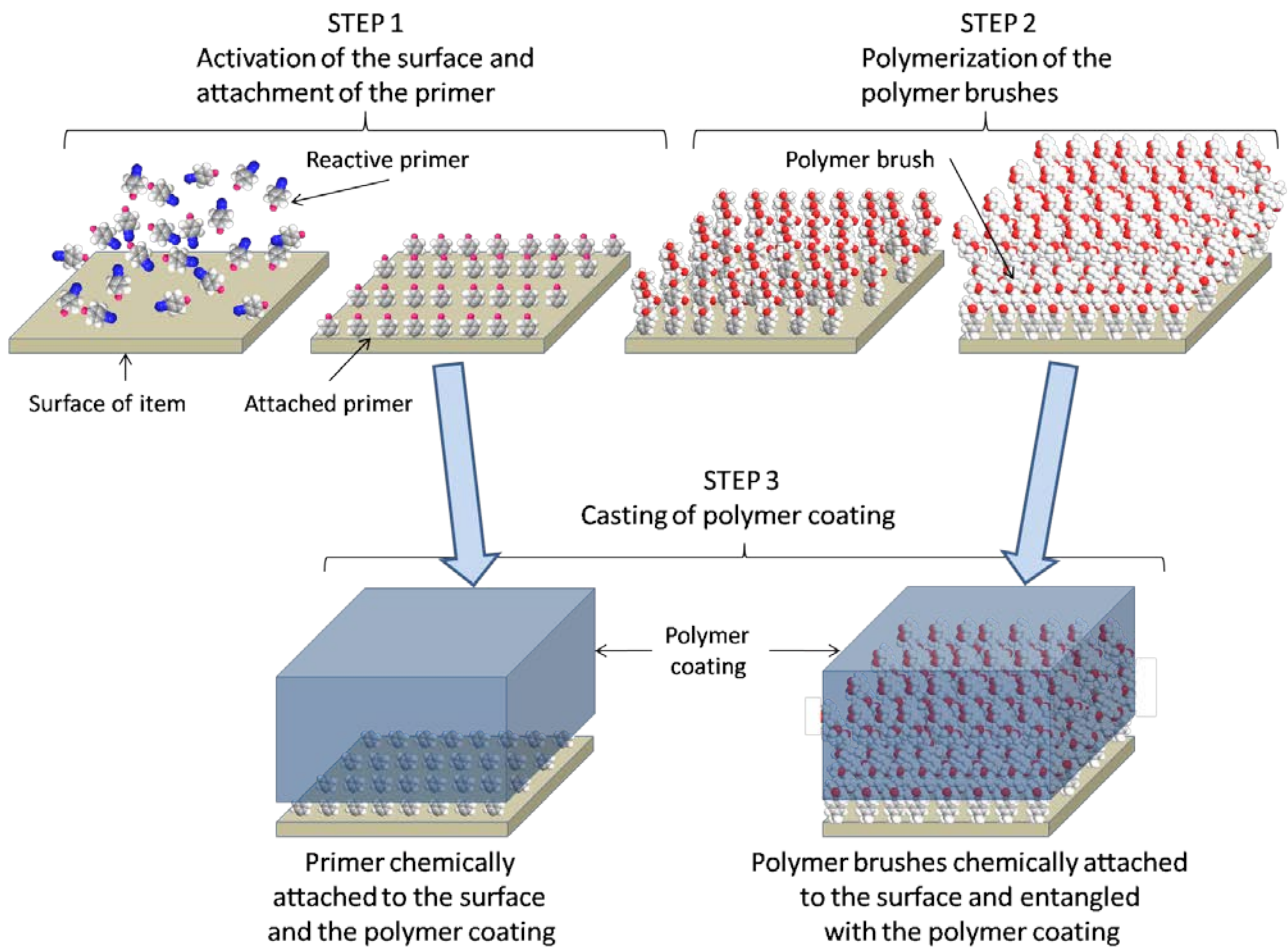




Electrochemical Science and Technology



A two day conference



Electrochemical Science and Technology Conference 2012

We are glad to welcome all of the 34 participants to the Danish Electrochemical Society's two day conference on Electrochemical Science and Technology at Aarhus University October 11-12, 2012. This year program contains 16 oral and 7 poster presentations covering a broad range of aspects of electrochemistry. The main talk of the conference will be given by Prof. *Frédéric Kanoufi*, ESPIC Paris. One of the objectives of the conference is to generate a forum for exchange of knowledge and to strengthen the collaboration between industry and academia. We hope that you will have an interesting and informative conference.

We will like to thank Elplatek for sponsoring the student awards and Aarhus University for hosting the conference.

Torben Lund

(Chairman of Danish Electrochemical Society)

Mogens Hinge

(Chairman of the local organization committee)

Program Thursday 11/10

- 14:30-15:00 14:30-15:00 Arrival to Aarhus University, Fredrik Nielsensvej 4, Bygning 1421
8000 Aarhus C, in Meeting room 2.2.
- 15:00-16:00 General Assembly in the Danish Electrochemical Society
- 16:00-16:05 Welcome by Mogens Hinge, Department of Engineering, AU

Mini Symposium: Electrochemical Surface Modifications (Chair: Torben Lund)

- 16:05-16:50 *Kim Daasbjerg*, AU: Radical Ways of Functionalizing Surfaces
- 16:50-17:20 *Allan H. Holm*, Grundfos: Electrochemistry at Grundfos; joining of materials and water treatment
- 17:20-17:40 *Mie Lillethorup*, AU: Investigating Charge Transfer Processes in Ferrocene-containing Polymer Brushes
- 17:40-18:00 *Jesper Vinther*, AU: Redox-Active Layers Originating from Electrogenerated Acid Facilitated Electrografting of Aryltriazines
- 18:00-19:00 Check-in hotels, Tour at Chemistry, and Poster session in meeting room 2.2
- 19:00 - ? Conference dinner, Dept. of Chem. Cantina, Langelandsgade 140, 8000 Aarhus C.



Program Friday 12/10

- 9.00-9.05 Opening of the conference, Kim Daasbjerg
 9.05-9.55 Invited Talk: *Frédéric Kanoufi*, ESPIC Paris Tech-CNRS: Inspecting the Local Reactivity of Surfaces from Their Electrochemical Triggering
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 10.25-10.40 Coffebreak

Oral presentations Session 1: Surface coatings (Chair: Mogens Hinge)

- 10.40-12.00 *Svava Davíðsdóttir et al*, DTU, Investigation of Photocatalytic Activity of Titanium Dioxide Deposited on Metallic Substrates by Plasma Technique
Rajnish Dhiman, SDU, SiCNanomaterials as Pt Catalyst Supports for Proton Exchange Membrane Fuel Cells
Torben Lund et al, RUC, The Role of N-Additives in Dye Sensitized Solar Cells
Lisbeth M. Ottosen et al, DTU, Electrokinetic Desalination of Portuguese Azulejo Tiles – Effect on Salt Crystals in the Interface between Biscuit and Glaze

- 12.00-13.00 Lunch

Oral presentations Session 2: Hydrogen production (Chair: Kim Daasbjerg)

- 13.00-14.20 *Juan Manuel Paz-Garcia et al*, A physiochemical and Numerical Model for Electrokinetics Transport
Cicilia Kjartansdottir et al, DTU, Durable electrodes for Alkaline Water Electrolysis
Sune Egelund et al, Siemens, High-Efficiency, Low Cost Electrodes for Alkaline Electrolysis
Anders Thygesen, DTU, Upgrading of Straw Hydrolysate for Production of Hydrogen and Phenols in a Microbial Electrolysis Cell (MEC)

- 14.20-15.20 Poster Session and coffee

Oral presentations Session 3: E (Chair: Steen U. Pedersen)

- 15.20-16.00 *Shaung Ma Andersen et al*, SDU, Interaction Between Nafion Ionomer and Noble Metal Catalyst for PEMFC's
Anders Bentien et al, AU, Experimental Evaluation of Electrokinetic Energy Conversion Efficiencies for Power Generation in Ion-Conductive Nano-Porous Membranes
 16.00-16.15 Student awards
 16.15-16.25 Closing remarks



Abstracts for Minisymposium

Thursday 11/10 16:00 – 18:00



Radical Ways of Functionalizing Surfaces

Kim Daasbjerg and Steen U. Pedersen

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 kdaa@chem.au.dk

Our recent research efforts are mainly concerned with the area of functionalized surfaces. To ensure an extraordinarily high stability of the modified layer the organic molecules are attached covalently to the conducting surface using electrografting. This method, being a fairly recent development in modified electrode research, may be carried out by oxidation of amines, aliphatic alcohols or aryl acetates or by the widely used reductive procedure involving aryl diazonium salts [1].

A common feature of all these procedures is that they involve radicals. Because of the high reactivity of radicals the electrode derivatization is usually very effective, leading to the formation of intertwined multilayers. Recently, we have succeeded in developing new tools [3,4] for controlling the structuring of the layers in the fast radical reactions, thereby enhancing the versatility of this new important modification method. In this manner a near-monolayer in a two-step “formation-degradation” process [4] as well as thick organic films using a mediating effect may be produced [5]. Furthermore, through in-situ generation of aryl diazonium salts from a reaction between the corresponding aryl triazenes and an electrogenerated acid (produced at the electrode surface), highly ordered aryl tethered films become obtainable. Also, unusual scanning electrochemical microscopy (SECM) patterns may be achieved using this procedure (Figure 1) [6].

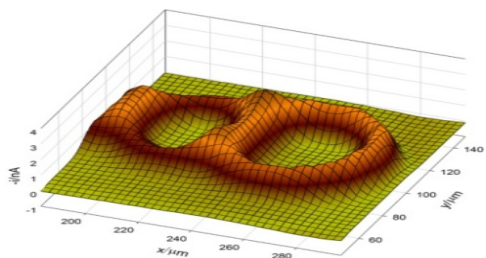


Figure 1. SECM image obtained at a 10 μm Pt ultramicroelectrode tip electrode (using ferrocene as redox probe) on a pyrolyzed photoresist film already modified by electrolyzing an aryl triazene and *N,N'*-diphenylhydrazine simultaneously at the substrate and tip electrodes, respectively, in 0.1 M $\text{Bu}_4\text{NBF}_4/\text{acetonitrile}$.

Finally, our progress toward the central objective of rational design of larger covalently modified molecular systems (including graphene) will be described, as will efforts toward creating new industrial coating solutions.

References

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- [2] (a) Malmos, K.; Iruthayaraj, J.; Pedersen, S. U.; Daasbjerg, K. *J. Am. Chem. Soc.* **2009**, 131, 13926–13926. (b) Malmos, K.; Iruthayaraj, J.; Ogaki, R.; Kingshott, P.; Besenbacher, F.; Pedersen, S. U.; Daasbjerg, K. *J. Phys. Chem. C* **2011**, 115, 13343–13352.
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- [5] (a) Ceccato, M.; Bousquet, A.; Hinge, M.; Pedersen, S. U.; Daasbjerg, K. *Chem. Mater.* **2011**, 23, 1551–1557. (b) Bousquet, A.; Ceccato, M.; Hinge, M.; Pedersen, S. U.; Daasbjerg, K. *Langmuir* **2012**, 28, 1267–1275.
- [6] Kongsfelt, M.; Vinther, J.; Malmos, K.; Ceccato, M.; Torbensen, K.; Knudsen, C. S.; Gothelf, K. V.; Pedersen, S. U.; Daasbjerg, K. *J. Am. Chem. Soc.* **2011**, 133, 3788–3791.



Electrochemistry at Grundfos; Joining of Materials and Water Treatment.

Allan H. Holm

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An annual production of more than 16 million pump units makes Grundfos one of the world's leading pump manufacturers. But where does electrochemistry fit into the picture? The presentation will provide an overview of two areas in which Grundfos utilises electrochemistry and electrochemical principles; strong and durable adhesion between otherwise incompatible materials and electrochemical methods of minimising fouling in water treatment. A large part of the work has been carried out in collaboration with university partners and we will discuss the technical motivations behind the investigations and illustrate how the collaborations have been used to clarify potentials and limitations as well as opened new areas of interest.



Investigating Charge Transfer Processes in Ferrocene-containing Polymer Brushes

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^bCenter for Oxygen Microscopy and imaging (COMI), Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark

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Charge transfer processes in redox polymer modified electrodes constitute a field of considerable interest with numerous important applications [1,2]. Recent advances in the living polymerization techniques, such as atom transfer radical polymerization (ATRP), offer the possibility to synthesize well ordered polymer brush structures. Such ordered redox polymer films represent an interesting platform in the study of charge transport phenomena.

We have developed electrodes modified with poly(ferrocenylmethyl methacrylate) brushes and investigated the charge transport through these surface films. Interestingly, the rate of electron transfer through the redox polymer brush system significantly depends on the nature of the anchoring layer between the substrate and the polymer chains as evidenced from electrochemical measurements as well as by ellipsometry, X-ray photoelectron spectroscopy (XPS), and polarization modulation-infrared reflection absorption spectroscopy (PM-IRRAS). The anchoring film originates from a diazonium-based ATRP-initiator containing a tertiary alkyl bromide functionality[3] and simply by changing the grafting conditions the characteristics of the initiator film may easily be varied.

More recently, studies evaluating the charge transport processes in the brushes from the solution site using scanning electrochemical microscopy (SECM) have been started. SECM analysis allows characterizing the electroactive layers without contribution from the anchoring layer. Hence, a very accurate determination of the charge transfer kinetics between immobilized redox species might be obtained

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REDOX-ACTIVE LAYERS ORIGINATING FROM ELECTROGENERATED ACID FACILITATED ELECTROGRAFTING OF ARYLTRIAZENES

Jesper Vinther^{1,2}, Joseph Iruthayara¹, Marcel Ceccato¹, Kurt Gothelf^{1,2}, Steen Uttrup Pedersen¹, and Kim Daasbjerg¹

Interdisciplinary NanoscienceCenter (iNANO), Aarhus University,

¹*Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark*

²*Center for DNA Nanotechnology (CDNA), Danish National Research Foundation, jvinther@chem.au.dk*

The mechanism of electrogenerated acid (EGA) facilitated electrografting (EGAFE) of aryltriazene (Figure 1, left) was studied in detail using Electrochemical Quartz Crystal Microbalance (EQCM), ellipsometry and X-ray Photoelectron Spectroscopy (XPS) techniques. The results demonstrate that EGAFE can occur via double potential step chronoamperometry. The first step is the electrochemical oxidation of the EGA agent to generate protons which in turn protonate the aryltriazene to form the corresponding aryldiazonium salt close to the electrode surface. The second step is the electrochemical reduction of the aryldiazonium salt, resulting in the electrografting of aryl groups. The film generated in the EGAFE of 4-(3,3'-dimethyltriaz-1-enyl)benzyl-1-ferrocene carboxylate (DMTF) consists of a densely packed layer of ferrocenyl groups with nearly ideal electrochemical properties. The reversible mass change observed by EQCM during the charging/discharging cycle of the ferrocenyl layer (Figure 1, right) clearly indicates the dynamic nature of the grafted layer wherein the counter ions move in and out of the film having a porosity determined by the applied potential.

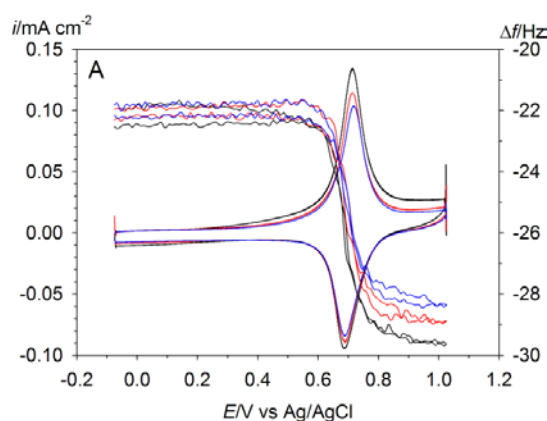
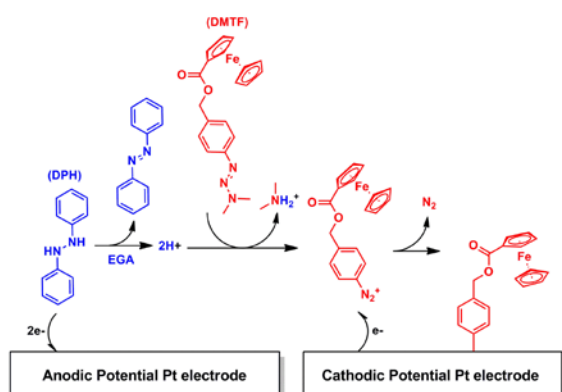


Figure 1. Left: Mechanism suggested for EGAFE of the aryltriazene DMTF. Right: First three voltammograms and frequency change recorded for a EGAFE of DMTF on Pt surface.



Abstracts for Talks

Friday 12/10 09:00 – 16:00

Program

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- 9.55-10.25 *Palle S. Jensen et al*, DTU: Incorporation of Metallic Nanoparticles into Surface Molecular Assemblies for Enhancement of Long-Range Protein Interfacial Electron Transfer
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- Rajnish Dhiman*, SDU, SiCNanomaterials as Pt Catalyst Supports for Proton Exchange Membrane Fuel Cells
- Torben Lund et al*, RUC, The Role of N-Additives in Dye Sensitized Solar Cells
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INSPECTING THE LOCAL REACTIVITY OF SURFACES FROM THEIR ELECTROCHEMICAL TRIGGERING

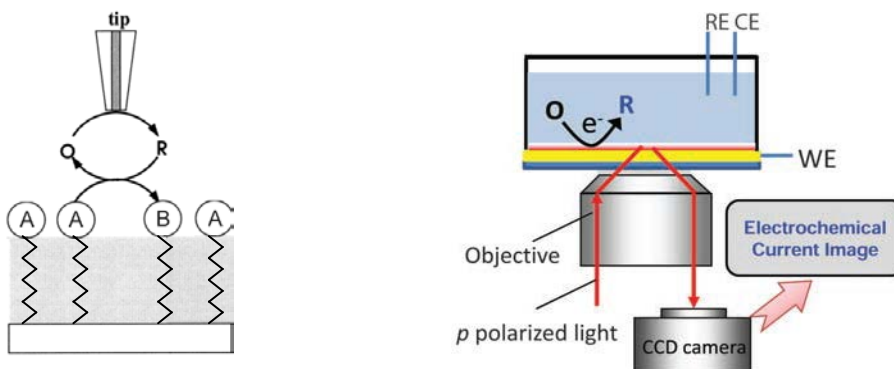
Frédéric KANOUI¹, Sorin Munteanu¹, Catherine COMBELLAS¹

¹ESPCI ParisTech-CNRS, Physicochimie des Electrolytes, Colloïdes et Sciences Analytiques, France, frederic.kanoui@espci.fr

Electrochemistry allows the creation of a great diversity of chemical reactants. It may be nicely used to modify the chemical and physical properties of different conductive or insulating surfaces. To do so one needs to generate and control fluxes of reactants close to a surface. One approach, based on local probes microscopies, consists of scanning a probe above a surface to interrogate and control its local physical and/or chemical properties (1). Indeed, Scanning Electrochemical Microscopy, based on microelectrodes tips, allows probing and transforming various interfaces.

Another approach consists of coupling the electrochemical actuation of a surface to a local in-situ and real time optical detection, owing to a microscopy imaging technique. For example, Surface Plasmon Resonance (SPR) was recently used to detect the local heterogeneity of a charge transfer reaction at an electrode (2).

This contribution will illustrate with recent works from our group how both approaches of local in-situ electrochemical inspections allow getting insight into surface transformation reactions.



Schematic approaches for surface reactivity inspection by scanning probe microscopy (left and 1) or coupled opto-electrochemical imaging (right and 2).

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(2) Tao N. and coll. *Science* **2010**, 327, 1363.



INCORPORATION OF METALLIC NANOPARTICLES INTO SURFACE MOLECULAR ASSEMBLIES FOR ENHANCEMENT OF LONG-RANGE PROTEIN INTERFACIAL ELECTRON TRANSFER

Palle S. Jensen¹, Qijin Chi¹, Jens Ulstrup¹

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A key challenge in nanoscale bioelectronics is to improve the efficiency of distant electron transfer of biological molecules. This objective could be achieved by integration of proteins and enzymes into specific matrices (e.g. nanoparticles) to assemble hybrid nanostructures. In this work, several types of gold nanoparticles (AuNPs) with sizes in the range 3-4 nm have been synthesized and characterized. The assembly of two-dimensional arrays of protein-AuNP hybrid bioconjugates on aAu(111) have been achieved, where the proteins (e.g. cytochrome *c* and azurin) have similar size to the AuNPs. Long-range interfacial electron transfer of cytochrome *c* and azurin have been investigated by electrochemistry, showing a significant enhancement of kinetics in comparison with reference systems without AuNPs. Possible mechanisms are discussed in the context of nanoparticle electronic effects.

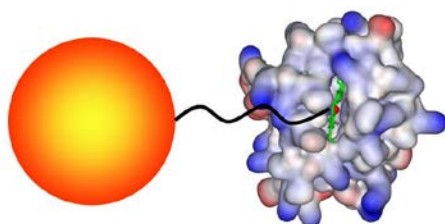


Fig. 1 Schematic illustration of aAuNP-protein bioconjugate

References:

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- (2) E. Katz, I. Willner, *Angew. Chem., Int. Ed.*, **2004**, 43, 6042.
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Investigation of photocatalytic activity of titanium dioxide coating deposited on metallic substrate by plasma technique

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Titanium dioxide (TiO_2) in the anatase crystalline structure corresponds to one of the most powerful photocatalytic 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. These special properties have increased the interest of TiO_2 as a technologically important material capable of being used in many industrial and everyday-life applications.

Metallic material such as stainless steel and lightweight 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.

Since the indented use of titanium dioxide coating is on various substrates it is important to have detailed investigation and knowledge of how the metallic substrate influences the photocatalytic properties. In this investigation, TiO_2 coating were made on aluminium alloy (AA1050) and stainless steel (S316) substrate using pulsed DC reactive magnetron sputtering. The photocatalytic activity was measured using three techniques namely: (i) electrochemical methods such as Open Circuit Potential (OCP) with and without UV-light. Linear sweep voltammetry, electrochemical Impedance Measurement (ii) Kelvin probe microscopy (iii) Optical measurements using reflection. Microstructural investigation was carried out by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Atomic force microscope (AFM)

The photocatalytic properties of TiO_2 film on different substrate varies significantly even though the characterization of SEM-figures, AFM and XRD indicated approximately identical TiO_2 film e.g. consisting of anatase phase, and having approximately thickness of 1,3. The TiO_2 coating on stainless steel has signified higher photocatalytic properties than TiO_2 on aluminium. The reason for the variance of the photocatalytic properties can be observed from the electrochemistry measurements and the phenomenal can be explained from the intersection between the metallic sample and the coating.



SiCNanomaterials As Pt Catalyst Supports For Proton Exchange Membrane Fuel Cells

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Fuel cells are seen as a prime future perspective for generation of clean energy. Their performance can only be accomplished by the proper selection of a catalyst support material to achieve the optimum life and price of the working cell. SiC holds many interesting properties as a potential catalyst support for the Proton Exchange Membrane Fuel Cells (PEMFCs). SiCNanomaterials have been prepared from nano-porous carbon black (Vulcan[®] XC-72) as a nano scale template by two different reactions, the first involving the reaction of carbon with SiO and, the second, direct reaction of silicon and carbon under a continuous Ar flow. The SiCnanocrystals obtained from solid phase reactions are free from agglomeration and have a granular morphology with particles size in the range of 50-150 nm, while those obtained from reaction with SiO holds the nano-porosity with particles size of 25-35 nm. Ptnano-catalysts have successfully been deposited by the polyol method, which is conventionally used for catalyst deposition over the several carbon based supports. These SiC based catalysts have been characterized for electrochemical activity and the results obtained are promising, which might indicate SiC as an alternative catalyst supports for PEMFCs.



The role of N-additives in Dye sensitized solar cells

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Dye-sensitized solar cells (DSC) have been extensively studied in the last decade as a promising renewable energy source because of their potential inexpensive manufacturing technology compared to silicon cells [1]. The solar to electricity efficiency of the DSC is enhanced by the addition of nitrogen additives like 4-*tert*-butylpyridine and 1-methylbenzimidazoles to the electrolyte. It is commonly accepted that the N-additives is adsorbed on the TiO₂ surface and change the conduction band of TiO₂ to more negative potentials. This increases the V_{oc} of the DSC and thereby the efficiency. The N-additives, however also play a key role in relation to the thermal stability of DSC ruthenium dyes at elevated temperatures (> 80 °C). On one hand N-additives may reduce the lifetime of the ruthenium dyes with the general structure RuLL'(NCS)₂ by thiocyanate ligand substitution as shown in eq. (1).



On the other hand dye degradation becomes much faster if the N-additive is removed from the electrolyte. A hypothesis will be suggested to explain the "N-additive protection effect" of the ruthenium dyes against reactions with other electrolyte components as solvent and mediators.

References

- [1] A. Hagfeldt, G. Boschloo, L.C. Sun, L. Kloo, H. Pettersson, Dye-Sensitized Solar Cells, Chemical Reviews, 110 (2010) 6595-6663.



Electrokinetic desalination of Portuguese Azulejo tiles – Effect on salt crystals in the interface between biscuit and glaze.

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Ceramic tiles are an important part of Portuguese cultural heritage and are worldwide appreciated. Azulejo tiles decorate inner and outer walls of churches, gardens, private houses, railway stations and a series of other buildings. Many azuljeo tile panels are damaged due to salt accumulation. Salts can crystallize on the surface or under the glaze, leading to severe damage as glaze lifting, fractures, scaling and granular disintegration.

Conservation actions today follow one of two approaches: either the tiles are removed from their support for ex-situ treatment (immersion in distilled water) before they are placed in the original place again or in-situ treatment of the azulejo panels by poulticing. Although poulticing is a well established technique, the results are still variable and unpredictable. Thus there is a need for a new in-situ technique which is gentle to the fragile azulejos.

Removal of salts from azulejos using an external DC field (electrokinetics) might be a potential method during conservation actions. The electrokinetic method has already experimentally been shown efficient for salt removal from natural stones, single bricks and from brick wall sections. Previously, few experiments have been made on electrokinetic desalination of single tiles, as well. These first experiments showed successful desalination when looking at average salt concentrations in the biscuit, however, it is the salt concentration in the interface between biscuit and glaze, which is the most important to decrease, as salt crystallization here causes disintegration of the glaze. The present study is focussed on this interface during electrokinetic desalination. Laboratory experiments are made with Portuguese XVIII century tiles which were removed from the panels due to salt decay. Before and after electrokinetic treatment the salt concentrations in the interface are evaluated using SEM-EDX.



A PHYSICOCHEMICAL AND NUMERICAL MODEL FOR ELECTROKINETIC TRANSPORT

**Juan Manuel PAZ-GARCIA¹, Björn JOHANNESSON¹, Lisbeth M. OTTOSEN¹,
Alexandra B. RIBEIRO², José Miguel RODRÍGUEZ-MAROTO³**

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³*Dept. of Chemical Engineering, University of Malaga, Spain, maroto@uma.es*

A physicochemical model is proposed for the mathematical description of electrochemically-induced transport processes, such as those taking place during electrokinetic treatments.

The model is based on the solution of the transient Nernst-Planck-Poisson system of partial differential equations. It includes the transport of water through the porous media due to capillary forces and electroosmosis, and the monitoring of the degree of saturation, the pH value and the porosity. Additionally, a comprehensive set of chemical and electrochemical reactions is included involving solid, gaseous and aqueous species and water in both the electrolyte and the solid structure.

A numerical model has been built for the mathematical solution of the proposed physicochemical model. This numerical model is based on a finite elements method for the integration of the transient system of partial differential equations, coupled with a Newton-Raphson method for computing chemical equilibrium. Electrochemical reactions are implicitly included in the finite elements method as part of the numerical procedure for the solution of the nonlinear system of equations.

The physicochemical and numerical model is described in a generalized manner. Therefore, it can be used to simulate a wide range of electrokinetic treatments in different inhomogeneous matrices, such as electro-desalination of construction materials and sculptures, electrokinetic remediation of contaminated soil or electrokinetic injection of matter into porous systems.



DURABLE ELECTRODES FOR ALKALINE WATER ELECTROLYSIS

Cecilia KJARTANSDOTTIR¹, Lars Pleth NIELSEN², Per MØLLER³

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

²*Danish Technological Institute, Denmark, lpn@teknologisk.dk*

³*Technical University of Denmark, Denmark, pm@mek.dtu.dk*

According to the World of Energy Outlook 2010, made by the International Energy Agency, renewable energy is the answer for a more secure, reliable and sustainable future. This implies that a larger fraction of the consumed energy will have to come from fluctuating renewable energy sources such as wind, sun and water. Thus, new alternatives will have to be developed enabling load management and energy storage that matches fluctuating consumer demands. Using the excess electrical power from the renewable energy sources to produce hydrogen via water electrolysis, offers the possibility of increased production capacity and load management with no greenhouse emissions.

A variety of water electrolysis systems have been proposed developed and constructed over the years. Alkaline electrolysis is the most mature commercial water electrolyte technology and offers the advantage of simplicity and is the current standard for large-scale water electrolysis system [1]. However, finding low cost electrode materials that are both efficient and having long term stability is one of the remaining challenges within the field of alkaline water electrolysis.

In the present work, physical vapour deposition (PVD) process, subsequent alloy formation followed by alkaline leaching is used to fabricate high surface area Ni-based electrodes for alkaline water electrolysis. Electrochemical measurements show that relatively good cathodic efficiency can be reached with the developed surface. High resolution scanning electron microscope images reveal large surface area with pores down to a few nanometers.

Durability tests carried out in a commercially produced electrolyser from GreenHydrogen.dk [2] operated with surplus power from wind turbines indicates no serious mitigation in electrode efficiency for at least 9.000 hours.

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High-efficiency, low cost electrodes for alkaline electrolysis

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With the increasing shortage of fossil fuels, hydrogen has been proposed as an essential future energy carrier and storage medium in a sustainable energy infrastructure. The introduction of hydrogen as new energy-carrier requires large scale production on a mega- or even terawatt scale – preferably without the depletion of natural or fossil resources as seen in high temperature reformation of hydrocarbons.

In this context water electrolysis is being investigated as a possible way of converting surplus energy from fluctuating sources into hydrogen acting as the new energy carrier.

A recently launched interdisciplinary project, carried out between Siemens Corporate Technology, GreenHydrogen and different research groups from The Technical University of Denmark (DTU), focuses on improving the present electrolyser-technology. The main vision in this project is to create a low-cost and highly effective route towards large scale hydrogen manufacture. A key element in this case is the selection and application of electro-active and durable coatings.

The presentation covers the main goals of the recently initiated PhD-projects in progress by the two authors, including a description on how electrochemistry is applied in the research and pursuit for suitable materials which are both catalytically active and durable in an electrolysis-application.



UPGRADING OF STRAW HYDROLYSATE FOR PRODUCTION OF HYDROGEN AND PHENOLS IN A MICROBIAL ELECTROLYSIS CELL (MEC)

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In a microbial electrolysis cell (MEC), hydrolysates produced by hydrothermal treatment of wheat straw was used for hydrogen production during selective recovery of phenols. The reactor volume based H_2 production rate was $0.025 \text{ m}^3 \text{ m}^{-3} \text{ h}^{-1}$ and equivalent to a COD (chemical oxygen demand) removal rate of $17 \text{ g m}^{-3} \text{ h}^{-1}$. The microbial community in the anode biofilm was adapted by establishment of xylose degrading bacteria of the Bacteroidetes phylum (16%) and *Geobactersulfurreducens* (49%). During the process, 61% of the chemical oxygen demand was removed as hydrogen at 64% yield. The total energy production yield was 78% considering the energy content in the consumed compounds and the cell voltage of 0.7 V. The highest hydrogen production was equivalent to $33 \text{ g m}^{-3} \text{ h}^{-1}$ and was obtained at pH 7–8 and 25°C. Accumulation of 53% phenolic compounds in the liquor was obtained by stepwise addition of the hydrolysate during simultaneous production of hydrogen from consumption of 95% for the hemicellulose and 100% of the fatty acids. Final calculations showed that hydrolysate produced from 1 kg wheat straw was upgraded by means of the MEC to 22 g hydrogen (266 L), 8 g xylan, and 9 g polyphenolics for potential utilization in biobased materials.



Interaction between Nafionionomer and noble metal catalyst for PEMFCs

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The implement of Nafion impregnation in electrode structure (catalyst layer) decreasing the noble metal catalyst loading by a factor of ten [1], is one of the essential mile stones in the evolution of Proton Exchange Membrane Fuel Cells' development among the application of catalyst support [2] and electrode deposition [3] etc. In fuel cell reactions, both electrons and protons are involved. Impregnation of Nafionionomer in catalyst layer effectively increases the proton-electron contact, enlarge the reaction zone, extend the reaction from the surface to the entire electrode. Therefore, the entire catalyst layer conducts both electrons and protons so that catalyst utilization in the layer is improved dramatically. The catalyst layer will in turn generate and sustain a higher current density. One of the generally adapted methods to impregnate Nafion into the catalyst layer is to mix the catalysts directly with the Nafion, especially supported catalysts, and then use the resulting mixture to fabricate the catalyst layer. The mixing ratio, mixing condition and most important interactions, between Nafionionomer and the catalysts/support (of different surface area, wetting property, and porosity) play a significant role in the performance of the final electrode product. In this work, ex situ study of Nafionionomer isothermal adsorption on catalysts / support materials is carried out. Experimental technique and method are improved based on earlier experience. Observation of Nafionionomer in aqueous solution is assisted by ^{19}F fluorine nuclear magnetic resonance spectroscopy (^{19}F -NMR).

References

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- [2] Petrow H. G. et al. U.S. Pat. No. 4,166,143 1979.
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Experimental evaluation of electrokinetic energy conversion efficiencies for power generation in ion-conductive nano-porous membranes

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In membranes the basic mechanism for electrokinetic effects is the coupling between the movement of ions and water and can be utilised for converting pressure (kinetic) energy into electrochemical energy or vice versa. E.g. power generation where movement of water from a pressure gradient drag ions along and creates a streaming potential (v). The electrokinetic energy conversion efficiency increases with the figure-of-merit $\beta = \frac{v^2 \cdot \sigma}{\kappa_H}$, where σ is the ion conductivity and κ_H is the hydraulic permeability and measurement of the three independent transport properties can be used for estimating the electrokinetic energy conversion efficiency. Investigations of electrokinetic effects for energy conversion has for the past decade regained attention with focus on applications within pumping in nano-fluidics where most experimental work is focused on clean-room fabricated nano-pores. Up to now ion-conductive membranes has not been considered for electrokinetic energy conversion. Here, we present initial experimental evaluation of the electrokinetic figure-of-merit of nano-porous ion-conductive membranes and estimate the conversion efficiency to be of the order up to 10 % in the present membrane and electrolyte concentration. It is anticipated that even higher efficiencies can be found in more rigorous studies.

This relatively large efficiency is very promising with respect to using ion-conductive membrane as a future decentralised energy source powered by solar/waste-heat or combustion created pressure differences. In that range fuel cells, thermoelectric materials and solar cells are competing technologies. Two major advantages of electrokinetic energy conversion is the versatility with respect to energy source in comparison to fuel cells or manufacturing price in comparison to semiconductor based thermoelectric materials or solar cells.



Abstracts for Posters



REDOX GRAFTING OF DIAZOTATED ANTHRAQUINONE: NEW INSIGHTS

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The recently introduced term “redox grafting” refers to the electrochemically driven reactions of surface modification involving the redox active groups of the modifier. This process is brought about by an electron transfer from the surface of an electrode to the species confined to the surface which are capable not only of storing but also transmitting the charge to the outer part of the layer, thus making possible further reactions at the film-solution interface. If the newly added layer has redox stations (carbonyl, nitro groups) then the process would replicate itself upon a favorable potential, resulting in up to 1 μm film thicknesses.

A suitable system for fundamental studies of charge propagation events through conductive multilayers is the 1-anthraquinonyl (AQ) based films due to their reduced tendency for chemical degradation. In the present work the anthraquinone-1-diazonium tetrafluoroborate salt (AQD) was utilized to investigate the formation of AQ multilayers. Electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D) technique was shown to be suitable for *in-situ* studying of the electrografting process. By the combining the cycling voltammograms with the frequency and dissipation changes from EQCM-D we have confirmed the proposed electron and solvated electrolyte transfer events accompanying electrografting.¹

References:

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A MODEL FOR COMPETITIVE ELECTROLYTIC REACTIONS INVOLVING GASEOUS SPECIES

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A model is presented for the calculation of the faradic efficiency of chloride oxidation with respect to the water oxidation reactions in electrolytic processes of salted water. This model is designed to predict the ionic flux of incoming H^+ or outgoing Cl^- into an electrolyte as a consequence of these competitive electrolytic reactions. In the model, gases from the reactions, i.e. O_2 and Cl_2 , form mixed gas bubbles which are freely released from the surface of the electrode with a constant total pressure, P_T (atm), equal to the pressure of the surrounding atmosphere, as:

$$P_{Cl_2} + P_{O_2} = P_T$$

Using the Nernst equation, partial pressures of the different components are obtained as a function of the concentration of aqueous chloride and the pH value at the vicinities of the electrodes. In this context, electrochemical potentials for the half reactions are assumed to have the same value, being the partial pressures the determining factor.

$$E_{Cl_2} = E_{O_2}$$

Generally, Nernst equation predicts high faradic efficiency of water electrolytic reaction with respect to chloride. Bubble overpotential, a specific form of concentration overpotential due to the evolution of gas at either the anode or cathode, is included in the model to fit the evolution of chloride to the experimental results.



ASSESSMENT OF THE PERFORMANCE OF AN EDTA-ENHANCED ELECTROKINETIC REMEDIATION OF A CONTAMINATED SOIL

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The use of BCR sequential extraction procedure at heavy metals contaminated soils for the prediction of the behaviour of some remediation techniques has proven to be an interesting tool. The success of these predictions are mainly observed for those techniques which are based on the mobilization of the toxic metals by acid, and the predictions can be correlated to the metals mobilized in the first fraction of the BCR, which uses acetic acid. Thus, when other mobilization agents are used, such as chelatant agents, the use of batch extraction experiments can be a useful tool for the prediction of the behaviour of techniques such as EDTA-enhanced electrokinetic remediation (EKR). We explore this issue using the same contaminated soil of Linares with the main details given in other papers presented at this conference.

The electrokinetic experiments were performed in two small methacrylate columns (3.2 cm² cross section area and 2 cm length) that hold about 15.5 g of the water saturated soil each one. The two columns are electrically connected in series, thus assuring that the same electrical charge flows through both columns. All the experiments were performed at a constant current density of 2 mA cm⁻². The addition rate of the ligand is about half of the circulating rate of electrical charge through the soil. Thus, one mol of ligand is added to the cathode compartment for each 2 moles of electrical charge (e⁻) circulated. If it is assumed that di-acid ethylenediaminetetraacetate anions are the main carriers of the electrical charge at the catholyte-soil boundary surface this addition rate would prevent the depletion of EDTA anions in the catholyte.

Contrary to the expected results, Pb was not recovered at the anode, and about a 4% was recovered at the cathode. Furthermore, an electroosmotic flow of about 1.7 mL h⁻¹ was observed from the anode toward the cathode. Therefore, the Pb-EDTA complex ions are undergoing two transport phenomena in opposite directions: electromigration toward the anode and electroosmosis toward the cathode. This could explain the no removal of Pb from the soil. The confirmation of such hypothesis requires the mathematical simulation of the process which is the future work to be performed.

Acknowledgements: The authors acknowledge the financial support of the Spanish Government through the project ERMES, CTM2010-16824.



ASSESSMENT OF THE PERFORMANCE OF HNO₃-ENHANCED ELECTROKINETIC REMEDIATION OF A CONTAMINATED SOIL

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When an electrical potential difference is applied between two electrodes inserted in the soil, the ions in the pore aqueous phase (including the heavy metal ions) are mobilized by electromigration towards the electrode of opposite charge where they are recovered, in a technique known as electrokinetic remediation (EKR). Frequently, water electrolysis reactions occur at the electrodes and generate an alkali and an acid front that migrate through the soil in opposite directions. This creates two possible problems: The basic front can cause metals precipitation and a low electrical-conductivity zone can arise in the region where the two fronts meet. To prevent these problems, an enhancement of the EKR technique consists in the addition of an acid to the cathode compartment.

This work studies the feasibility of a nitric acid-enhanced EKR of a soil from the ceased mining district of Linares (Spain). The soil samples for this study were collected at 10-30 cm depth, from a zone downstream from some slag heaps. The values obtained for the total concentrations of the most representative metals, in mg kg⁻¹, were Pb: 45200 ± 700, Mn: 2300 ± 200; Cu: 530 ± 16 and others in lower concentrations such as Zn, As, etc. A sequential extraction procedure is performed for each of these metals, indicating that their mobility is quite different, with more than 80% of the Pb soluble at a pH value about 2.4, whereas only about 50% of the Cu is solubilized at that pH value.

The very low hydraulic conductivity of this soil (below 10⁻¹⁰ m s⁻¹) makes EKR the only technique to be considered among the in situ ones. The electrokinetic experiments were performed in two small methacrylate columns (3.2 cm² cross section area and 2 cm length) that hold about 15.5 g of the water saturated soil each one. The two columns are electrically connected in series, thus assuring that the same electrical charge flows through both columns. All the experiments were performed at a constant current density of 2 mA cm⁻². Nitric acid solution is adequately added to the cathode compartments in order to hold the pH of the catholyte at a constant value. Around a 27% of the Pb in the soil was recovered at the cathode whereas the concentration of Pb in the half of the soil closer to the anode was reduce below 10% of the initial one.

Acknowledgements: The authors acknowledge the financial support of the Spanish Government through the project ERHMES, CTM2010-16824.



ASSESSMENT OF THE PERFORMANCE OF ACETIC ACID- ENHANCED ELECTROKINETIC REMEDIATION OF A CONTAMINATED SOIL

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When studying the remediation of soils contaminated by heavy metals the BCR fractionation has proven a very useful tool for the prediction of the performance of some techniques. On another paper presented at this conference we presented the results obtained for the remediation of a soil from the mining district of Linares (Spain) contaminated by heavy metals, mainly by Pb using the electrokinetic remediation (EKR) enhanced by the addition of nitric acid at the cathode compartment. In this case we use acetic acid instead.

The BCR results indicate that more than 80% of the Pb present in the soil is recovered in the first step of the fractionation analysis which uses acetic acid. Therefore we decided that EKR should give a good performance when enhanced by acetic instead of nitric acid.

The experimental setup and procedure is the same described in the other paper: two methacrylate columns electrically connected in series that hold 15.5 g of water saturated soil each, and which are crossed by a constant current with a density of 2 mA cm^{-2} . In this case, an acetic acid solution is adequately added to the cathode compartments in order to hold the pH of the catholyte at a constant value automatically controlled.

The recovery of Pb at the cathode is similar to that obtained with the strong acid enhancement (around a 30% of the Pb). Also the concentration profiles of Pb in the soil column are similar for the two types of enhancement. Nevertheless, the acid consumption rates at the cathodes are extraordinarily different. The protons addition rate for the acetic acid is more than four fold higher than that needed with the nitric acid, and than the rate of charge circulating through the soil. On the other hand, the time required for the achievement of a similar efficiency in the clean-up is 2.5 fold higher for the nitric acid than for the acetic.

The explanation of such differences requires the mathematical simulation of the process, which is the next step in the research work.

Acknowledgements: The authors acknowledge the financial support of the Spanish Government through the project ERHMES, CTM2010-16824.

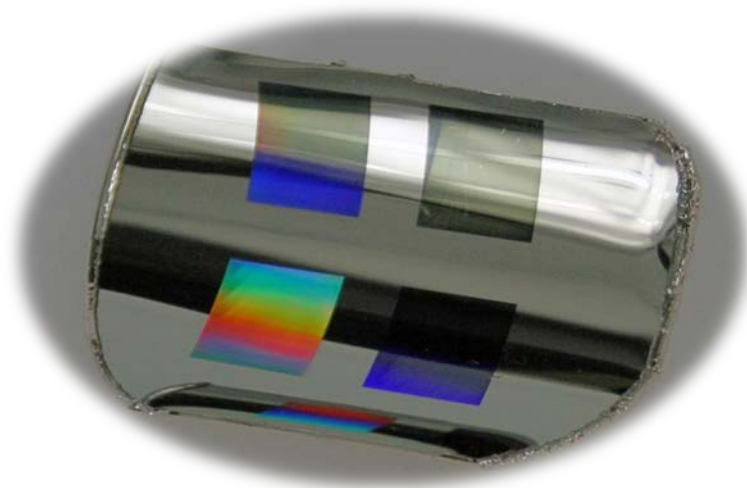


Electrochemical planarization of surfaces for micro- and nano-structuring

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By micro- and nanostructuring a surface it is possible to obtain self-cleaning properties, structural colors, light absorption, hydrophobicity, anti-stiction, increased friction or surface joining properties. The vision of the Danish High Technology platform “NanoPlast” is to develop and implement a technology that enables the use of nanostructured surfaces on injection moulded plastic components. The aim is to use nanotechnology in the production of plastic parts, where nanostructures are transferred from the surface of the injection moulding tool to the surface of the moulded plastic parts. This will enable new creative surface functionalities such as self-cleaning surfaces and structural colours in cheap plastic parts. The technology developed in the NanoPlast platform will enable nanostructures on free form moulded products. Today, mass production of nanostructured injection moulded surfaces can only be done when manufacturing planar items such as CDs and DVDs. In order to produce well defined micro- and nanostructures on the injection moulding tool, critical requirements are made to the surface roughness. As high precision polishing of the complex 3D surfaces of the injection moulding tool are extremely costly and time consuming, electrochemical processes have been sought for planarization of the surface. In this presentation, pulsed and DC deposition of Cu, Ni/Co alloy is attempted reduce surface roughness, and effect of pH and [Co] is investigated.





ELECTROCHEMICAL CHARACTERISATION OF ATMOSPHERIC PLASMA SPRAY COATINGS FOR WATER ELECTROLYSIS

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Raney nickel coatings (50/50 NiAl) for hydrogen electrodes were produced by atmospheric plasma spraying (APS) using different powders and spray parameters. The coatings were characterised using a specially adapted electrochemical testing method. The disc specimens were mounted in a holder that restricts exposure to the coating at the centre (Ø11 mm, 1 cm²). Testing was performed in a three-electrode cell consisting of the disc specimen (Ø11 mm), a nickel counter electrode and a mercury/mercury oxide reference electrode. The test solution was 25% KOH maintained at 70 °C throughout the test. Subsequent to activation and conditioning of the specimen, a galvanodynamic scan was performed from 0 to -300 to +300 mA/cm².

Compared with non-coated nickel, the NiAl coatings provide a considerable improvement (i.e. reduction) in cell voltage, even at a small coating thickness of 30 µm. A wide range of coatings produced by APS have been tested this way. The best performance is observed for a coating with 100 µm thickness and it is mainly ascribed to improved cathode properties. No additional improvement was observed by increasing the coating thickness further to e.g. 300 µm. The electrochemical performance is determined by a complex relationship between the applied spray parameters and the obtained microstructure. This relationship is not yet fully understood, but the tests show that very high efficiencies can be obtained for Raney nickel coatings deposited by APS. Further optimisation of the promising NiAl electrode surfaces will require improvement of the anode side.



WIRING UP SINGLE MOLECULE ELECTRONICS

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Preliminary results in design and production of single molecule electronics are presented. Artificial DNA nanostructures are designed for the organization of functional materials to create nanoelectronic devices. DNA origami, in which a long single strand of DNA is folded into a shape using shorter staple strands, can display nm-resolution patterns of binding sites, in principle allowing controlled arrangements of organic oligomers, carbon allotropes, silicon nanowires, or quantum dots. DNA origami are synthesized in solution and precisely deposited on SiO₂ between prefabricated nano-sized metal wires (Figure 1, left) by use of electron-beam lithography. Using a 4-point probe setup, electronic conductivity is measured across single molecules (Figure 1, right).

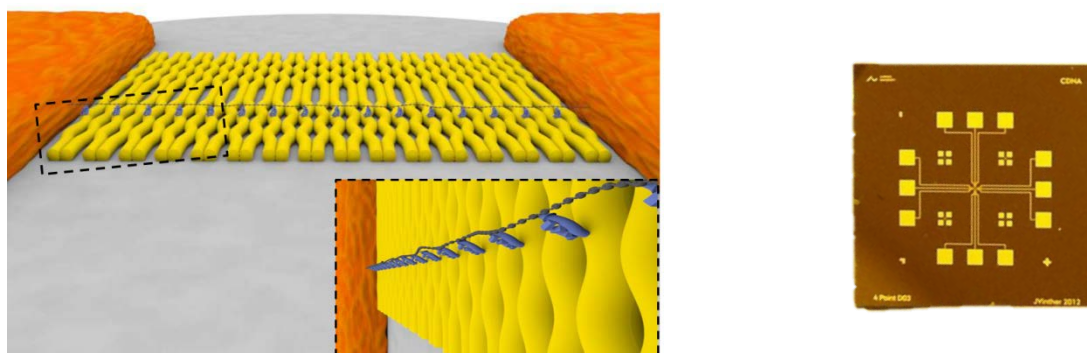


Figure 1. Left: Animation by Niels V. Voigt, illustrating a single molecule directed between two metal wires by a surface deposit DNA origami. Right: Silicon chip with twelve micro fabricated gold wires, bridging the macroscopic domain with the microscopic domain.



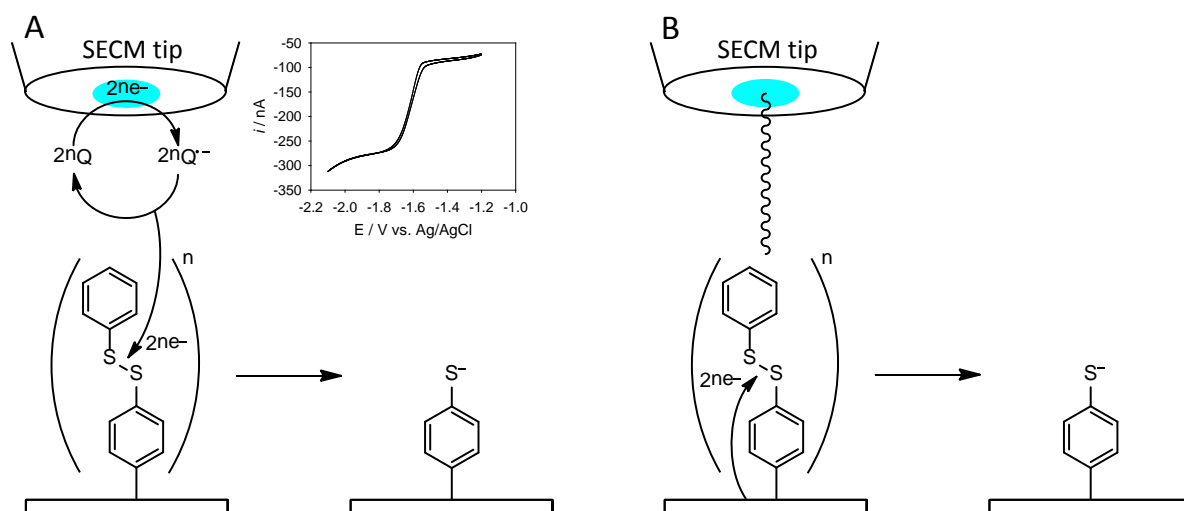
Using Scanning Electrochemical Microscopy (SECM) to Create Monolayer Patterning *via* Multilayer Degradation

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A top-down method was developed to generate a surface pattern of a single organic monolayer containing a thiophenyl functionality. This new strategy exploits the possibility of reducing disulfide units incorporated in an electrochemically grafted multilayer¹, either by film degradation *via* a tip generated electron carrier (mediated cleavage, Scheme 1A) or by confining the electric field lines to the tip-substrate gap by using the SECM tip both as the counter and reference electrodes (direct cleavage, Scheme 1B). The reactivity of the exposed thiophenyl groups makes this strategy suitable for fabrication of a variety of microarrays to serve, e.g., as biosensors. The time dependent evolution of the pattern in conjunction with time-resolved simulation was used to gain insight into the kinetics of the film degradation in two dimensions, i.e., the vertical and lateral pattern propagation.



[1] L. T. Nielsen, K. H. Vase, M. Dong, F. Besenbacher, S. U. Pedersen, K. Daasbjerg. J. Am. Chem. Soc



Conducting and Ordered Carbon Films Obtained by Pyrolysis of Covalently Attached Polyphenylene and Polyanthracene Layers on Silicon Substrates¹

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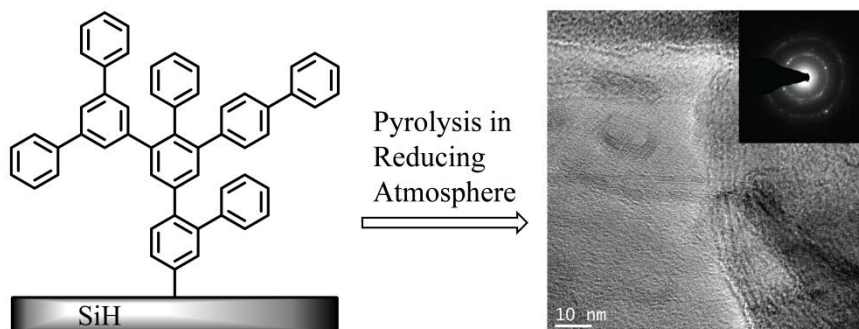
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Graphite-like thin films with excellent electrode properties were obtained by pyrolysis of nanometer thick electrografted layers of polyphenylene and polyanthracene layers on silicon substrates in forming gas atmosphere. The pyrolyzed grafted films, characterized by using different surface analytical techniques, consist of graphite-like layers of 5 to 26 nm crystallite thickness with electrochemical properties similar to those of pyrolyzed spin coated photoresist films. Hence, pyrolysis of covalently bonded organic layers is an alternative approach to obtain very thin conducting carbon films strongly attached to a substrate. Further, this technique can be applied to substrates of any geometrical structure, in contrast to spin coating techniques. It is suggested that thin graphite-like films on silicon produced in this manner could serve as substrate for spectroelectrochemical investigations of surface reactions by attenuated total reflectance experiment or in the production of optically transparent electrodes.



[1] *Journal of Materials Chemistry*, 2012, **22**, 18172-18180



Eco Chemie – MetrohmAutolab

Eco Chemie was founded in 1986 and is since 1999 a member of the Metrohm group. Since October 1st, 2009 our official company name is MetrohmAutolab, reflecting the customer oriented combination of the worldwide Metrohm sales and support organization and the high quality Autolab series of instruments.

ISO 9001:2008 certified, MetrohmAutolab has been setting the benchmark in electrochemical research instrumentation for more than two decades. With base in Utrecht, The Netherlands, MetrohmAutolab designs and manufactures Autolab instruments, accessories and software for electrochemistry.

Known for innovation, the Autolab was the first commercial digital potentiostat/galvanostat, that was completely computer controlled. Our latest software package NOVA has again set a high standard for powerful electrochemical research software.

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