



Electrochemical Science and Technology Conference 2014

9-10 October



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Program Thursday 9/10

- 14:00-14:45 General Assembly in the Danish Electrochemical Society
- 14:45-14:50 Welcome by Johan Hjelm (Chairman)
- 14:50-15:35 Invited speaker: *Jesper H. Wandrup*, R&D Radiometer Aps: A clinical and Analytical Review of Electrochemical Sensor Development in Radiometer in Relation to Optimal Monitoring of Critically ill Patients
- 15:35-16:20 Invited speaker: *Lo Gorton*, Professor, Department of Biochemistry and Structural Biology, Lund University, Sweden: Electrochemical Communication between Bacterial Cells/Biological Membranes and Electrodes
- 16:20-16:40 Coffee break**
- 16:40-17:00 *Svava Davíðsdóttir*, DTU – Division of Materials and Surface and Engineering: Interfacial structure and photocatalytic activity of magnetron sputtered TiO₂ on conducting metal substrates
- 17:00-17:20 *Kirill Bordo*, DTU: Electrochemical profiling of multi-clad aluminium sheets used in automotive heat exchangers
- 17:20-17:40 *Visweswara Gudla*, DTU – Department of Mechanical Engineering: Anodizing of Al-Zr and Al-Ti model alloys: Microstructure and Optical appearance
- 17:40-18:00 *Iosif Fromondi*, Metrohm Autolab B.V. : Measuring raw signals in electrochemical impedance spectroscopy
- 18:00 Dinner**

Program Friday 10/10

- 09:00-09:45 Invited speaker: *Dermot Diamond*, Professor, Co-founder and Director of the National Centre for Sensor Research, Dublin City University, Ireland: Calixarenes as ionophores in ion-selective electrodes
- 09:45-10:30 Invited speaker: *Tim Albrecht*, Associate Professor, Imperial College London – Department of Chemistry: Functionalized solid-state nanopores for biosensing applications
- 10:30-10:50 Coffee break**
- 10:50-11:10 *Chiara Canali*, DTU – Department of Micro-and Nanotechnology: Impedance-based detection for facing new challenges in biotechnology – Enhanced 3D sensing, conductometry and electrode functionalization
- 11:10-11:30 *Christopher Schulz*, Lund University – Department of Biochemistry and Structural Biology: A cellobiose dehydrogenase biosensor tuned by cations to study the decomposition of lactose/ibuprofen containing tablets
- 11:30-11:50 *Kamrul Hasan*, Lund University: Photo-microbial fuel cell based on cyanobacteria for harnessing solar energy
- 11:50-12:10 *Torben Lund*, RUC: Modification of TiO₂-based dye-sensitized solar cell photo anodes by chemical and electrochemical grafting strategies



12:10-13:30 Lunch and poster session

13:30-13:50 *Ioannis Spanos*, KU Nano-science Center: Structural disordering of de-alloyed platinum bimetallic nanocatalysts – Its role on oxygen reduction reaction activity and nanoparticle stability

13:50-14:10 *Aleksey Nikiforov*, DTU Department of Energy Conversion and Storage: Non-Pt catalysts for intermediate temperature water electrolysis

14:10-14:30 Coffee break

14:30-14:50 *Kristian Bastholm Knudsen*, DTU Department of Energy Conversion and Storage: A Study of e-transportation through Li_2O_2 , the main discharge product in the Li-O_2 battery

14:50-15:10 *Daniel Minzari*, IPU: Electrochemical preparation of injection moulding tools for micro- and nanostructuring

15:10-15:30 *Marie Lund Traulsen*, DTU Energy Conversion: In operando raman spectroscopy as a tool for investigation of solid oxide electrodes

15:30 Closing remarks



Short CV



Dr. Wandrup is Principal of Medical Scientific Affairs in R&D of Radiometer, Copenhagen, Denmark.

In 1973 he earned a University degree, Cand Scient (MSc) in organic and physical chemistry at the University of Copenhagen.

In 1980 he became a Medical Doctor, MD at the University of Copenhagen. In 1989 he got his Danish medical specialist license in Chemical Pathology and earned Danish University degree of medicine as Dr. med. (DMSc – Doctor of Medical Science) on a thesis with the title: *Towards Optimality in Potentiometric Measurements of Calcium Ion Activity in Blood. Ionized Calcium in Neonates.*

Dr. Wandrup has done clinical training in internal medicine, abdominal surgery, neonatology and pediatrics and chemical pathology. After 11 years career in the Danish Hospital system he joined Radiometer.

Dr. Wandrup has published several peer reviewed scientific articles regarding analytical and clinical aspects of Multi-Profile Blood Gas Analysis. As an expert in BG-biosensor technology and an MD specialist of Chemical Pathology he has very actively served and contributed to several CLSI (Clinical and Laboratory Standards Institute, USA) publications on laboratory standardization of blood gas analysis as well as electrolytes.



A Clinical and Analytical Review of Electrochemical Sensor Development in Radiometer in Relation to Optimal Monitoring of Critically Ill Patients

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Principal Specialist of Clinical Scientific Affairs, R&D Radiometer Aps, Denmark.

ABSTRACT

Objective: To review important clinical and analytical aspects of electrochemical sensor development in Radiometer in relation to optimal monitoring of critically ill patients.

Summary of review: Monitoring is a crucial part of the care of the critically ill patient in the intensive care and emergency department as the physiological response to critical illness is linked strongly to outcome.

In this clinical setting demands for fast Multi-profile blood gas analysis have led to the development of fast, sensitive and selective potentiometric and amperometric electrochemical sensors for clinic use.

In present review various important analytical and clinical factors which might affect the performance characteristics of such electrochemical sensors in the clinical setting are to be discussed.



Lo Gorton is Professor at Lund University (chair), Faculty of Natural Sciences, Department of Analytical Chemistry since 1997.

He received his Ph.D in 1981 with the Thesis: A Study of Modified Electrodes and Enzyme Reactors, and he was appointed Docent at Lund University in 1986.

Lo Gorton is the author of more than 450 papers in international periodicals, and the special issue of Bioelectrochemistry, 76(1-2), 2009, (Advanced Design of Electron-Transfer Pathways Across Biomolecular Interfaces) was dedicated to Lo Gorton on the occasion of his 60th birthday. He is also the editor of "Biosensors and Modern Biospecific Analytical Techniques", , Vol. XLIV of Comprehensive Analytical Chemistry, Elsevier, Amsterdam, 2005 and the invited author of 12 chapters in scientific books. Lo Gorton is member of the editorial board of more than 10 international Journals on electrochemistry and analytical topics. Lo Gorton has received several international awards: "The most highly cited paper authored by a Swedish scientist in the field of Physical, Chemical and Earth Sciences between Jan 1995 and June 1999" (2000, ISI); "Professor Honoris Causa of the University of Bucharest" (2000); "Visiting Honorary Professor" at Xiangfan University (2010); "Fellow of the International Society of Electrochemistry" (2012); International DropSens Award for "Best Research Work in Applied Electroanalytical Chemistry" (2012); "Katzumi Niki prize in Bioelectrochemistry" awarded by the Bioelectrochemical division of the International Society of Electrochemistry (2013/2014).

Lo Gortons current scientific interests are: Bioelectrochemistry and spectroelectrochemistry especially the electrochemistry of NAD(P)⁺/NAD(P)H, mediated and direct electron transfer reactions between redox proteins/enzymes/whole living cells and electrodes, chemically modified electrodes, biofuel cells, biosensors and their use in flow analysis, nanostructured electrode materials. Other of his research topics are Immobilised enzymes, flow injection analysis, liquid chromatography, mass spectrometry, polysaccharide hydrolysing enzymes and their use for analysis and characterisation of derivatised cellulose, hemicellulose and starch.

Website: http://www.cmps.lu.se/biostruct/people/lo_gorton/



Electrochemical Communication between Bacterial Cells/Biological Membranes and Electrodes

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Electrochemical transfer (ET) communication between bacterial cells and electrodes can usually be obtained through the use of freely diffusing monomeric redox mediators. Previously we have, however, also shown that flexible osmium redox polymers can work as efficient mediators for a number of both Gram – as well as Gram + bacteria and electrodes, clearly showing that the mediator does not need to pass the inner membrane to be able to shuttle the charge between the cells and the electrode [1]. In some restricted cases ET can be obtained directly between the bacterial cells and the electrode, e.g. between *Geobacter* sp. and *Shewanella* sp. and various carbon electrodes [2,3]. Here it will be shown that the current density from *Shewanella oneidensis* MR-1 to graphite electrodes in the presence of lactate can be increased at least four times by the use of an Os-polymer with an E° -value of 0.221 V (vs Ag|AgCl, sat. KCl) compared with the use of naked graphite [4]. Further increases in the current density for bioelectrocatalysis can be obtained by exchanging ordinary graphite electrodes for electrospun carbon fibres. For example for 18 mM lactate the current density increased from 10 to 120 $\mu\text{A}/\text{cm}^2$ [5]. Currently we are also investigating the effect of feeding the cells with cis-platin, which causes the cells just to grow but not to divide. When comparing normal cells with cis-platin treated cells it is possible to get current densities up to six times higher with the treated cells [6]. We have now extended our studies to include photosynthetic organisms/membranes. Successful electrochemical communication between isolated photosystem I and II and electrodes have been known for some time [7,8] however, here we report on electrochemical communication between whole viable photosynthetic bacterial cells (*Rhodobacter capsulatus* [9] and *Leptolyngbia* sp.) as well as with eukaryote systems (thylakoid membranes from spinach [10], the eukaryote unicellular algae *Paulschulzia pseudovolvox*) and electrodes through the use of osmium redox polymers.

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Professor Dermot Diamond

**Funded Investigator: INSIGHT Centre,
Director: National Centre for Sensor Research,
Dublin City University, Dublin 9, Ireland.**

Dermot Diamond received his Ph.D. and D.Sc. from Queen's University Belfast (Chemical Sensors, 1987, Internet Scale Sensing, 2002), and was Vice-President for Research at Dublin City University (2002-2004). He has published over 300 peer-reviewed papers in international journals, is a named inventor in 18 patents, and is co-author and editor of four books. He is director and founding member of the *National Centre for Sensor Research* (www.ncsr.ie) at Dublin City University, and an SFI-funded investigator in the INSIGHT Centre (<http://www.insight-centre.org>). In 2002, he was awarded the inaugural silver medal for Sensor Research by the Royal Society of Chemistry, London, and in 2006 he received the DCU President's Award for research excellence. In May 2014, in recognition of his academic contributions and achievements, he was admitted to Membership of the Royal Irish Academy. His research is focused on the fundamental science of stimuli responsive polymers, the development of futuristic autonomous chemical sensing platforms, and the use of analytical devices and sensors as information providers for wireless networked systems i.e. building a continuum between the digital and molecular worlds.

Details of his research can be found at www.dcu.ie/chemistry/asg.

Abstract: Danish Electrochemical Society Annual Meeting, 2014

This paper focuses on the context of early research into the use of calixarenes as ionophores in ion-selective electrodes and explains the basis for their exquisite selectivity in terms of the 3D arrangement of polar binding sites [1]. However, in order to make chemical sensors with long effective lifetimes, this polar cavity must be associated with an overall non-polar molecular character, in order to ensure that the binding sites do not leach rapidly into aqueous sample media. Furthermore, while selectivity demands a significant binding constant (at least for the primary target ion), this cannot be too large, or binding becomes irreversible, leading to device failure. I will also review the trend towards solid-state sensor configurations compatible with printing technologies and low-cost mass production. To achieve this goal, the electrode internal-filling solution must be replaced with a solid material capable of emulating the mixed conductance behaviour that (in conventional electrodes) is very effectively delivered by the combination of the internal electrolyte and the Ag/AgCl internal reference electrode [2]. These solid-state electrodes can be incorporated into configurations that open up new potential applications for these sensors, such as wearable platforms for monitoring ions in sweat [3]. If time allows, I will introduce some recent exciting developments in remotely controlled microdroplets that are capable of moving to specific locations on demand due to changes in the local chemical environment. The droplet movement, reminiscent of chemotaxis, can be controlled using localised photochemically or electrochemically generated chemical gradients in the droplet vicinity. I will suggest that these droplets are a natural progression in the concept of a chemical sensor from conventional bench-top electrodes, through solid-state miniaturised devices, to mobile multi-functional droplets.

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Tim Albrecht studied Chemistry at the University of Essen (1995-2000) and obtained his PhD from the MPI of Bioinorganic Chemistry in Muelheim a.d. Ruhr and the TU Berlin, Germany, under the supervision of Prof. P. Hildebrandt (2003). His PhD project focused on interfacial charge transfer studies of artificial and natural heme proteins using single-crystal electrochemistry, surface-enhanced and resonance Raman spectroscopy, and electrochemical Scanning Tunnelling Microscopy. From 2003-2006, he was a Marie-Curie postdoctoral fellow in Professor Jens Ulstrup's group at the Technical University of Denmark in Lyngby, and worked on single-molecule charge transport in small transition metal complexes, biomolecules and nanoparticles in electrochemical environments. He accepted a Lecturer position in the Department of Chemistry at Imperial College London in 2006 and was promoted to Senior Lecturer in 2011. He has been awarded the Tajima Prize of the International Society of Electrochemistry in 2013 and is currently Visiting Professor at the Kavli Institute/TU Delft.

His research interests span a wide range of subjects, centred on the physical and chemical properties of charged interfaces in solution and charge transport at the nanoscale. Specific application areas include single-molecule biosensing with solid-state nanopores, molecular and spintronics, as well as the surface science of copper leaching.

Functionalized solid-state nanopores for biosensing applications

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Solid-state nanopore devices are a new class of sensors for the structural and compositional analysis of biopolymers such as DNA, RNA and peptides, as well as biomolecular complexes.[1] Typically, they consist of a liquid cell, separated into two compartments by a thin, solid-state membrane. A single, nanometer-sized opening in the membrane (the "nanopore") connects these two compartments and allows for the exchange of ions and liquid between them. Upon application of an electric field across the membrane, charged biopolymers are pulled through the nanopore one-by-one, modulating the ion current in a characteristic way. This modulation in the current-time trace can then be related to the properties of the translocating biomolecule and perhaps even to the composition of the analyte. Therefore DNA sequencing has been a long-term goal and major driving force in the field, since the approach would be fast, inexpensive and not require any labelling. Unfortunately, the implementation of these promises has proven very difficult. Some of the reasons are the lack of control of DNA motion in the nanopore; insufficient spatial and temporal resolution (i.e. to resolve individual bases or base pairs); and the lack of specificity of the sensing region.[2]

However, these challenges can be overcome, as we and others have shown. In my presentation, I will discuss a select number of examples from our own work and put them into context with the state-of-the-art in the field.

These examples include the use of bipotentiostatic electrodeposition, with *in situ* ion current feedback through the pore, as a tool for fabricating sub-10 nm metallic pores; [3] SERRS-based detection of translocation events and plasmonic enhancement in the nanopore; [4] embedding of electrode junctions in the nanopore and the notion of tunnelling-by-sequencing; [5,6] and the integration of glass nanopipettes with droplet microfluidics. [7] In addition to DNA, we have also studied small proteins, such as insulin, and complexes between DNA and proteins, for example p53, single-stranded binding protein (SSB) and methylation-specific antibodies. In this context, nanopore sensing proves to be a valuable biophysical tool and may find applications in gene profiling or molecular barcoding.

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Interfacial structure and photocatalytic activity of magnetron sputtered TiO₂ on conducting metal substrates

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The photocatalytic behaviour of magnetron sputtered anatase TiO₂ coatings on copper, nickel, and gold were investigated with an aim to understand the effect of metallic substrate and coating-substrate interface structure. Stoichiometry and nano-scale structure of the coating was investigated using X-ray diffraction, Raman spectroscopy, scanning and Transmission electron microscopy. Photocatalytic behaviour of the coating was investigated using optical spectrophotometry measurements and electrochemical methods via photo voltage, photocurrent, and scanning kelvin probe microscopy measurements. Nature of the metal substrate and coating-substrate interface had profound influence on the photocatalytic behaviour. Nickel substrate has reduced the required photon energy for TiO₂ excitation, while TiO₂ coating on copper showed higher band gap attributed to quantum confinement. However, the TiO₂ coating on gold exhibited behaviour typical of easy transfer of electrons to and from the conduction band, therefore require only a small amount of photon energy to make the TiO₂ coating conductive



ELECTROCHEMICAL PROFILING OF MULTI-CLAD ALUMINIUM SHEETS USED IN AUTOMOTIVE HEAT EXCHANGERS

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Aluminium alloys are widely used in all types of heat exchanger applications in automotive, e.g. in radiators, air conditioner evaporators, exhaust gas recirculation (EGR) and water charge air cooling (WCAC) systems. This is due to the favourable combination of properties, such as low density, high thermal conductivity and good corrosion resistance. During the last two decades, mechanical assembly in the production of heat exchangers has been continuously replaced by brazing of aluminium alloys. This change was caused by cost and safety requirements as well as recycling issues [1]. Brazed heat exchangers are generally manufactured from clad aluminium sheet materials where a high melting point core alloy, typically Al-Mn (AA3xxx), is clad on one or both sides with a low melting point alloy Al-Si (AA4xxx) family.

The effects of the coolant composition on the corrosion of aluminium-based heat exchanger materials have been extensively studied [2]. On the other hand, corrosion occurring on the outer side of heat exchanger tubes is also a very important issue and is currently a blocking point for continued down-gauging and weight reduction of several types of heat exchangers. Recently significant increase in this air-side corrosion resistance has been achieved by using clad sandwich materials with multiple layers of different alloys.

In the present work, we employ a combination of micro-scale electrochemical measurements and glow discharge optical emission spectroscopy (GDOES) sputtering to investigate the corrosion propagation in a four-layer Al structure containing a copper-free AA3xxx interlayer on the air-side [3, 4]. The changes in the microstructure of the material caused by brazing are investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The results are compared to those obtained for a conventional three-layer product.

References

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Anodizing of Al-Zr and Al-Ti model alloys: Microstructure and Optical appearance

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Anodized aluminium alloy components are extensively used in various applications like architectural, decorative, and automobile either for corrosion protection, optical appearance or both. However, recent increase in the use of recycled aluminium alloys for sustainability and environmental friendliness has made it difficult to control the optical appearance of the anodized surface due to variations in microstructure and more importantly due to higher amounts of intermetallic phases. The current work focuses on understanding the behaviour of intermetallic phases during anodizing and their specific effect on optical appearance of the anodized Al surfaces with respect to light scattering and absorption. Binary Al-Zr and Al-Ti based model alloys were prepared by magnetron sputter coating and later heat treated to form Al-Zr and Al-Ti based intermetallic phases in an Al matrix. Anodizing behaviour of these dual phase coatings was studied and the obtained optical appearance was characterized using reflectance spectroscopy, which measures diffuse and total reflectance from a surface. Metallurgical and microstructural characterization using SEM, FIB-SEM TEM, GD-OES, GI-XRD and SKPFM was carried out to investigate the effect of coating microstructure, anodizing parameters, and electrochemical nature of intermetallic phases on appearance of anodized layer. Microstructure of the coating is found to have great influence on the appearance of anodized layer due to presence of completely or partially oxidized intermetallic phases in the anodized layer which modifies the visible light absorption and scattering phenomenon.

Keywords: Magnetron sputtering, aluminium coating, anodizing, appearance, TEM



ECO CHEMIE – METROHM AUTOLAB

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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 Metrohm Autolab, 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, Metrohm Autolab has been setting the benchmark in electrochemical research instrumentation for more than two decades. With base in Utrecht, The Netherlands, Metrohm Autolab 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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IMPEDANCE-BASED DETECTION FOR FACING NEW CHALLENGES IN BIOTECHNOLOGY: ENHANCED 3D SENSING, CONDUCTOMETRY AND ELECTRODE FUNCTIONALIZATION

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The outstanding advances of the biotechnological research have raised increasing demand for solid analytical methods with a special focus on application within medical and pharmaceutical sciences, tissue engineering and health care. We developed different impedance-based methods for real-time monitoring of 3D cell cultures and their metabolic activity. Planar vertical electrodes can be applied in different 2, 3 and 4 terminal configurations in a multiplexing-like approach to provide spatially distributed information on cell proliferation for *in vitro* tissue cultures (Figure 1A). The same setup can be used for estimating the influence of mammalian cell proliferation on medium conductivity (Figure 1B) and therefore characterizing the culture in terms of its biochemical activity. Moreover, this approach allows evaluating the overall 3D environment, even in terms of the scaffold architecture supporting cell organisation, proliferation and differentiation (Figure 1C). We are currently developing protocols for electrode functionalization to eliminate protein and cell adhesion to enhance detection reproducibility and electrode reusability using the same setup described above. For this purpose, chemical modifications performed in aqueous solvents are explored making them suitable for on-line modification of electrodes in polymeric perfusion-based cell culture systems.

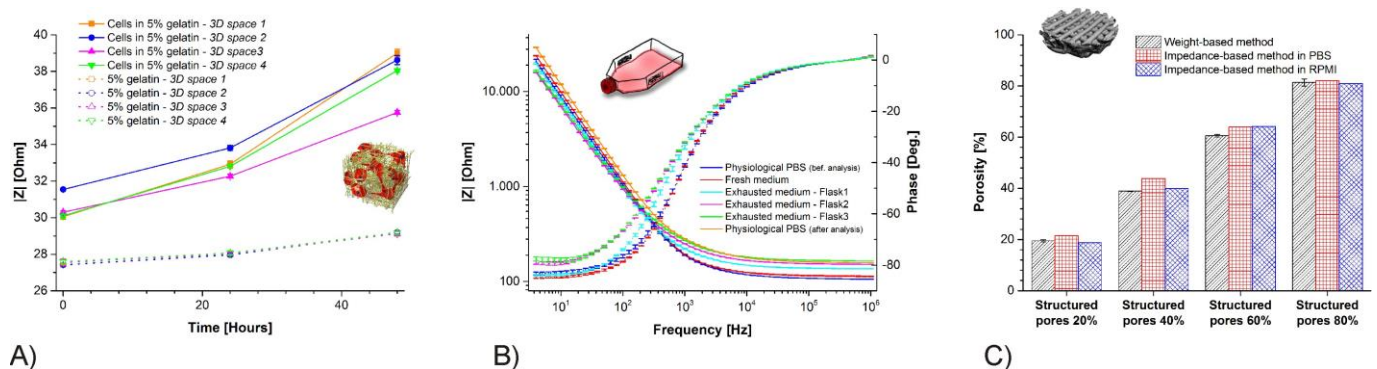


Figure 1. A) Spatial monitoring of cell growth for a 3D culture embedded in a 5% (w/v) gelatin scaffold ($|Z|$ at 4 kHz over time). B) Influence of mammalian cell proliferation on medium conductivity. C) Evaluation of porosity for different 3D cell culture scaffolds.



A cellobiose dehydrogenase biosensor tuned by cations to study the decomposition of lactose/ibuprofen containing tablets

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Cellobiose dehydrogenase (CDH, EC 1.1.99.18) is an extracellular fungal redox enzyme, which has shown promising properties for applications in both biosensors and biofuel cells. It is a two domain enzyme composed of a catalytic, FAD containing dehydrogenase domain, connected through a polypeptide linker region with a cytochrome *b* domain. The natural substrate is cellobiose, but also other sugars such as lactose or glucose can be oxidised efficiently. CDH is capable of directly delivering the electrons gained from the oxidation of the substrate to an electrode without the need of possibly toxic mediators.

Here we present the basic working principle of a CDH biosensor. The recently found beneficial effect of soluble, divalent cations as Ca^{2+} and immobilised polycations as polyethylenimine (PEI) and polydiallyldimethylammonium chloride (PDADMAC) on the electrochemistry of CDH is highlighted and discussed. Taking advantage of the beneficial effects of cations on CDH, a biosensor was constructed to quantify the release of the filling material lactose from polymer matrix tablets containing ibuprofen. Therefore a fast and easy sample preparation procedure using the polycation PEI to precipitate denaturing SDS present in the samples taking only 20 min was developed and is presented. The time dependent release of hydrophilic lactose was investigated with a CDH biosensor premodified with PDADMAC and was compared to the release of the hydrophobic ibuprofen. The time dependence of the release of both substances on the composition of the release medium was investigated enabling to elucidate the release mechanism of the drug. Since lactose is commonly used as a filling material for drug containing tablets the developed CDH biosensor has potential to be generally used in the pharmaceutical development of tablet formulations.



PHOTO-MICROBIAL FUEL CELL BASED ON CYANOBACTERIA FOR HARNESSING SOLAR ENERGY

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Life depends on photosynthesis, a process by which green plant, algae and photosynthetic bacteria convert sunlight into chemical energy¹. Cyanobacteria account for 20-30% of global photosynthetic activity and their electrogenic conduit might be exploited to photo-bioelectrochemical devices². Recently the most metabolically versatile purple bacteria, *Rhodobacter capsulatus*³ has been shown to communicate with osmium redox polymer modified graphite electrodes.

In this presentation, photo-electrochemical investigations conducted with cyanobacteria (*Leptolyngbya* sp.) immobilized on electrodes by flexible Os^{2+/3+} functionalities. Photosynthetic constituents in cyanobacteria were excited with a visible light source and the subsequent electron transfer from them to the electrode has been documented by cyclic voltammetric and chronoamperometric measurements. A significant photocurrent density ($\approx 8.64 \mu\text{Acm}^{-2}$) was observed while the cyanobacterial cells were embedded in the osmium polymer matrix. Moreover the photocurrent improved to $\approx 48.2 \mu\text{Acm}^{-2}$ when 1 mM ferricyanide was added to the electrolyte. These findings could have significant implications in the near future for photosynthetic energy conversion.

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Modification of TiO_2 -based dye-sensitized solar cell photo anodes by chemical and electrochemical grafting strategies

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²University of Science HCMC, Vietnam

Dye-sensitized solar cells (DSCs) have been studied extensively the last two decades.¹ From an economical point of view, DSCs are highly interesting because the manufacturing costs of DSCs are significantly lower than the costs of silicon cells. Furthermore, DSCs are very well suited for building integration e.g. as semi-transparent glass facades.¹ The most common used mediator in the DSC is the I^-/I_3^- two electron redox pair. The standard potential of this pair is however too negative compared with the applied dyes. In order to decrease the potential mismatch between the dye and the redox mediators several alternative mediator systems have been investigated including various $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ complexes.¹ A drawback is that the back electron transfer from the photoanode to the oxidized form of one electron mediators e.g. Co^{III} k_{rec2} (see Figure 1) is much faster than to I_3^- . In order to reduce the back electron transfer from the photoanode to the mediator R^+ and the oxidized dye S^+ we have applied electrochemical and chemical grafting strategies to attach an electrical isolation layer of mono and multilayers of organic molecules on the TiO_2 photoanode.

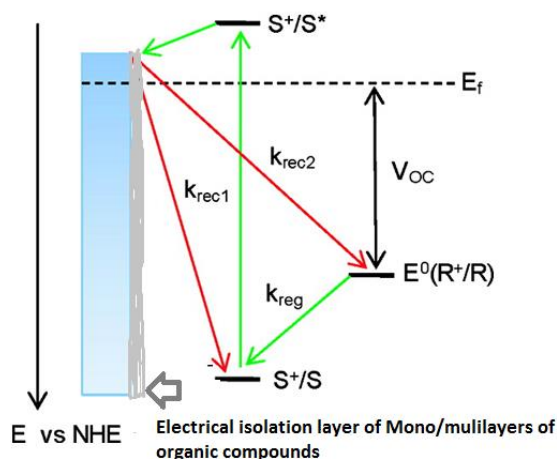


Figure 1 Energy level diagram of the DSC. The red arrows show the unwanted back electron transfer reactions to the mediator R^+ and sensitizer S^+ .

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STRUCTURAL DISORDERING OF DE-ALLOYED PLATINUM BIMETALLIC NANOCATALYSTS: ITS ROLE ON OXYGEN REDUCTION REACTION ACTIVITY AND NANOPARTICLE STABILITY.

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Alloying platinum with transition metals like cobalt, change the electronic properties of the synthesized nanoparticles (NPs), thus enhancing their stability during accelerated stress tests (ASTs) and their activity towards the oxygen reduction reaction (ORR). Pt_xCo_{1-x} colloidal nanoparticles of varying Pt:Co ratios, in the range of 2-3nm in diameter, were synthesized using a simple modified toolbox colloidal synthesis approach. Subsequent de-alloying of the Pt_xCo_{1-x} colloidal nanoparticles by a simple hydrochloric acid washing treatment has a clear impact on ORR activity and the stability of the NPs, as evidenced by electrochemical measurements. Structural disordering due to alloying and de-alloying enhance the ORR activity and the stability of the as-prepared alloys. On the other hand, excessive alloying and de-alloying, as in the case of PtCo₆ NPs, has the opposite effect.



NON-PT CATALYSTS FOR INTERMEDIATE TEMPERATURE WATER ELECTROLYSIS

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Water electrolysis is recognized as an efficient energy storage supplement to a renewable energy production. The most effective modern water electrolyzers are based on the use of polymeric proton-conducting membrane electrolytes (PEM), e.g. Nafion[®]. However, there is a great challenge for their widespread commercialization: high cost and low abundance of the catalytic materials (Pt, IrO₂) and use of Ti or other expensive construction materials.

An alternative could be to develop an intermediate temperature (200-400 °C) water electrolyzer (ITWE) without expensive platinum and IrO₂ catalysts, and with cheap electrolyte and construction materials. The first step to this goal might be achieved by creating a simulation system for the initial tests, which could consist of molten alkali metal dihydrogen phosphates (e.g. KH₂PO₄) as supported liquid phase electrolytes.

In this paper, the results of electrochemical study of transition metals (tungsten, molybdenum, niobium and tantalum) carbides in molten KH₂PO₄ at 260 °C are presented. All the results were compared with platinum. WC demonstrated better performance than Pt as a catalyst for hydrogen evolution reaction. The catalytic activity of metal carbides decreased in the row WC > Pt ≈ Mo₂C > NbC > TaC.

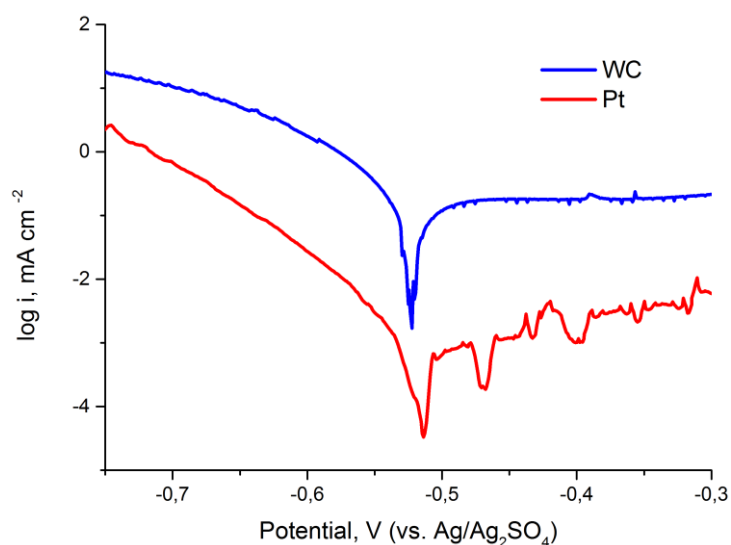


Fig. 1. Tafel-plots of WC-coated and Pt electrodes. 260 °C. Molten KH₂PO₄, Ag/Ag₂SO₄ reference electrode



A study of e^- transport through Li_2O_2 , the main discharge product in the Li- O_2 battery

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In the field of energy storage devices the pursuit for cheap, high energy density, reliable secondary batteries is at the top of the agenda. The Li- O_2 battery is one of the possible technologies that, in theory, should be able to close the gap, which exists between the present state-of-the-art Li-ion technologies and the demand from new electric consuming technologies, such as EVs [1].

However, the Li- O_2 battery still suffers greatly from high overpotentials during oxygen reduction and evolution reactions (discharge and charge, respectively), poor rechargeability, and decomposition of salts and solvents etc. [2] [3]. In order to improve the electrochemical performance of the Li- O_2 batteries; it is crucial to understand the fundamental mechanisms that governs and limits the system during electrochemical operation.

Here we present a redox probing study of the deposition product lithium peroxide, Li_2O_2 , using an outer-sphere redox shuttle, cobaltocene, to determine the change in heterogeneous rate constant as a function of the depth of discharge (and thus the thickness of the deposited Li_2O_2 layer) by electrochemical impedance spectroscopy. The results yield a limiting Li_2O_2 thickness of ~19 nm before sudden death, i.e. a dramatic increase in overpotential upon discharge, due to the insulating nature of Li_2O_2 .

Additionally, this work includes the determination of diffusion coefficients and concentrations of various species, such as $\text{O}_2^{0/2-}$, using macro- and microelectrodes.

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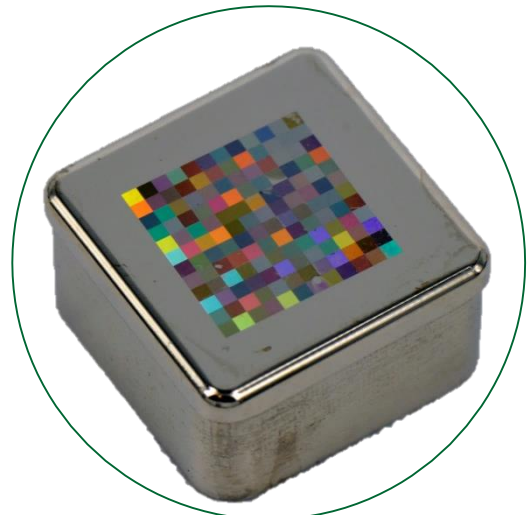
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Electrochemical preparation of injection moulding tools for micro- and nanostructuring

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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 inexpensive 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 to the surface quality must be observed. In this presentation, some of the challenges that are faced when combining industrial tool machining with clean room nano-fabrication techniques are described. In the Nanoplast project, combinations of mechanical and electrochemical surface planarization has been used in order to obtain surface qualities that are sufficient for a given application. Further, a surface homogenization process is used for obtaining a uniform, nano-crystalline substrate for the structures. Surface planarization has been attempted by using pulsed and DC electroplating in Cu, Ni and Ni/Co baths, with the intent to reduce surface roughness while still observing the geometry tolerances. For pulsed plated NiCo, the effect of pH, [Co] and pulse parameters has been investigated, and key findings will be presented.





IN OPERANDO RAMAN SPECTROSCOPY AS A TOOL FOR INVESTIGATION OF SOLID OXIDE ELECTRODES

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Solid oxide electrodes are important in a number of technologies including solid oxide fuel cells, solid oxide electrolysis cells, gas sensors and electrochemical gas purification. The electrodes operate at elevated temperatures (300-900 °C), while they are subjected to gas flow and electrical polarisation.

Conventionally, the solid oxide electrodes have been studied by electrochemical techniques during operation, and then analyzed *post-mortem* using electron microscopy, elemental analyses etc. However, for a correct interpretation of the electrochemical response from the electrodes, it is desirable to do *in situ* monitoring with techniques capable of resolving specific chemical changes that occur in real time. For instance Raman spectroscopy may yield insight into the presence of segregated oxide species or contaminating impurities on the electrodes during operation.

In the work presented here, Raman spectroscopy has been applied *in operando* to study electrochemical gas purification, more specific electrochemical reduction of NO_x, on lanthanum strontium manganite (LSM) electrodes. One LSM electrode was modified with Ba, and *in operando* Raman studies revealed the presence of a new oxide phase that showed a strong dependence on the applied electrical potential. These results illustrate how *in operando* Raman spectroscopy expands our understanding of why Ba-modified LSM electrodes show higher NO_x conversion during electrochemical gas purification compared to un-modified LSM electrodes.

Due to the great potential of combining *in operando* Raman spectroscopy with electrochemical characterisation, DTU Energy Conversion decided in 2014 to invest in a set-up dedicated to this purpose. At the end of the talk a short description will be given of this set-up, and the future plans will be described for combined *in operando* Raman spectroscopy and electrochemical characterisation at DTU Energy Conversion.



In-situ FTIR spectroscopy of the electrochemical interface during oxygen reduction on commercial platinum catalysts

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The development and application of in-situ spectroscopic techniques to monitor processes is one of the major challenges in modern catalysis.^{1, 2} This is especially challenging for electrocatalytic processes, which take place at the electrochemical interface and involve adsorption processes of reactants and intermediates, but also specific adsorption of counter anions – so called spectator species.³ A detailed understanding of the complex behavior of the interface that controls electrochemical reactions is needed in order to establish a materials by design approach. Only a limited number of spectroscopic methods exist that allow probing the interface during a continuing reaction. Here we present the first real in-situ Fourier transform infrared (FTIR) spectroscopy study of the electrochemical interface between a carbon supported fuel cell catalyst and the (sulfuric acid) electrolyte during the oxygen reduction reaction (ORR) with well-defined mass transfer. For this purpose a special fabricated electrode is used where the catalyst layer is spray coated on top of an ATR crystal equipped with a structured gold contact layer and applied to our recent developed in-situ ATR-FTIR wall jet electrode setup⁴. The designed interface allows tracking of several potential dependent processes; changes in the carbon support induced by oxidation, water expulsion at the interface, and (bi-)sulfate adsorption on the platinum particles and the carbon support. This enables us to scrutinize the role of specific adsorption of (bi-)sulfate anions in the strong inhibition process of the ORR on platinum catalysts. The (bi-)sulfate adsorption behavior is discussed in relation to measurements on carbon black without platinum. Correlation of the band intensities vs. the measured oxygen reduction current reveals that the anion adsorption on platinum does not block the ORR directly, but the onset of oxide formation with the concomitant conversion of the adsorbate layer reducing the anion coverage is the decisive blocking mechanism

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MEASURING RAW SIGNALS IN ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Iosif Fromondi¹, Esben Dam²

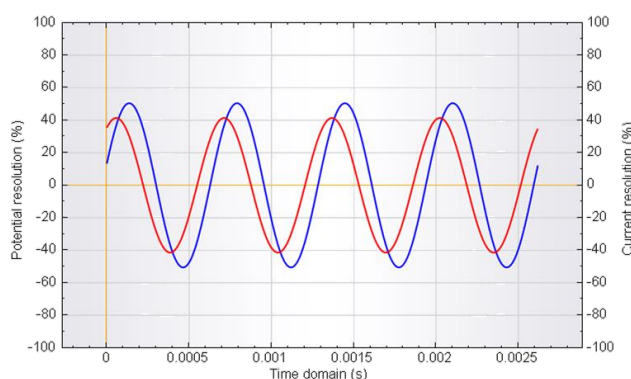
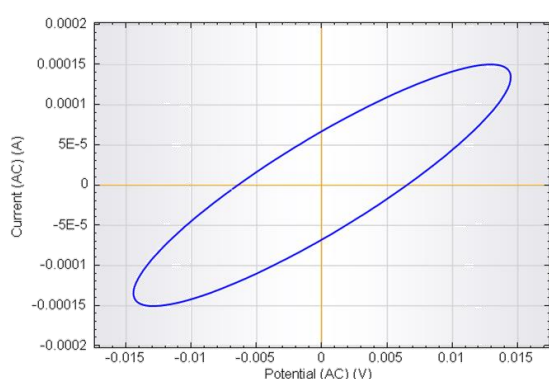
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Electrochemical Impedance Spectroscopy (EIS) involves the study of the variation of the impedance of an electrochemical system with the frequency of a small-amplitude AC perturbation. In practice, the time-domain of the input and output signals are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

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

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



A typical Lissajous plot for a linear system (left) and resolution plots (right) showing large resolution values for both Potential (AC) and Current (AC).



Investigations on the electro-catalytic ORR activity of shaped Pt nanoparticles

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The oxygen reduction reaction (ORR) is the cathode reaction in fuel cells and attracts huge attention of scientists. Platinum is the most active element as catalyst material for the ORR, but the metal is very pricy and its reserves are depleting, which seriously restricts its application in mass products. Therefore people invest enormous effort into enhancing the catalytic activity of platinum.

Shaped nanoparticles of platinum are specifically interested as model catalysts and lots of development has been already obtained. For example, Tian has made a breakthrough to synthesize shaped THH platinum nano-crystals enclosed with high index facets, which show excellent electrocatalytic activities towards the oxidation of small organic molecules such as ethanol and formic acid [1]. Due to the high surface energy, the shaped particles may also show unique catalytic activities towards ORR.

In this work, we have synthesized THH platinum nanocatalysts as is shown in figure 1 and applied it towards the ORR in different base electrolytes. The results are compared to polycrystalline Pt and commercial Pt black.

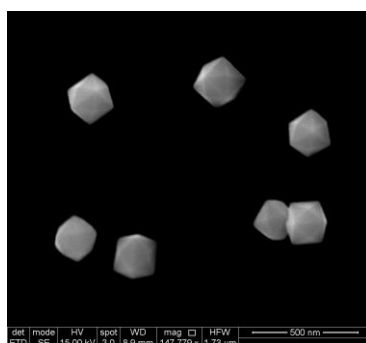


Figure 1. SEM image of the shaped Pt nanoparticles as synthesized.

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HIGH TEMPERATURE STUDY OF LSM MICROELECTRODES

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The oxygen electrode in solid oxide fuel cells and electrolyses cells is usually a composite porous electrode composed of yttria stabilized zirconia, YSZ, as the ionic path and strontium substituted lanthanum manganite, LSM, as the electronic phase. Although studied for many years it is still not clear whether the reaction is confined to a narrow zone along the triple phase boundary, TPB, where the gas phase is in contact with both the electronic and the ionic phase, or a substantial part of the reaction takes place on the surface of the LSM grains.

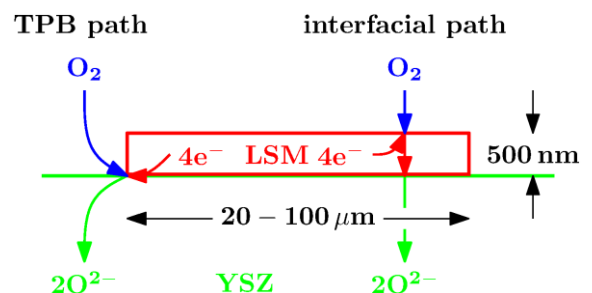
The oxygen electrode reaction was studied on microelectrodes having a simple geometry, and with dimensions where contribution from the TPB as well as the interfacial reaction could be expected. Since these reactions are in parallel and scales with the electrode perimeter and the area, respectively, the overall current can be written as

$$i = i_{TPB} + i_i = a \cdot d + b \cdot d^2$$

where d is the diameter of the electrode. Thus, the distribution of the electrode reaction can – in principle – be determined from the dependence on the electrode size.

Impedance measurements as well as cyclic voltammetry was carried out in a Controlled Atmosphere High Temperature Scanning Probe Microscope, CAHT-SPM, in the temperature range 660-860°C in oxygen, air and nitrogen.

The results confirm previous similar studies, namely, that the reaction is confined to the TPB path at high oxygen partial pressures, whereas the interfacial process is dominating at low oxygen pressures.





Blood-Gas Analyzer with Solid State Sensors

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On modern hospitals and especially at Intensive Care Units (ICU) there is an increasing demand for blood gas analyzers that are *simpler, faster, better*. The analyzers are preferentially placed at the “Point of Care” i.e. near the bed of patient on the ICU.

“Blood Gas” is short for measuring the respiratory parameters pO_2 , pCO_2 and pH, while measurement of cNa^+ , cK^+ , cCa^{2+} , and cCl^- monitors the electrolyte balance. Finally $cLac$ and $cGlu$ reports on the metabolic status of the patient.

ABL90 – Flex meets these requirements by introducing miniaturized sensors comprised of thick-film, screen-printed, solid state sensors all 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 metabolite sensors 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.

The Solution Pack contains calibrating solutions, quality control solutions and rinse-solutions. The *faster* 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 μ 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. In this context it has not been 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 regenerated 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*.



ELECTROCHEMICAL R&D ACTIVITIES AT IRD FUEL CELLS A/S

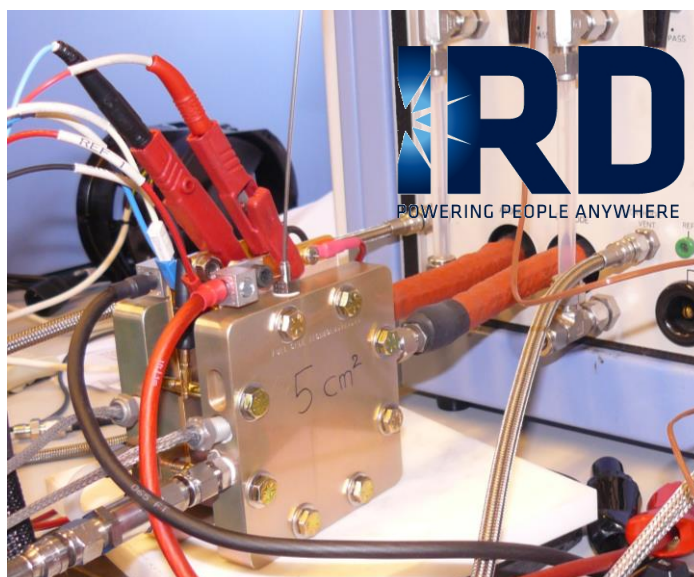
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IRD Fuel Cells A/S is a private Danish fuel cell (FC) and electrolyser cell (EC) company specialised within the polymer electrolyte membrane (PEM) technology, including direct methanol (DM) fuelling technology. The company produces FC and EC systems and components and has a long tradition within electrochemical research and development. Thus IRD has comprehensive electrochemical testing facilities at its premises in Svendborg and Albuquerque, New Mexico, USA, and the company participates in a great number of publicly and privately funded national and international R&D projects in close collaboration with a broad range of academic and private groups.

The extensive R&D work aims at developing the optimal solutions for the customers, partners and the product portfolio of the company. On the component and subcomponent level there are activities within catalysts, polymers, electrodes, membrane-electrode assemblies (MEAs) and bipolar plates. These activities are carried out by dedicated electrochemists, engineers and other scientists. The electrochemical techniques applied in the IRD laboratories include rotating disc electrode (RDE), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and polarisation (IV) characterisation. Accelerated stress testing (AST) through electrochemical ageing is applied as an important means to assess the durability and lifetime of the various components.

This poster will give a brief overview of some of the basic and advanced electrochemical R&D activities continuously going on at IRD in order to efficiently provide sustainable power to the world.





Impedance Spectroscopy for SOFC Stack Diagnostics

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As SOFC technology is moving closer to a commercial break through, methods to measure the “state-of-health” of operating stacks are becoming of increasing interest. Electrochemical impedance spectroscopy (EIS) is a powerful technique that carries information about both kinetic and mass transport and concentration gradient related losses in an electrochemical cell during galvanic discharge. An operating stack is subject to compositional gradients in the gaseous reactant streams, and temperature gradients across each cell and across the stack, which complicates detailed analysis.

This methodology can be used to detect possible minor changes in the supply of gas to the individual cells, which is important when going to high fuel utilizations. The fuel flow distribution provides important information about the operating limits of the stack when high electrical efficiency is required.

Furthermore, the time dependent performance changes that takes place over the first few hundred hours of operation were monitored using EIS and could be assigned to anode cermet related changes.