Voltammetry. An improvement of the electrochemical properties of co-doped polyaniline has been developed. It was demonstrated that co-doping of polyaniline with titanium ions and protonic acid has a significant effect in expanding the electrochemical activity of polyaniline in comparison with polyaniline doped only with protonic acid. Using titanium ions for doping polyaniline can be considered an efficient approach for the improvement of the electrical conductivity of polyaniline.

## Polymer planar electrodes for cellular sensing

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*Submitted for poster presentation*

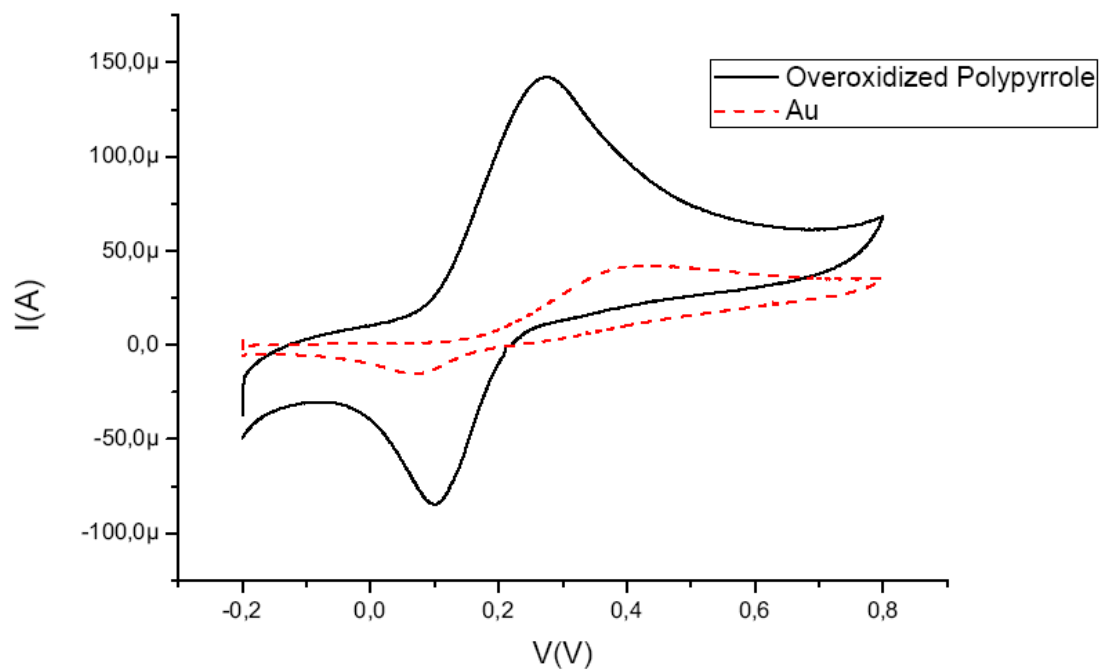
In this paper the modification of planar gold microelectrodes for electrochemical extra-cellular sensing using conductive polymers will be presented. The modification is done in order to increase the sensitivity and compatibility of the system to live cells, as well as protecting the gold surface in order to increase the lifetime of the sensor.

The main goal of the microelectrodes is to detect single cell (pheochromocytoma PC12) exocytosis events through amperometric and voltammetric measurements. The material under investigation is polypyrrole (PPy), which was chosen due to its conductivity and versatility. This material has already been shown to have good dopamine detection properties, especially when it is treated with doping [1] or overoxidation [2].

Electrodeposition by the cyclic voltammetry method was chosen for depositing PPy on microelectrodes. This method allows the deposition of PPy on only selected electrodes on a chip, making possible the specific functionalization of different electrodes. We studied the electrodeposition of a film of polypyrrole on gold. This was done both on macro- and on microelectrodes. We showed that the thickness of the film is important for the allowed spacing between electrodes, as thicker films increase the electrode dimensions and eventually bridge small gaps between electrodes. The thickness also effects the adhesion of the PPy to the electrodes; the larger the thickness the smallest the adhesion.

The polypyrrole film was modified as well by overoxidation using chloride, dodecylsulfate, sulphate and polystyrene sulfonate counterions. The performance of the modified electrodes after injection of dopamine in a microfluidic system was then compared to the performance of bare gold electrodes. The experiment showed that the modification with the dodecylsulfate counterion increased the electrochemical response (figure 1). After some time the PPyOx needs to be renewed. This is done by cyclic voltammetry in Phosphate Buffer Solution, as reported in the literature [3]. In this work the voltages used for the cleaning have to be lower, due to the fact that cells are growing on top of the electrodes.

Finally, the dopamine release from PC12 cells after triggering with a KCl solution was measured with the PPyOx modified electrodes. These preliminary experiments showed that the electrochemical response is higher as from the bare gold electrodes. Future work will include testing this system with microelectrodes and addressing the issue of proper exocytosis triggering.



**Figure 1:** Comparison of cyclic voltametry of 350  $\mu\text{M}$  dopamine in 0,1 M phosphate buffer solution at uncoated gold electrode and overoxidized polypyrrole coated electrode.

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# Characterization of nanoporous gold electrodes by electrochemical methods

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Keywords: nanoporous gold, Electrochemistry, Cyclic voltammetry, Electrochemical Impedance Spectroscopy, dealloyed time

Nanoporous gold (np-Au) as a novel electrode material has obtained extensive attention [1-3]. It has many advantages for microelectrodes, especially the large surface to volume ratio compared with conventional Au electrodes.

In this work, we use simple microfabrication techniques to create np-Au electrodes. The various pore sizes of np-Au were obtained by dealloying four types of AgAu alloys in nitric acid. For comparison, the deposited parameters of conventional Au were kept the same as the gold deposited conditions of AgAu. A FEI Nova 600 NanoSEM scanning electron microscope (SEM) with Oxford Instruments EDX system and a Ka X-ray photoelectron spectrometer from Thermo Scientific were used to acquire the morphology of different np-Au electrodes and analyze the elemental composition of deposited and dealloyed electrodes, respectively. The impedance of the np-Au samples, compared with conventional Au electrodes, was characterized using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The same electrochemical techniques were also used to investigate the influence of dealloyed time on the nanoporous gold. Ferri/ferro-cyanide  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  solution was used for the impedance measurements. Both the cyclic voltammogram and the Nyquist plots of the different samples reveal that the np-Au electrodes have much lower impedance than the conventional Au electrode. It is also found that the impedance of np-Au electrode generally decreases with the increase of the pore size. The optimized dealloyed time was determined by CV and EIS measurements, which was proved as well by the results of SEM and EDX.

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# **Stability of Au and Pt working electrodes and Ag/AgCl reference electrodes in Gamble's solution for engineered nanoparticles toxicity characterization**

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Engineered nanoparticles (ENP), particles with at least one dimension  $\leq 100$  nm, have attracted a great deal of interest during recent years, due to their many technologically interesting properties. However, some of these properties have given rise to concern that they may be harmful to humans [1-5]. In this study, a representative of the interstitial fluid of the deep lung, Gamble's solution [6], was employed to investigate the stability of different electrodes in order to characterize the redox activity between the Gamble's solution and engineered nanoparticles. The redox activity indicates the toxicity of the nanoparticles. Later, we will fabricate a portable sensor device to measure the amount and the toxicity of the particles. Gamble's solution was buffered with sodium phosphate to keep the pH at a constant value of 7.4. The investigated electrodes were; a commercial Au working electrode cleaned by several different methods [7] and also with a thiol modification on the surface, Pt working electrodes of different sizes, commercial and self-made, and commercial Ag/AgCl reference electrodes with KCl and self-made ones without KCl. Using open circuit potential time (OCPT) measurement in Gamble's solution, Pt working electrode showed a significantly higher stability and reproducibility than Au electrodes with the thiol surface modification or cleaned by any method. A commercial Ag/AgCl reference electrode from Gamry Instruments showed higher stability than one from CH Instruments.

This project is a part of "NANODEVICE - Novel Concepts, Methods, and Technologies for the Production of Portable, Easy-to-Use Devices for the Measurement and Analysis of Airborne Engineered Nanoparticles in Workplace Air", a research project funded by the European Commission in the context of the 7th Framework Program.

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# Galvanic series for metals and alloys used in electronic circuit board assemblies .

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## Abstract:

Corrosion reliability of electronic devices has inherently reduced today due to the demand for miniaturization, increased levels of contamination resulting from production practices, and implementation of new technologies with little regard to corrosion issues such as the use of no-clean fluxes together with the use of multiple materials, potential bias, and humidity exposure. Contamination on a printed circuit board assembly (PCBA) can be either process, application or handling oriented. The most common contaminations found on a PCBA are traces of no clean flux residue and human sweat or finger print due to handling. When these contaminations combine with moisture, an electrolyte solution is formed that contains ions causing conductivity in the solution, which on a biased component form a typical electrochemical cell.

In order to study the effect of such electrolyte solutions on the printed circuit board (PCB) materials, the electrochemical behavior of various metallic materials and coatings have been investigated using a micro-electrochemical set up with a tip resolution of 1 mm – 300  $\mu\text{m}$ . Open Circuit Potential (OCP) measurements and potentiodynamic polarization experiments were carried out and mixed potential behavior between various couples were evaluated. A galvanic series consisting of OCP values of various materials have been developed in 10 % of no clean flux solution and 10 % of sweat solution (according to the ISO standard ISO 3160-2 which comprises of 20g/l NaCl, 17.5g/l  $\text{NH}_4\text{Cl}$ , 5g/l acetic acid and 15g/l d,l lactic acid with the pH adjusted to 4.7 by NaOH). The galvanic series have been made by listing the open circuit potential of the different metals and alloys, and analyzing the mixed potential behavior between the anodic and cathodic polarization behavior of specific galvanic couplings such as Copper, Nickel and Gold, used in edge connectors, and mobile pad systems. The anodic and cathodic behavior of the coupling materials provides practical information about their corrosion performance under biased condition. Thus, from the galvanic series developed, the relative corrosion behavior of the electronic materials containing contaminants and exposed to high humidity can be assessed, and help the selection of materials for various applications based on their corrosion behavior.



## **Relation between alloy composition, surface finishing and optical properties when anodising aluminium**

Lightweight aluminium is a key part of the green technology of the future. The possibility of manufacturing low weight products and thereby increasing energy efficiency in e.g. the transport sector is very important. Moreover the aluminium is very easy and cheap to recycle, but the recycled (secondary) aluminium contains a lot of impurities making it less efficient to use than the newly extracted (primary) aluminium. Inter metallic particles of impurity element formed during casting and subsequent thermo-mechanical treatment in the secondary aluminium is the source of problems and secondary aluminium is therefore more obvious for casting than as wrought aluminium.

It was found that alloy composition, microstructure and surface finishing prior to anodizing all have an influence on the optical properties of the anodized surface. In this paper the effect of surface finishing on the optical property of the anodized layer has been investigated in detail for three commercial aluminium alloys namely 1050, 6082, and 5754 using photospectrometry, SEM, GDOES and XRD. It was found that the optical property of the anodized layer depends on the prior surface finishing and alloy composition, and that specular and diffused reflection varied depending on the above parameters.

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## NOVEL ELECTROCHEMICAL MICROFLUIDIC DEVICE FOR DRUG COMPOUNDS CHARACTERISATION

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Only about 1 out of 10,000 chemical compounds screened for applicability in the drug industry is found to be safe and effective [1]. Despite constantly rising drug development expenditures, the number of newly discovered and approved drugs has recently stagnated. Pharmaceutical development processes thus require innovative methods to analytically assess compounds in a cost-efficient manner. This paper reports a novel electrochemical microfluidic device designed for evaluating a compound's absorption *via* the partition coefficient. This parameter reflects lipophilicity, a key parameter used to biopharmaceutically and pharmacokinetically profile drug compounds.

Studies of ionic species distribution at the interface between two immiscible electrolyte solutions (ITIES) can elucidate physiochemical mechanisms of drug behavior *in vivo*[2]. Measuring the cyclic voltammogram (CV) and presenting the transfer potential as a function of pH in form of partition diagram gives an overview of the partition behavior of a drug compound and provides information on the partition coefficient as well as pK<sub>a</sub> of the compound (figure 1). The first systems for drug studies using ITIES involved large interfaces and phase volumes[3]. However, nowadays electrochemistry at ITIES focuses on designing the sensors based on micro interfaces. Examples of such micro-ITIES based sensors such as microscale pores in silicon membranes[4] or nanopipettes[5] or systems using droplets of organic or aqueous phase[6]. A microfluidic PMMA-based device for studying partitioning of ionizable drugs at ITIES by CV, that works in concordance with drug research processes trends seeking to conserve compounds for which only limited amounts are available is presented. The fabricated miniaturized device presented allows physicochemical characterization but also can be used as a sensor. It reduces reagent consumption and is suitable for integration with flow-based analytical methods such as high performance liquid chromatography.

The fabricated microfluidic device demonstrates potential as a powerful tool for the simple, fast and reliable drug compounds studies with future applicability to novel pharmaceutical research including drug-protein interaction.

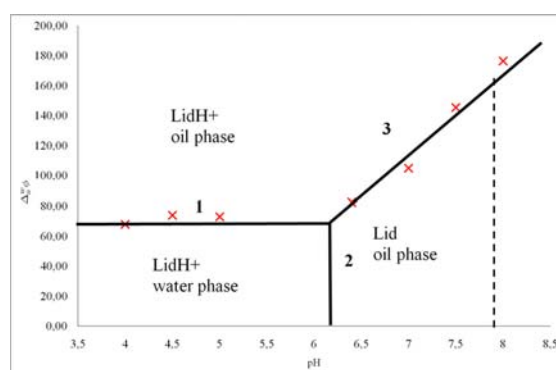


Figure 1. Ionic partition diagram of lidocaine measured at oil/water interface. The experimental points (x) represents measured half-wave potentials from CV

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# Preparation of Nafion 117™-SnO<sub>2</sub> Composite Membranes using an Ion-Exchange Method

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Nafion 117™-SnO<sub>2</sub> composite membranes were successfully prepared using an ion-exchange method. SnO<sub>2</sub> was incorporated into Nafion 117™ membranes by ion-exchange in solutions of SnCl<sub>2</sub> · 2 H<sub>2</sub>O in methanol, followed by oxidation to SnO<sub>2</sub> in air. The content of SnO<sub>2</sub> proved controllable by adjusting the concentration of the ion-exchange solution.

The prepared nanocomposite membranes were characterized by XRD and <sup>119</sup>Sn MAS NMR while the in-plane proton conductivity was found to decrease with SnO<sub>2</sub> content when evaluated with EIS. However, the conductivity was comparable to Nafion™ at SnO<sub>2</sub> contents below 8 wt%.

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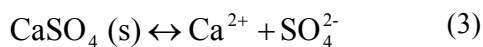
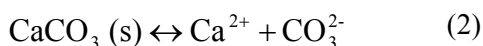
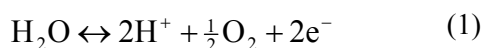
**Title:**

**The impact of calcium ions on the electrokinetic desalination of sulfate from stone: Preliminary results**

**Abstract:**

Salt can produce damage on porous materials like sandstone and bricks. The salts are transported into the pores in the material with moisture and due to the evaporation, the solution becomes super saturated and the salt can precipitate. Na<sub>2</sub>SO<sub>4</sub> is particularly damaging because of its increasing volume caused by hydration leading to a crystal pressure high enough for the material to crack.

In laboratory, an experimental setup with a clay containing CaCO<sub>3</sub> in the electrode compartments is used. The advantage of using clay with a relative high content of CaCO<sub>3</sub> in the electrode compartments is the buffer capacity. The production of acid at the anode (1) can decrease the pH in the part of the sample nearest to the anode. The carbonate containing clay (2) can avoid the pH drop by formation of bicarbonate and calcium ions are released and they will be the ions that can be transported into the sample instead of the protons. A side effect of the buffering from the anode compartment can be the generation of a calcium front in the stone sample and, as consequence; it can produce precipitation of CaSO<sub>4</sub> in the pores of the material (3). In this study it was evaluated if the calcium front can be a limiting factor for the desalination of sulfate from porous stone materials due to precipitations of CaSO<sub>2</sub> ( $K_{sp} = 4.93 \cdot 10^{-5}$ ). For the experiments 3 different stones were used.



By the current setup with CaCO<sub>3</sub> containing clay in the electrode compartments for the electrokinetic desalination of SO<sub>4</sub> the Ca concentration in the stone increased due to electrokinetic treatment. Voltage during the electrokinetic desalination is highest in samples with the highest pore concentrations of Ca and SO<sub>4</sub> and can be explained by precipitations of CaSO<sub>4</sub>. A significant increase in Ca combined with the unchanged SO<sub>4</sub> content for prolonged electrokinetic treatment indicates that precipitation of CaSO<sub>4</sub> can be the limiting factor for the effectiveness of the electrokinetic desalination of SO<sub>4</sub>. Nevertheless, the sodium reduction is increased with the prolonged duration for the electrokinetic treatment so; this limiting factor does not stop the electrokinetic process itself. It only affects to the sulfate reduction.

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