Book of Abstracts

SMCBS 2007

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Published October 2007, ISBN 83-89585-18-9

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Revision: 24.0.41, 2007-10-24 19:24 GMT

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Welcome

The present booklet contains programme and abstracts of invited tutorial lectures, as well as contributed keynote lectures, short oral communications, and posters of the jointly organised 3rdInternational Workshop on 'Surface Modification for Chemical and Biochemical Sensing', SMCBS'2007, and XVI International Meeting of the Electrochemical Section of the Polish Chemical Society. We are pleased and feel honoured to host over a dozen of distinguished scientists who have kindly accepted our invitation to present tutorial lectures.

Interdisciplinary permeation of concepts between chemistry, biology, physics, materials science, microelectronics, and engineering has inspired important new ideas in several research fields including sensing and biosensing. For constructing chemical or biochemical sensors, surfaces of solid substrates are modified for selective or, in some cases, even specific analyte detection. The use of sensor-based analytical procedures, originally focused on chemical and biochemical tests, is gaining increasing interest, among others, in environmental toxicity testing, for ecosystem monitoring, clinical diagnosis and therapy, as well as testing of crops and foods of animal origin. The recent increase of interest in the sensor-based detection techniques is manifested by the increase of the number of both scientific papers published and patents registered. Toward this interest, a series of our Workshops is organized. Being encouraged by success of the 1st and 2nd International Workshop on Surface Modification for Chemical and Biochemical Sensing in 2003 in Białowieża and in 2005 in Kazimierz Dolny, respectively, we hope that also the present 3rd SMCBS' 2007 Workshop in Włodowice will successfully become a platform for researchers to meet in order to discuss in-depth, exchange, and generate ideas that will stimulate new, and most expectantly, collaborative research.

Apparently, electrochemical aspects of chemical and biochemical sensing dominated previous Workshops and most participants were either electroanalytical chemists or users of electroanalytical techniques. As an extension of this trend, the present Workshop is co-organized by Electrochemical Section of the Polish Chemical Society as a continuation of the 32-year old tradition of International Meetings of this Section.

The Organising Committee thanks all those who contributed to the workshop. Our gratitude is particularly due to the authors of the contributions, to the persons chairing sessions of the Workshop and members of the International Advisory Board.

On behalf of the Organising Committee, we welcome all Workshop participants and readers of the present book.

Włodzimierz Kutner and Marcin Opałło

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Programme

Sunday, 4 November

Registration and Lunch
Sunday afternoon, 4 November, 12:00

1st Bus Departure to Wlodowice
Sunday afternoon, 4 November, 14:00

2nd Bus Departure to Wlodowice
Sunday afternoon, 4 November, 15:00

Dinner
Sunday evening, 4 November, 19:30

Monday, 5 November

Breakfast
Monday morning, 5 November, 8:00

Session 1
Monday morning, 5 November, 9:00

9:00 Tutorial lecture

Scanning electrochemical microscopy - a tutorial lecture

Wolfgang Schuhmann

Ruhr-Universität Bochum, Anal. Chem. - Elektroanalytik & Sensorik (ELAN), Universitätsstr. 150, Bochum 44780, Germany

e-mail: wolfgang.schuhmann@rub.de

The tutorial lecture will provide an overview of scanning electrochemical microscopy (SECM) and its prerequisites, limitations and fields of applications.

The main aspects will be:

- Scanning probe microscopy as a tool for gathering localized physical, topographic and electrochemical information.
- System set-up, imaging modes, achievable resolution. Combination with electrochemistry.
- Fabrication of micro- and nanoelectrodes and specific characteristics
- Feedback mode, generator collector mode, impedance and redox competition mode of SECM
- Application of SECM in biosensor development, material research, micro- and nanostructuring of surfaces, catalyst evaluation

9:40 Keynote lecture

Shearforce-based distance control in scanning electrochemical microscopy

Mathieu Etienne[1], Alain Walcarius[1], Wolfgang Schuhmann[2]

1. *Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME), 405, rue de Vandoeuvre, Nancy 54600, France* **2.** *Ruhr-Universität Bochum, Anal. Chem. - Elektroanalytik & Sensorik (ELAN), Universitätsstr. 150, Bochum 44780, Germany*

e-mail: etienne@lcpme.cnrs-nancy.fr

Scanning electrochemical microscopy (SECM) allows for the direct high-resolution vizualization of local variations in the (electro)chemical reactivity of solid/liquid, liquid/liquid, and even liquid/air interfaces. For a solid/liquid interface, as the electrode probe approaches the surface in the solution, its current, due to reduction or oxidation of freely-diffusing electroactive species, decreases over an insulating material (negative feedback) and increases over conductive material (positive feedback). These phenomena are often used in *classical* SECM to determine the tip-to-sample distance for relatively flat and homogeneously conductive samples. The SECM feedback mode has also been used for high resolution imaging of topographic changes and conductivity variations [1].

However, use of current feedback information for positioning *and* imaging is only possible for well-defined systems and is inappropriate for surfaces exhibiting complex topography and complex conductivity or for probes that do not consume (and produce) electroactives species (i.e. potentiometric probes).

Moreover, current feedback is strongly dependant on the radius of the electrode/probe. The gap between the electrode and sample surface must be within one radius of the electrode to achieve enough current feedback to control positioning. Thus, small electrodes required for higher spatial resolution must be positioned closer to the surface. The experiment is very delicate on flat surface and almost impossible on a sample showing complex topographic features.

One possible strategy to overcome these limitations is the implementation of a shearforce-based distance control in SECM, that allows to dissociate tip-positioning and electrochemical measurement. Tip-to-sample distance is then determined with a good accuracy using shearforce dampening of the electrode tip vibration. We used a non-optical detection based on two piezoelectric plates mechanically attached to the body of the electrode [2]. The first one stimulates the tip oscillation, while the second one is used to measure the response of the system. The setup is rather easy to implement on potentiometric [3,7] or amperometric [4] electrodes, and can be used to perform SECM experiments in feedback [2,3] or generation/collection modes [4-6]. One important question to be discussed is the performance of the tip positioning as it is a very critical parameter for the good operation of the electrochemical measurement.

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10:00	Keynote lecture

Porphyrination of III-V compound semiconductor surfaces for detection of exhaled breath indicators of physiological status

Scott D. Wolter[1], Michael A. Garcia[1], Maria Losurdo[2], Joseph Bonaventura[3], Giovanni Bruno[2], William V. Lampert[4], April Brown[1]

1. *Electrical and Computer Engineering, Duke University, Durham, NC 27708, United States* **2.** *Institute of Inorganic Methodologies and of Plasma, IMIP-CNR, and INSTM, via Orbana, Bari 4-70126, Italy* **3.** *Nicholas School for the Environment, Duke University, Durham, NC 27710, United States* **4.** *U.S. Army Research Office, Research Triangle Park, NC 27709, United States*

e-mail: woltersd@duke.edu

Chemical functionalization of III-V compound semiconductor van der Pauw (VDP) sensors is being studied by our research group for defense, biological and environmental applications. The sensing mechanism rests upon adsorbate-induced changes in charge and surface potential, and follows a Langmuir gas adsorption kinetics model. Sheet resistance changes have been monitored as a function of analyte type, concentration, dilution in air and inert gases, and for long-term operation in our initial work using AlGaN/GaN, InAs, and InP materials [1,2]. This sensor platform and capabilities in our molecular beam epitaxy growth facility to modify semiconductor attributes enable us to expediently evaluate attachment chemistry and sensor effectiveness. This lecture reports on porphyrination of VDP surfaces as a biomimetic approach to selective detection of exhaled breath by-products linked to physiological status including respiratory and cardiac ailments. Surface chemistry and sensing modality have been studied for various protoporphyrin compounds (e.g. ferric-porphyrin chloride - *hemin*) functionalized to the semiconductor surfaces. These functional groups can be engineered, combined, and incorporated to fit desired specifications, and thus can be tailored for selective response to a broad range of analytes. Included in the analytes of interest in our ongoing work are nitric oxide, carbon monoxide, and their variants. The porphyrins are characterized by a central metal cation operative for selective sensing, amine linking groups which may be altered chemically to limit porphyrin aggregation, and carboxylic acid ligands which may be used as surface tethers. X-ray photoelectron spectroscopy and spectroscopic ellipsometry (SE) have been used to assess and optimize surface chemistry. Modifications in the electronic and chemical state of the semiconductor surfaces provide insight into chemical bonding. Interestingly, surface analysis has revealed upward band-bending of the valence band maximum indicating chemisorption of the functional groups, and evidence of carboxylate bonding preferentially to the anion of the semiconductor. SE analysis has been performed both *in-situ* and *ex-situ* to explore variations in porphyrin molarity and benzoic acid used as a ‘spacer’ to optimize surface coverage (following the chemistry protocol developed by Wu and Cahen & co-workers [3] on GaAs). The porphyrin and benzoic acid concentration (relative to dimethlyformamide solvent), along with the chemistry duration, were determined to directly correlate to surface coverage. Benzoic acid added to the porphyrin solution appears to prevent the formation of aggregates in favor of normal-to-surface orientation. We have also begun conducting temperature-dependent sensor measurements to learn more about the effects associated with analyte-surface interactions (i.e. thermodynamics and kinetics of adsorption-desorption processes) and initiating experiments on humidity effects on analyte detection. These results will be discussed and serve as a basis for discussion of exhaled breath sensors and future applications.

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10:20	Short communication

Increasing Biosensor Sensitivity by Length Fractionated Single Walled Carbon Nanotubes

Federico Tasca[1], Lo Gorton [1], Jakob B. Wagner[2], Gilbert Nöll[1]

1. *Lund University, Department of Analytical Chemistry, Lund SE-221 00, Sweden* **2.** *Lund University, Polymer and Material Chemistry, nCHREM, Lund 22100, Sweden*

e-mail: federico.tasca@analykem.lu.se

In this work the sensitivity increasing effect of single walled carbon nanotubes (SWCNTs) in amperometric biosensors depending on their average length distribution was studied. For this purpose the SWCNTs were oxidatively shortened and subsequently length-separated by size exclusion chromatography. TEM images of different fractions of SWCNTs were collected. Diaphorase embedded in an osmium redox polymer was blended with the shortened SWCNTs of different length. Depending on the average length of the SWCNTs the sensitivity of the amperometric biosensor model system towards oxidation of NADH could be increased up to a factor of five. The best performance could be achieved with SWCNTs of medium length. The linear range for NADH detection was between concentrations of 5 µM and 7 mM. The biosensor exhibited excellent electrocatalytic properties. Even at relatively high NADH concentrations the oxidative current was only limited by the diffusion rate of NADH.

Coffee break

Monday morning, 5 November, 10:35

Session 2

Monday morning, 5 November, 10:55

10:55 Tutorial lecture

Electrocatalysis and Bioelectrocatalysis at Network Films of Metal Nanoparticles and Carbon Nanostructures

Paweł J. Kulesza, Katarzyna A. Karnicka, Barbara Kowalewska, Magdalena Skunik, Beata Baranowska, Andrzej Ernst, Przemysław Ziaja, Krzysztof Miecznikowski, Malgorzata Chojak

Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland

e-mail: pkulesza@chem.uw.edu.pl

There has been a growing interest in the fabrication of organized monomolecular (monolayer) and multilayered assemblies at solid surfaces. Most of research concerns alkanothiols and their derivatives that can be successfully employed to obtain monolayer coverages on gold. An interesting alternative originates from the possibility of self-assembling inorganic (e.g. polyoxometallate) monolayers because they provide potentially better stability, and they undergo reversible stepwise electron transfer reactions of importance to such technologies as electrocatalysis, electrochromism, molecular electronics and sensing. We have recently pursued the concept based on multiple formation of two-dimensional arrays composed alternately of a conducting polymer, such as polyaniline or polypyrrole, and a heteropolyanion of molybdenum or tungsten. Monolayers of alkanothiolates are capable of passivating gold nanoparticles and producing alkanothiolate monolayer protected clusters of gold. They combine bulk and molecular properties within a nanometer scale material that is expected to yield novel and promising size-dependent electronic, optical and chemical properties. We have explore the ability of polyoxometallates (phosphotungstate, phosphomolybdate) to form self-assembled monolayers on metal (e.g. Pt or Au) nanoparticles (ca. 2-7 nm) or carbon nanotubes. Such polyoxometallate modified nanostructures can be linked together by ultra thin conducting polymer (polyaniline, polypyrrole, PEDOT) bridges. The formation, morphology, structural transformations and electrochemical properties of the nanoparticle containing three-dimensional network films are examined using cyclic voltammetry, potential step techniques, microgravimmetry, FTIR spectroscopy, STM and scanning electrochemical microscopy. The network films composed of polyoxometallates, ultra-thin conducting polymer layers and platinum or carbon nanostructures can produce interfaces with specific electrocatalytic properties towards reduction of such inert reactants as oxygen, hydrogen peroxide or bromate. Electrocatalytic systems that would be useful in biological media, or the systems utilizing biocatalysts (enzymes), have to operate in neutral solutions. Recently, there has been growing interest in the fabrication of stable highly effective bioelectrocatalytic systems for oxygen reduction, particularly with respect to potential applications in biofuel cells. Unless highly specific and expensive enzymes belonging to a group of proteins with the copper active centers, such as bilirubin oxidase or laccase, are considered, the reduction of oxygen in neutral media is a two-step process suffering from the formation of hydrogen peroxide as undesirable intermediate product. Although the above enzymes are capable of the effective four electron reduction of oxygen to water in neutral media, and significant progress have recently been made in their practical utilization, there is a need to look for alternate bioelectrocatalytic systems. To facilitate electron transfers between the electrode surface and the redox protein centers, the concept of co-deposition of multi-walled carbon nanotubes (CNTs) within the bioelectrocatalytic film has been recently proposed. Good electronic conductivity of CNTs, together with their mechanical stability, have made them attractive for potential applications in electrochemistry and bio-electrochemistry. Representative examples include cases of electrocatalytic reductions of hydrogen peroxide and oxygen. To stabilize composite films, we utilize multi-walled carbon nanotubes, that have been modified with ultra-thin layers of organic (e.g. 4-(pyrrole-1-yl) benzoic acid or ABTS) and inorganic metal oxo compounds. We expect here attractive interactions between anionic adsorbates and positively charged domains of the enzymatic sites. The other important issues are stability and mediating capabilities of adsorbates.

11:35 Keynote lecture

Electrochemical and Photochemical Patterning of Oxidized Boron-Doped Diamond Electrodes

Sabine Szunerits[1], Paolo Actis[1], Rabah Boukherroub[2]

1. *Institute National Polytechnique de Grenoble (INPG), 1130, rue de la piscince, Saint Martin d'Hères 38402, France* **2.** *Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN), Cité Scientifique Avenue Poincaré, Villeneuve d'Ascq 59652, France*

e-mail: sabine.szunerits@lepmi.inpg.fr

The ability to pattern surfaces with micro- and nanometer sized structures is currently a significant area of research. Lithographic and scanning probe microscopy techniques have been widely used to show the feasibility and the limits employing these different approaches. Micropatterned surfaces are of interest as they allow the controlled deposition of liquids or cells and site-specific immobilization of chemical and biological molecules, a critical step in many assays including diagnostic analysis, high throughput screening, and bioelectronic sensing. Boron-doped diamond (BDD) substrates have emerged over the years as attractive electrode materials and have gained remarkable interest for various applications due to their high chemical stability, good electrical conductivity, large potential window in aqueous electrolytes, and biocompatibility. Boron-doped diamond (BDD) electrodes are in addition interesting interfaces for the formation of micropatterns. The present work describes different approaches to incorporate electro- or photoactive groups on BDD for biomolecules immobilization. First, pyrrole-terminated BDD surface was prepared by chemical functionalization of oxidized BDD surface with N-(3-trimethoxysilylpropyl)pyrrole (TMPP). The reaction produces an organic layer covalently attached to the surface and bearing terminal electroactive pyrrole groups. The covalent linking of pyrrole units on the BDD surface allows formation of strongly adhesive conducting polymer films through electropolymerization. The micro- and nanopatterning of BDD with polypyrrole was achieved using either the direct mode of Scanning Electrochemical Microscope (SECM) or the newly developed electrochemical Scanning Near-field Optical Microscope (E-SNOM). The nanopatterning of BDD with polypyrrole using E-SNOM was achieved by constraining the current lines between ITO and the electro-optical tip, working as a counter electrode, by bringing the electro-optical probe into the near-field of the BDD interface. The essence of this deposition method is based on the generation of high concentrations of pyrrole radical cation monomers in the gap between the BDD electrode and the electro-optical tip, working in this case as a counter electrode. Depending on the method used polypyrrole dots with diameters in the range of 1-250 µm are electrogenerated. A second approach is based on the direct immobilization of biological molecules via photochemical reaction with surface-bound benzophenone.

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11:55 Keynote lecture

Proteins in biomimetic surface architectures

Renate L. Naumann, Wolfgang Knoll

Max Planck Institute for Polymer Research (MPIP), Ackermannweg 10, Mainz 55128, Germany

e-mail: naumannr@mpip-mainz.mpg.de

Renate Naumann and Wolfgang Knoll

Max Planck Institute for Polymer Research

Ackermannweg 10, 55128 Mainz (Germany)

naumannr@mpip-mainz.mpg.de

Membrane proteins represent a crucial class of biological agents. They are the key factors in many vital functions of the cell, such as nerve excitation, respiration, photosynthesis and transport of ions and nutrients. Attempts have been made to design model systems for their investigation which pinpoint bilayer lipid membranes to surfaces. The proteins are then reconstituted into the lipid membrane to form a biomimetic surface architecture which can be investigated by a combination of spectroscopic and electrochemical techniques.

Thiolipid-based tethered bilayer lipid membranes (tBLMs) have been used to incorporate porines, ion carriers and channels such as hemolysin, valinomycin, melittin, gramicidin [1], MaxiK, the M2 channel of the AChR. The kinetics of ion transport through these moieties has been analysed using impedance measurements as a function of various parameters, such as ion concentration, transmembrane potential, leak resistance etc. The spectra are simulated using the computer program Spice designed to analyze bioelectrochemical processes. Larger complex proteins such as the cytochrome c oxidase from *Rh. sphaeroidis*, CcO, are incorporated in the so-called **protein-tethered bilayer Lipid membrane (ptBLM)** developed in our laboratories [2]. Recombinant CcO solubilized in detergent is immobilized in different defined orientations on a chemically modified gold surface to a nickel chelating nitrilo-triacetic acid (NTA) surface. The CcO monolayer is reconstituted into the lipid by substitution of detergent molecules with lipids using in-situ dialysis or adsorption. An overview is given of the investigations performed so far on this system in our laboratories, in particular using electrochemistry in combination with surface-enhanced ATR-FTIR spectroscop), and surface enhanced resonance Raman spectroscopy (SERRS) [3]. When the protein is immobilized with the cytochrome c binding side directed towards the electrode and reconstituted *in-situ* into a lipid bilayer, it is addressable by direct electron transfer to the redox centers. Electron transfer to the enzyme via the spacer, referred to as electronic wiring, shows an exceptionally high rate constant. This allows to perform a kinetic analysis of all four consecutive electron transfer steps within the enzyme. Structural changes of the peptide backbone are deduced from spectral changes of certain bands (e.g. Amide I), which are assigned to specific redox states of the redox centers. These spectral changes are monitored by Surface Enhanced ATR-FTIR Spectroscopy in the rapid scan and in the step scan mode. Stationary measurements at different fixed potentials show that redox transitions occur in all four redox centers. Time-resolved measurements, applying repeated potential pulses allow to follow the change of the redox state of the Cu_A, the heme a and the heme a_3 center as a function of time. Time constants of the transitions are obtained by fitting three parameter exponentials to the time dependent absorption data [7].

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12:15 Keynote lecture

Bioanalytical studies based on lectin-carbohydrate interactions measured by QCM and SPR techniques

Bengt Danielsson, Gulnara R. Safina, Srimathi Soundararajan

Lund University, Pure and Applied Biochemistry Department, Getingevägen 60, Lund SE-22100, Sweden

e-mail: bengt.danielsson@tbiokem.lth.se

Biosensors use a combination of biological receptor compounds and the physical or physical-chemical transducer directing real-time monitoring of specific biological events. Surface plasmon resonance (SPR) technique is a powerful optical biosensing technique for non-label affinity interaction analysis. Lectins as biological receptor molecules and Biacore 3000 as optical transducer were employed for bacteria differentiation. The lectins were covalently immobilized on Biacore CM5 chips and the sample solution containing glycoproteins (or serum), endotoxin (lipopolysaccharide) or whole bacterial cells was flowed over the surface. The obtained lectin binding patterns correlated well with theoretical patterns derived from carbohydrate structures of glycoproteins and endotoxins. The experiment with whole bacteria showed possibility to distinguish bacteria with cross-reactivity in immunoassay (*Citrobacter freundii* and *Escherichia coli* O157) by using of the lectin panel. The expression of carbohydrate structures on the outer side of the bacteria was required for increase the sensitivity of measurement. Similar results were obtained using a prototype of a commercial QCM device. The glycoprotein studies aimed at investigation of the suitability of lectin-array based analysis in liver disease diagnosis. One question is whether whole serum can be used as sample or if the glycosylation of discrete proteins needs to be studied for correct diagnoses.

12:35 Short communication

Selective Photorelease of Active Chemicals Locked by the Flavoprotein Dodecin

Gilbert Nöll, Martin Grininger, Dieter Oesterhelt, Sibylle Trawöger, Eva-Kathrin Sinner, Madlene Von Sanden-Flohe, Bernhard Dick, Tanja Nöll

Lund University, Department of Analytical Chemistry, Lund SE-221 00, Sweden

e-mail: gilbert.noll@analykem.lu.se

Dodecin from *Halobacterium salinarum* is a dodecameric, hollow-spherical flavoprotein which contains six flavin binding sites. In each binding site, two flavins are arranged in an aromatic tetrade between two tryptophan residues. Dodecin binds not only native but also artificial flavins with high binding affinities. The dissociation constants for flavin binding to dodecin were determined by titration of the fluorescent ligand with the apoprotein at room temperature. When incorporated into apododecin, the flavin fluorescence is quenched, probably by electron transfer from tryptophan to the excited flavin state. Reduction of the flavin ligand induces the dissociation of the holocomplex into apododecin and free flavin. Inspired by the binding mode and the redox characteristics of dodecin, we are developing an electrochemically active flavin modified electrode surface (electrode - molecular wire - flavin) which is able to bind or release dodecin apoprotein triggered by the redox potential. Possible applications range from the control or transport of single molecular assemblies containing dodecin apoprotein, up to the development of bioelectrochemical data storage devices with an electrochemical input (write) and an optical (fluorescence sensitive) output (read). Additionally we have synthesized flavin ligands which can be tethered to various molecules of interest by an amide or an ester bond. Irradiation of dodecin with blue-light in the presence of EDTA results in photochemical reduction of these flavins followed by their release. We are working on a protein based molecular transport system triggered by light. This system will allow the binding and release of functional molecules tethered to flavins.

Lunch

Monday afternoon, 5 November, 13:00

Session 3

Monday afternoon, 5 November, 14:30

14:30 Tutorial lecture

A new approach to theoretical modeling of membrane potential

Andrzej Lewenstam[1,2,3], Witold Kucza[2,3], Tomasz Sokalski[1], Robert Filipek[2,3], Johan Bobacka[1], Marek Danielewski[2,3]

1. *Abo Akademi University, Center for Process Analytical Chemistry and Sensor Technology ProSens (PROSENS), Biskopsgatan 8, Turku 00410, Finland* **2.** *AGH University of Science and Technology, Faculty of Materials Science and Ceramics (AGH UST), Mickiewicza 30, Kraków 30-059, Poland* **3.** *AGH University of Science and Technology, Interdisciplinary Centre for Materials Modelling, MSC, al. Mickiewicza 30, Kraków 30-059, Poland*

e-mail: alewenst@abo.fi

Existing theoretical interpretations of membrane potential used in biology and in chemistry are based on assumptions of total or local equilibrium and electroneutrality or *quasi*electroneutrality. This practice allows simplifying calculus; however, it does not allow access to time domain and non-equilibrium membrane potential. The paradox is in fact that non-equilibrium membrane potential is a prerequisite of biological life and majority of applications of membrane-based sensors. Many practical applications of ion-selective membrane electrodes (ISEs) are impeded simply because of lacking interpretation of variability of selectivity coefficients and detection limits over time. For this reason, we use the Nernst-Planck-Poisson (NPP) equations to pave access to the time-domain. The NPP equations allow predicting and visualizing the selectivity and the low detection limit variability over time as well as assessing the influence of other physico-chemical parameters e.g. membrane thickness, main to interfering ion concentration ratios and ion diffusibility. In this way, the conditions under which measured selectivity coefficients are true (unbiased) and detection limits can be optimized.

This work is supported by the Polish State Committee for Scientific Research via grant KBN 3 T09A 175 26, and by the Finnish Academy via the Process Chemistry Centre (PCC) at Abo Akademi University, Finland.

15:10 Keynote lecture

Surface Potentials: the Unexplored Way to Develop Sensors for Small Organic Ions and Large Biomolecules

Luc J. Nagels

University of Antwerp, Department of Physics, Antwerp, Belgium University of Antwerp, Department of Chemistry, Groenenborgerlaan 171, Antwerp 2020, Belgium

e-mail: luc.nagels@ua.ac.be

Many materials develop surface potentials when they are in contact with water solutions. With ISE sensor surfaces, these potentials change when they are contacted by certain cations or anions, due to non-faradaic phenomena. The selectivity of these sensors is mostly not as high as generally thought, certainly not for organic ionic substances. This selectivity is often adjusted by adding a molecule which has strong interactions with the analyte ion, a so-called ionophore. Despite the enormous activity in the field of macrocyclic or podand receptor molecules, good ionophores are still lacking for organic ionic molecules. The situation is better for anionic- than for cationic organic substances. Several examples of successful ligands for anionic organic molecules will be demonstrated. However, ISE selectivity for organic ions is mostly dominated by their lipophilicity (logP). This will be shown by recent examples where ISE sensors were used as a novel detection system in HPLC. The system uses a signal transformation algorithm to obtain a concentration related tracing. The analyte molecules varied from organic sulphonate and sulfate detergents and biochemicals over carboxylic acids from food industry, to pharmaceuticals. The detection limits are excellent, except for hydrophilic cationic compounds. For the latter substances, better organic ionophores and membrane components should be developed. Surprisingly, highly charged molecules such as DNA also performed very well. They yielded unexpected calibration curves (slopes) and very good detection limits. Their responses were slower than the ones of the smaller molecules. This effect was attributed to high mass transfer resistance. These data on highly charged and large biomolecules in the HPLC application receive support from recent literature data on totally different applications. This opens new exciting possibilities for the use of ISE's in the (bio)sensor area.

15:30	Keynote lecture

Potentiometric Ag^+-sensors based on conjugated polymers

Johan Bobacka[1], Zekra Mousavi[1], Ari Ivaska [1], Andrzej Lewenstam[1,2]

1. *Abo Akademi University, Process Chemistry Centre, Laboratory of Analytical Chemistry, Biskopsgatan 8, Turku FIN-20500, Finland* **2.** *AGH University of Science and Technology, Faculty of Materials Science and Ceramics (AGH UST), Mickiewicza 30, Kraków 30-059, Poland*

e-mail: johan.bobacka@abo.fi

Conjugated, electrically conducting, polymers are multifunctional materials that are of great interest in the area of chemical sensors [1], including potentiometric ion sensors [2,3]. For many years, one of the main challenges has been to obtain functionalized conjugated polymers showing high selectivity towards specific ions. We have found that conjugated polymers, including polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3-octylthiophene) (POT), show a selective potentiometric response to silver(I) ions in aqueous solution [4-6]. The selectivity to Ag^+ seems to be a common feature of several conjugated polymers and the doping ions do not play a crucial role. Oxidation of conjugated polymers such as PPy and PEDOT by Ag^+ causing electroless deposition of metallic Ag onto the conjugated polymers is well described in the literature [7]. However, we have found that chemically synthesized POT shows a selective response to Ag^+ although POT remains in the undoped form, as shown by UV-vis spectroscopy [5]. This indicates that the presence of metallic Ag in the conducting polymer is not a prerequisite for the potentiometric response to Ag^+. In the case of POT, the potentiometric response to Ag^+ is therefore related mainly to interactions between Ag^+ ions and sulfur atoms of the conjugated polymer backbone. Additionally, Ag^+ ions may interact via π-coordination with double bonds present in conjugated polymers. Conjugated polymers represent a new class of Ag^+-selective membranes.

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15:50	Short communication

Miniature planar ion selective chloride electrodes and their application to blood serum analysis

Przemysław Bieganowski[1], Elżbieta Zwierkowska[2], Selim Achmatowicz[2], Magdalena Maj-Zurawska [1]

1. *University of Warsaw, Department of Chemistry, Pasteura 1, Warsaw, Warszawa 02-093, Poland* **2.** *Institute of Electronic Materials Technology (ITME), Wólczyńska 133, Warszawa 01-919, Poland*

e-mail: bieganowski@chem.uw.edu.pl

Recently many studies have been undertaken in order to construct miniature potentiometric sensors having good analytical properties in terms of potential stability, detection limit, linear range and slope of the calibration plot. In the field of ion selective electrodes with solid-contacted membranes, significant improvements have been achieved by introducing a redox couple or lipophilic redox active self-assembled monolayer between the membrane and metal substrate. Especially attractive is the possibility to introduce an intermediate layer, having both ionic and electronic conductivity, placed between the ion-selective membrane and the metallic contact. Conducting polymers possess this function. The aim of this work is to investigate the characteristic of miniature planar chloride electrodes and their application to blood serum analysis. The electrodes contain solvent polymeric ion selective membrane deposited on various supports. The ion selective membrane consists of an ion exchanger methyl-tri-n-tetradecylammonium chloride (MTTACl) or methyl-tri-n-dodecylammonium chloride (MTDACl), a plasticizer bis-(2-ethylhexyl) sebacate (DOS) and poly(vinyl chloride) (PVC) (high molecular weight) or polyurethane (Tecoflex) as a polymeric matrix. In the case of polyurethane membrane some amount of potassium tetrakis [3,5(bis(trifluoromethyl)phenyl] borate (KtFPB) is also added to improve the conductivity of the membrane. The electric contact on the support is a screen printed silver layer. Between this layer and the ion selective membrane various intermediate layers are present. Various compositions of intermediate layers were tested to provide electrodes exhibiting stable potential readings and long lifetime of their practical utility. In one case the silver layer is covered electrochemically with gold (3 µm), then the next layer containing soluble conducting polymer poly(3-octylthiophene) (POT) ((wt. %): 29.7%POT, 29.7%PVC, 39.6% MTTACl,1% 3-aminopropyltriethoxysilane) is applied. In the other case the silver layer is covered by screen printed graphite, then the next layer containing POT ((wt. %): 33%POT, 33%PVC, 34% MTDACl) is applied. The electrodes show Nernstian behavior during at least two months. The electrodes containing polyurethane as polymeric matrix show slightly better characteristics. The chosen electrodes were investigated under flowing through conditions to determine chlorides concentration in quality control serum samples (QCS). The results were compared with the results obtained using commercial potentiometric clinical analyzer (KONE, Finland) and with concentration values given by QCS producer. The comparison indicates the possibility of application of investigated electrodes to blood serum analysis.

Coffee break

Monday afternoon, 5 November, 16:05

Session 4

Monday afternoon, 5 November, 16:30

16:30	Keynote lecture

Surface Modification of Carbon Materials for Electrocatalysis: From Catalyst Development to the Hierarchical Build-up of Electrode Structures

Michael Bron

Ruhr-Universität Bochum, Anal. Chem. - Elektroanalytik & Sensorik (ELAN), Universitätsstr. 150, Bochum 44780, Germany

e-mail: michael.bron@rub.de

Despite the huge progress in the field of polymer electrolyte membrane fuel cells (PEM-FCs) during the last two decades, there are still some drawbacks, which have to be overcome in the course of fuel cell commercialisation. One of these is related to electrocatalysis: Typical electrocatalysts for PEM-FCs consist of nanoparticles of Pt or its alloys, which are deposited onto a conducting carbon black. While Pt is still the most active metal for the cathode process in PEM fuel cells, namely the oxygen reduction reaction (orr) in acid environment, it is rather expensive, and still exhibits large overvoltages for the orr. Alternative approaches are therefore pursued in the development of active and stable electrocatalysts. One of these alternatives, which will be discussed in this presentation, uses iron-nitrogen centres incorporated into the surface of a carbon black. Such surface-modified carbons can prepared from a variety of precursors, like metalloporphyrins and -phthalocyanines, metal salts together with acetonitrile or metal complexes of e.g. phenanthroline. These precursors are deposited onto the carbon and submitted to an appropriate heat treatment step at 500 to 900 °C, in which the active electrocatalyst forms. The properties of the carbons used in the preparation, like surface area and nitrogen content, strongly influence the activity of the derived electrocatalysts. Recently, we have successfully modified carbon nanotubes with catalytically active centres. We were able to show, that the electrocatalytic activity of these nanotubes depends on their structural parameters (length and diameter). However, catalyst development for fuel cells can not just focus on catalyst activity. Further important points are the investigation of catalyst selectivity (i.e., the ratio of water to H_2O_2 formation) as well as the overall electrode structure of the so called gas diffusion electrodes, which is rather complex and includes at least two layers (catalyst layer as well as gas diffusion layer) and additives. In order to optimise electrode structure, a hierarchical approach would be desired, in which an appropriate substrate is modified step by step to build up a gas diffusion electrode, e.g. by the growth of carbon fibers and tubes and subsequent deposition of electroactive species like Pt nanoparticles or electropolymerized metalloporphyrines. First steps in this direction are currently carried out in our laboratories. The methods we use for investigating the catalytic active materials include RDE (rotating disc electrode), impedance and SECM (scanning electrochemical microscope) measurements.

16:50	Keynote lecture

Nanomaterials at the surface of chemical sensors

Jan Labuda, Adriana Ferancova

Slovak University of Technology in Bratislava, Institute of Analytical Chemistry (STU), Radlinskeho 9, Bratislava 81237, Slovakia (Slovak Rep.)

e-mail: jan.labuda@stuba.sk

Nanotechnology and nanomaterials become popular at the construction of devices such as chemical sensors, biosensors, electromechanical and analytical systems, diagnostic instruments, etc. as they enable manipulations on the supramolecular level. Nanomaterials characterized by at least one dimension smaller than 100 nm possess new possibilities of controlling the properties of signal transducers, new signal transduction technologies, new matrices for immobilization of biomolecules, redox mediators, markers, indicators, etc., and leads to lowering the detection limits. Nanomaterials are also of interest for miniaturization of the sensors and preparation of nanoelectrode arrays and offer new environmental, biomedical and *in vivo* applications. Nanomaterial structures involve, for example, carbon or metal nanotubes, nanoshells, nanofibers, other carbon nanostructures such as fullerenes and diamonds, nanorods and nanowires, nanoscale assemblies, nanoclusters and nanoparticles, as well as nanocomposites. In this paper, examples of the chemical modification of the surface of electrochemical and optical sensors by nanomaterials as well as by recognition elements with nanomaterials as the markers will be presented together with its effects on the sensitivity and selectivity of chemical analysis.

Acknowledgement: The work was supported by the Grant Agency VEGA of the Ministry of Education of Slovakia (Project No. 1/2462/05) and the Ministry of Education of the Slovakia (Application Research Project).

17:10 Short communication

Metalloporphyrin modified glassy carbon electrodes for oxygen reduction: Investigation of local electro-catalytic activity

Ayodele O. Okunola, Xingxing Chen, Kathrin Eckhard, Michael Bron, Wolfgang Schuhmann

Ruhr-Universität Bochum, Anal. Chem. - Elektroanalytik & Sensorik (ELAN), Universitätsstr. 150, Bochum 44780, Germany

e-mail: ayodele.okunola@ruhr-uni-bochum.de

The development of suitable catalyst materials for oxygen reduction in the cathode half-cell reaction of PEM fuel cells has received tremendous attention in recent years. Metalloporphyrins supported on carbon blacks have proven to be potential candidates as suitable modification materials for the cathode with two and four electron reduction of oxygen to hydrogen peroxide and water respectively, as reported in literature. Heat treatment of these catalysts at temperatures between 400°C and 900°C has lead to enhanced stability. Basic investigations on those materials in principle use dip- or drop- coating techniques and sometimes combined with a heat treatment [1, 2]. Such modified surfaces have been applied extensively in the catalytic reduction of oxygen. An immediately observable limitation however is the possibility of quantifying effectively, the porphyrin-loading in the case of dip or drop coated materials and a drastic reduction in catalytic activity in the case of a heat-coated surface due to a destruction of the heat polymerized metalloporphyrin under high temperature conditions. In order to obtain quantifiable porphyrin loadings as modification materials, electro-polymerized metalloporphyrins of Fe and Mn using pulse potentials or cyclic votammetric deposition procedures have been established. Fundamental parameters such as ring substituents, porphyrin loading and their effects on activity and stability for oxygen reduction have also been investigated, with Fe-porphyrins showing better initial activity but Mn-porphyrins have shown better stability. A combination of two transition metalloporphyrins of Fe and Mn was also investigated. A further step was then taken to visualize the local electro-catalytic activity using scanning electrochemical microscopy (SECM). An estimation of the number of electrons involved in the oxygen electro reduction, to water or hydrogen peroxide was attempted, using the redox competition mode of scanning electrochemical microscopy (RC-SECM) [3]. Details of experimental procedures and results shall be discussed.

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17:25 Short communication

Novel lectin-based quartz crystal microbalance biosensor for the identification of the pathogenic bacteria

Gulnara R. Safina, Bengt Danielsson

Lund University, Pure and Applied Biochemistry Department, Getingevägen 60, Lund SE-22100, Sweden

e-mail: gulnara207@hotmail.com

The development of the sensitive, rapid and simple methods for the detection of the pathogenic bacteria in the biological and food samples is the important problem which requires the special analytical approaches. The flow-through assay for screening of the pathogenic bacteria presence using lectin-based quartz crystal microbalance (QCM) biosensor has been proposed. The biosensor makes it possible to identify the bacteria presence using lectins immobilized on the surface of QCM crystal which bind specifically to the certain oligosaccharides present on the cell wall of the bacteria injected. For the obtaining of the biosensing part of the analytical device amine coupling procedure has been used. Firstly, the clean working surface of the crystal was treated with 11-mercaptoundecanoic acid (thiolization step) in order to obtain thiol self-assembled monolayers on its gold surface. Then the thiolized surface was activated on-line mode by sequential injections of the mixture of 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride (EDC), N-hydroxisuccinimide (NHS). Then, the on-line immobilization of lectin with following blocking of the surface with ethanolamine hydrochoride to prevent non-specific binding was carried out. In this work we used different lectins as ligands – Concanavalin A (ConA), lectins from Ulex europeaus (UEA), Maackia amurensis (MAL), Lens culinaris (LCA), wheat germ agglutinin (WGA) – and different strains of the pathogenic bacteria Campylobacter jejuni and Helicobacter pylori as analytes. Formation of the complex [lectin-sugar] on the surface of the crystal after injection of the bacteria leads to the decreasing of the oscillation frequency of the crystal due to the increasing of its mass that is an analytical signal. The working conditions of the biosensor – flow rate, pH of the working buffer, the dilution of the bacterial cells, the regeneration solution – have been found and optimized. All the measurements were carried out in phosphate buffered saline (pH 7.4), the dilution of the cells was 1:50. Using the lectins having different specificity to various sugar residues makes it possible to distinguish and identify the different bacterial strains. It has been found that ConA revealed wider variety of the specificity to different bacteria observed. Lectin from UEA, vice versa, can bind only certain strains of Helicobacter pylori. Glycine with pH 2.5 was used as a regeneration solution which is able to remove the formed [lectin-sugar] complex from the crystal surface without significant damage of immobilized ligand to make it ready for the next experiment The most important advantage of proposed sensor is the ability to carry out the label-free assay, which makes it possible to analyze the bacteria directly in the sample. The assay is sensitive, much more rapid than the conventional bacteriological analysis (assay time is about 20-30 minutes) and simple which makes it as an alternative technique for the bacteria detection.

Dinner

Monday evening, 5 November, 18:15

Poster session

Monday evening, 5 November, 19:15

19:15 Poster 1

Driving ion transfer across the toluene (trihexyl(tetradecyl)-phosphonium tris(pentafluoroethyl)trifluoro-phosphate) | water (electrolyte) interface with the MnTPP(III/II) redox system

Wojciech Adamiak[1], Masanori Satoh[2], Galyna Shul[1], Ewa A. Rozniecka[1], Jingyuan Chen[2], Frank Marken[3], Marcin Opallo[1]

1. *Polish Academy of Sciences, Institute of Physical Chemistry, Kasprzaka 44/52, Warszawa 01-224, Poland* **2.** *University of Fukui (U. Fukui), 3-9-1 Bunkyo, Fukui 910-8507, Japan* **3.** *University of Bath, Department of Chemistry, Claverton Down, Bath BA2-7AY, United Kingdom*

e-mail: wadamiak@ichf.edu.pl

Recently the ionic liquids have been applied as electrochemical solvents [1,2]. However, reports of electrochemical studies involving ionic liquid/water interface are scarce. Some of them utilize three phase boundary formed at the electrode/ionic liquid/water interface [3,4]. Typically in such a system an electric charge is generated by electrode reaction of the redox probe within ionic liquid deposited on the electrode surface. The electrode is immersed in the electrolyte aqueous solution. To keep electroneutrality within the organic phase the electrode reaction is associated with ion transfer across liquid/liquid interface [4]. The use of weakly coordinating solvents with low dielectric permittivity (e.g. toluene) ensures relatively good solubility of hydrophobic redox probes (e.g. porphyrinato metal complexes). Recently the solution of phosphonium-phosphate ionic liquid (cph.aph) in toluene as the suitable electrolyte system has been proposed [5]. Herein, the deposit of cph.aph supported toluene containing manganese(III) porphyrine (MnTPP) chloride as the redox probe was examined in terms of ion transfer across liquid/liquid interface. The effect of cph.aph concentration on UV-VIS spectra of MnTPP-toluene solution was examined. They are clearly affected by addition of the ionic liquid and observed changes may be considered as an evidence for axial ligation of ionic liquid anion to the porphyrine molecule. Cyclic and differential pulse voltammetry experiments were carried out at glassy carbon electrode modified with organic solution and immersed in aqueous phase. Reversible anion transfer occurs and it has been found that the peak potentials depend on the nature and concentration of the anion present in the aqueous phase. Analysis of data indicates that after immersion of the electrode into aqueous solution spontaneous anion exchange across liquid/liquid interface and equilibrium occurs. Then the Mn(III/II)TPP electro-reduction brings about anion transfer between organic and aqueous phase. Hydrophobic anions are transferred at more negative potentials and only for strongly hydrophilic anions (F^-, SO_4^{2-}) a change in mechanism are observed. The addition of cph.aph. shifts peak potentials towards more negative values. This effect may be assigned to stabilization of $Mn(III)TPP^+X^-$ (X = $PF_6^-ClO_4^-$, SCN^-, NO_3^-, Br^-) ion pairs in toluene by the ionic liquid.

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19:15 Poster 2

Determination of Dopamine in Presence of Ascorbate in Ultrathin Carbon Nanoparticle Composite Film Electrodes

Mandana Amiri[1], Saeed Shahrokhian, Frank Marken[2]

1. *Sharif University of Technology, Azadi Avenue, Tehran 14588, Iran* **2.** *University of Bath, Department of Chemistry, Claverton Down, Bath BA2-7AY, United Kingdom*

e-mail: mandanaamiri@yahoo.com

Carbon materials are widely used for modified electrodes in electroanalysis and in particular the recent development of a new range of nanocarbons has triggered many new developments in electrochemical sensing. In this report uniform carbon nanoparticles are employed in conjunction with a poly(diallyldimethylammonium chloride) or PDDAC binder. After suspension into water, the carbon nanoparticles with negative surface charge readily assemble onto surfaces which have been modified with PDDAC polycations. A layer-by-layer electrostatic assembly process is used to grow thin carbon nanoparticle films with ca. 5 to 6 nm average thickness increase per deposition layer at tin-doped indium oxide (ITO) substrates. Transparent and strongly adhering films of high electrical conductivity are formed and characterized in terms of their electrochemical reactivity. When immersed in aqueous 0.1 M phosphate buffer pH 7, each layer of CNP-PDDAC is adding an interfacial capacitance of ca. 10 mF cm^{-2}. Absorption into the CNP–PDDAC nanocomposite film is dominated by the sites in the PDDAC cationomer and therefore anionic molecules such as indigo carmine are strongly bound and retained within the film (cationic binding sites per layer ca. 150 pmol cm^{-2}). The characteristics of these ultrathin films as electrodes for adsorbed and for solution redox systems are explored and the selective determination of dopamine in the presence of ascorbate is highlighted as a potential sensor application. The determination of dopamine in the presence of ascorbateis a challenging problem for in vivo nerve cell investigations and it has led to new types of modified electrodes. For the mixed redox system ascorbate–dopamine in 0.1M phosphate buffer pH 7 cyclic voltammograms suggest a rapid and selective temporary poisoning process which causes the ascorbate oxidation to be suppressed in the second potential cycle. This effect is exploited for the detection of micromolar concentrations of dopamine in the presence of millimolar ascorbate.

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19:15 Poster 3

Incorporation of $RuSe_x$/C within nanostructural Ir matrices to enhance oxygen reduction

Beata Baranowska, Hanna Elzanowska, Magdalena Skunik, Paweł J. Kulesza

Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland

e-mail: bbaranowska@chem.uw.edu.pl

One of the main aims of the research on fuel cells is creating the most efficient electrocatalysts for oxygen reduction. The platinum based catalysts have been so far most commonly used systems for cathodes. However the problem is the high activity of Pt towards methanol oxidation, which reduces possibility of its using as cathode in Direct Methanol Fuel Cells (DMFCs) in which methanol crossover through the polymer membrane from the anode to the cathode can occur. Direct reaction of a fuel with catalyst at the cathode leads to its depolarization and to the drop of the cell power. An interesting alternative to Pt-based catalysts in DMFCs can be $RuSe_x$ nanoparticles, because of it's high methanol tolerance. But to make system more attractive, the potential of the oxygen reduction should be shifted towards more positive values. This feature has been recently achieved by us via modification of carbon-supported $RuSe_x$ nanoparticles with ultra-thin films of tungsten oxide (WO_3).

In this work we utilize the iridium nanoparticles (obtained by sol-gel method) as the addition to $RuSe_x$/C catalyst. Ir surface can be partially oxidized during potential cycling and as a result the mixture of Ir with mixed valent oxides (IrOx) is formed. Ir oxides are characterized by good electronic conductivity, the property necessary to enhance O_2 reduction. Apart from that, just like in the case of WO_3, iridium structures are highly active towards hydrogen peroxide reduction, thus supporting direct reduction of oxygen to water. The TEM images illustrate that nanostructural Ir makes compact polymeric type structure analogous to those previously observed for WO_3. It is reasonable to expect that IrOx may serve as a matrix for carbon-supported $RuSe_x$ particles. Analysis of voltammetric and RDE experiments shows that, after modification of $RuSe_x$ by iridium nanoparticles, better catalytic properties of the cathode, namely the positive shift of the reaction potential and the increase of the reaction rate (in comparison to bare $RuSe_x$ and Ir/IrOx systems) have been obtained.

19:15 Poster 4

Adsorption of As(III) and As(0) on the gold microelectrode

Anna Basa[1], Tadeusz Krogulec[1], Andrzej S. Baranski[2]

1. *University of Białystok, Institute of Chemistry, Hurtowa 1, Białystok 15-399, Poland* **2.** *University of Saskatchewan, 110 Science Pl., Saskatoon S7N5C9, Canada*

e-mail: abasa@uwb.edu.pl

Strong toxicity and carcinogenesis of arsenic has been the reason to develop many analytical techniques for controlling and determining its content in environmental samples, mainly in natural and drinking water [1]. Considering simplicity, low-cost, velocity and sensitivity of electrochemical methods, they have found wide application to arsenic determination. That was possible due to the electrode processes of arsenic compounds and therefore better knowledge of their mechanism is significant. Most of the studies were conducted on the large size electrodes: mercury, platinum [2] or gold [3,4], not many works were carried out on the microelectrodes [1]. It seems that the mechanism of the electrode processes occurring on the gold electrodes has not been completely explained in the literature yet. Cyclic voltametry studies carried out on the gold microelectrode show, that As(III) ions adsorb on the electrode surface. This phenomenon was not considered by other researchers, concerning electrode processes taking place on the gold. Our studies indicate, that As (III) adsorbed on the electrode surface is involved in the following reaction:

$$As(OH)_{3\,(ads)} + 3H^{+} + 3e^{-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} As_{(ads)} + 3H_2O$$

The product of this process, As(0), is also adsorbed on the electrode surface. The relation between the charge of As(III) adsorption/desorption peaks and (i) deposition potential, (ii) deposition time and (iii) As(III) concentration were measured. The monolayer charges and adsorption isotherms were determined for three electrolytes: 0.5 M H_2SO_4, 0.04 M borax and 0.1 M NaOH. The analysis indicates that adsorption of As(III) can be described by Frumkin isotherm, and also pH of the solution strongly affects the molecular interaction in the monolayer. The molecular interaction parameter changes from positive value ($g = 0.9$) in acidic conditions, to negative value ($g = -1$) in strong basic solution. The analysis of kinetics of investigated processes was carried out in range pH from 0 to 13. The standard rate constants of reaction were determined for different values of pH. The obtained values from $1.4\cdot10^{-6}\ s^{-1}$ to $9.2\cdot10^{-9}\ s^{-1}$ indicate the irreversibility of that process. The rate of the process decreases with pH increase.

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19:15 Poster 5

Synthesis of electroactive films of Prussian Blue: improvement of selectivity and stability of the advanced H_2O_2 transducer.

Anastasiya Borisova[1], Aleksandr G. Chuchalin[2], Eldar H. Anaev[2], Arkady A. Karyakin[1]

1. *Chemistry Department, Moscow State University, Leninskie Gory, 1-3, Moscow 119992, Russian Federation* **2.** *Pulmonology research institute, Moscow 105077, Russian Federation*

e-mail: avborisova@list.ru

The problem of monitoring of low levels of hydrogen peroxide is required in medicine, environmental control and in industry. There are known different methods of such detection, but electrochemical analysis is the most sensitive, selective and the cheapest method.

The construction of electrochemical sensor for hydrogen peroxide is based on advanced electrocatalyst for hydrogen peroxide reduction (Prussian Blue). The application of Prussian Blue modified electrodes for sensors and biosensors construction has been shown for the first time in our group [1]. To start mass production of sensors it is necessary to apply planar electrodes based on screen-printed technology as well as to simplify the procedure of electrodes modification by nano-scaled layers of Prussian Blue. We have been developed the new method of chemical deposition of nano-scaled films of Prussian Blue allowed to increase the reproducibility of sensors and to lower their cost. Analytical characteristics of developed sensors tested in FIA are: linear range of hydrogen peroxide detection $10^{-7} – 10^{-3}$ M, low response time (<1 min), operational stability >1000 measurements. Significant increase of the stability of Prussian Blue can be achieved by covering electrode by polymeric membrane (Nafion®). Under the constant flow of hydrogen peroxide with concentration 10^{-4} M sensor holds 100 % stability during more than 1 hour. Combining precipitation Prussian Blue with some organic polymers as polyaniline, polypyrrole and different substituted polypyroles make it possible to improve the analytical characteristics of sensors. The new fields of application of developed sensor for hydrogen peroxide have been defined. Sensor could be applied in clinical diagnostics for oxidative stress detection. Sensor has been used for development of novel method of non-invasive diagnostics of condensate of expired air in pulmonology.

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Acknowledgements. Financial support through RFFI 06-03-33013-a, RFFI-07-03-12211-innovation, grant of Federal Agency for Science and Innovation (2007) and IINTAS innovation 05-000007-429 and ISTC 32-09 are greatly acknowledged.

19:15 Poster 6

A new class of receptors for the development of biosensors: aptamers for clinical bio-markers

Sonia Centi, Alessandra Bini, Sara Tombelli, Maria Minunni, Marco Mascini

Università di Firenze, Dipartimento di chimica (DEPT), via della Lastruccia 3, Sesto Fiorentino 50019, Italy

e-mail: sonia.centi@unifi.it

Aptamers are an alternative to antibodies in their role as biorecognition elements in analytical devices. Aptamers are *in vitro* selected oligonucleotides that can bind with high affinity and specificity to a wide range of target molecules, such as proteins or other organic and inorganic molecules. They have been used in numerous investigations, as therapeutic or diagnostic tools and they have been recently employed in analytical chemistry, as immobilised ligands or in homogeneous assays. In this work the development of an aptamer-based biosensor (aptasensor) for C-reactive protein (CRP), an important clinical bio-marker, will be presented. CRP was the first acute-phase protein to be discovered (1930) and is a sensitive systemic marker of inflammation and tissue damage. It is produced by hepatocytes in response to the cytokine interleukin-6 and its plasma half-life is of 19 h. CRP is considered a marker of vascular inflammation and a risk factor for cardiovascular disease. It has also a prognostic value for patients with acute coronary syndrome. The average concentration of CRP in blood is 0.8 mg/l but levels may increase up to 500 mg/l in case of inflammation. An RNA aptamer specific for CRP has been coupled to a surface plasmon resonance transduction, for the development of a new generation of biosensors. The CRP-specific RNA aptamer is composed of 44 bases and the binding constant K_d was estimated to be 125 nM. Several immobilisation protocols have been studied and optimised. In particular, different spacers (polyT spacer composed of 20 thymines and a triethylene glycol spacer) have been attached to the 5’ end of the aptamer to study the effect of the vicinity of the oligonucleotide to the solid surface. Moreover, binding conditions such as binding buffer, ionic strength and pH, have been optimised. With the best working conditions, a detection limit for CRP of 0.005 mg/l was reached with good selectivity towards human serum albumin. This detection limit allows a high dilution (around 1000 times) of serum samples, in order to overcome matrix non-specific effects when analysing real samples.

19:15 Poster 7

Electrical Wiring of Living Bacillus subtilis Cells Using Flexible Osmium-Redox Polymers

Vasile Coman[1], Cecilia Hägerhäll[2], Lo Gorton[1]

1. *Lund University, Department of Analytical Chemistry, Lund SE-221 00, Sweden* **2.** *Lund University, Biochemistry, Getingevagen 60, Lund SE-22100, Sweden*

e-mail: Vasile.Coman@analykem.lu.se

Artificial mediators offer the possibility for an enhanced electron transfer between microbial cells and electrodes. The important role of these electron shuttles in whole cell biosensors and microbial fuel cells is to replace the natural electron acceptor (oxygen in case of aerobic bacteria, Fe(III) oxides/complexes in case of anaerobic organisms), thus preventing the problem of limiting concentrations. The polymeric mediators proved to exhibit efficient electron shuttling properties for multiple layers of microbial cells. They promote a stable binding on the electrode surface; therefore the problem of releasing possible human-toxic compounds in the environment is reduced. In the present study the application of two different flexible osmium redox polymers; poly(1-vinylimidazole)$_{12}$-[Os-(4,4′-dimethyl-2,2′-di'pyridyl)$_2$Cl$_2$]$^{2+/+}$ (osmium redox polymer I) and poly(vinylpyridine)-[Os-(N,N′-methylated-2,2′-biimidazole)$_3$]$^{2+/3+}$ (osmium redox polymer II) were investigated for efficient electrical wiring of gram-positive bacteria *Bacillus subtilis*. Their efficiency in wiring gram-negative bacteria was previously investigated [1,2]. The two Os-polymers differ in redox potential and the length of the side chains, where the Os$^{2+/3+}$-functionalities are located. The analytical characteristics of the microbial sensors were evaluated for determination of succinate, fumarate and glucose as substrates in both batch analysis and flow analysis mode using both gold and graphite electrodes. The influence of oxygen presence in the buffer on the current response was evaluated. The efficiency of the electron transfer with the osmium redox polymer was compared with that of a soluble mediator (ferricyanide).

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19:15	Poster	9

Electrochemical oscillations and bistability in the redox processes of mercury ions, coupled with the self-induced convection of Hg surface.

Maciej T. Gorzkowski, Rafał Jurczakowski, Marek Orlik

University of Warsaw, Faculty of Chemistry, Pasteura1, Warsaw 02-093, Poland

e-mail: gorzki@chem.uw.edu.pl

Electrochemical dynamic instabilities remain the subject of intensive studies oriented on the oscillations of the current flowing through the circuit, the oscillatory changes of the working electrode potential and also on the pattern formation on the electrodes. One of the typical sources of instabilities in electrochemical diffusion-migration systems is the existence of the negative differential resistance (NDR) in the current-potential characteristics of the given electrode process. In the systems studied so far such NDR regions were caused either by electrostatic repulsion of ions from reaction site in the double layer, the potential-dependent desorption of the catalyst, or adsorption of an inhibitor on the electrode surface, including even its partial blocking by the particularly compact adsorbate layer. The existence of galvanostatic oscillations is usually interpreted in terms of the hidden negative resistance (HNDR). In our work we described, for the first time, oscillations and bistability which are associated with the NDR region caused by **completely different mechanism** – the potential-dependent onset and decay of convection associated with the electroreduction of Hg(II) and Hg(I) ions at the mercury electrodes. These processes are known to induce strong convection of the Hg electrode [1]. The nonlinear phenomena were observed by us in various electrochemical reactors including the system resembling the "beating mercury heart" but operating on different basis (involving convection). In our experiments, under potentiostatic conditions the current oscillations were observed in the presence of ohmic drops, while under galvanostatic conditions the large-amplitude oscillations of the electrode potential (Fig. 1) were observed only in the presence of excess of chlorides, producing a permanently existing layer of calomel in contact with the mercury surface. The outline mechanism of those oscillations was suggested [2].

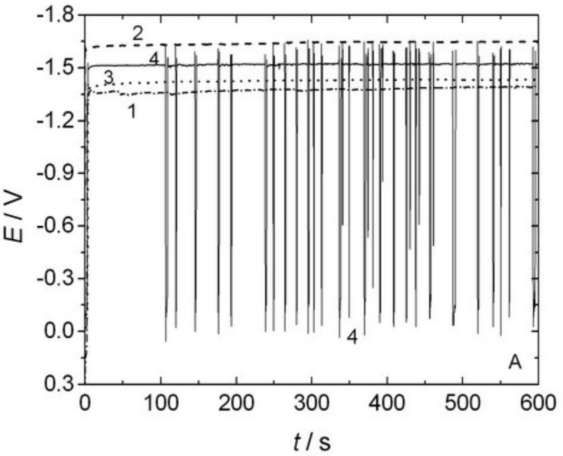

Figure 1. Steady-state currents (curves 1, 2 and 3) and spontaneous relaxation galvanostatic oscillations (curve 4) of the potential of a Hg electrode during the reduction of Hg(II) and Hg(I) ions in the presence of calomel layer.

It was also found that Hg^{2+} ions, undergoing fast surface synproportionation with Hg as the electrode material, are more efficient species than Hg$_2^{2+}$ for the onset of convection and thus oscillations. Our results enrich the set of electrochemical/oscillatory systems for the ones based on the alternate onset and decay of convection.

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19:15	Poster	10

Cu(II) detection at a carbon paste electrode modified by amorphous and ordered cyclam-functionalized mesoporous silica

Stéphanie Goubert-Renaudin[1], Mathieu Etienne[1], Yohann Rousselin[2], Frank Denat[2], Michel Meyer[2], Alain Walcarius[1]

1. *Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME), 405, rue de Vandoeuvre, Nancy 54600, France* **2.** *CNRS-Université de Bourgogne, ICMUB (LIMRES), Dijon, Dijon 21100, France*

e-mail: Stephanie.Renaudin@lcpme.cnrs-nancy.fr

Silica-based organic-inorganic materials combine the advantages of an inorganic backbone (mechanical stability, high porosity and possible control of pore size and 3D pore arrangement) and the chemical reactivity of organic groups [1]. Both organic and inorganic properties have strong influence on the adsorption of heavy metals in aqueous solution. Modifying electrodes with such materials can lead to an improvement of the sensitivity and selectivity of the sensor due to the preconcentration of the target analytes at open-circuit prior to their electrochemical detection by anodic stripping voltammetry [2,3]. Among polyazamacrocycles, cylam displays very interesting properties for sensing applications. It forms stable complexes with a large number of transition metals, in particular copper(II), and the complex properties can be tuned by a judicious choice of the organic groups attached to the macrocycle [4,5]. In the present work, cyclam molecules have been grafted onto the surface of silica materials displaying ordered (SBA15) and amorphous (K60) mesoporosity. Both hybrid materials have been dispersed in a carbon paste and the resulting modified electrodes have been successfully exploited for voltammetric detection of copper(II). The strong binding properties of cyclam towards Cu(II) species are kept when bound to silica and cyclam-functionalized silica acts as a powerful preconcentration agent. Surprisingly, a well-ordered silica does not improve significantly the electrode response, suggesting that the accumulation process may be restricted by chemical reactivity of immobilized cyclam towards Cu(II), rather than diffusion of the analyte into the silica network. The influence of interfering species (Co^{II}, Ni^{II}, Cr^{III}, …) on the electrochemical detection of Cu(II) and the analytical characteristics of the sensor have been studied.

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19:15 Poster 11

Bioelectrocatalytic dioxygen reduction at carbon nanotubes – silicate composite film modified electrode

Martin Jönsson[1], Katarzyna Szot[1], Jerzy Rogalski[2], Katarzyna A. Karnicka[3], Paweł J. Kulesza[3], Marcin Opallo[1]

1. *Polish Academy of Sciences, Institute of Physical Chemistry, Kasprzaka 44/52, Warszawa 01-224, Poland* **2.** *Maria Curie Sklodowska University, Department of Biochemistry, Pl. Sklodowskiej 3, Lublin 20-031, Poland* **3.** *Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland*

e-mail: martinj@ichf.edu.pl

A tin-doped indium oxide electrode was shown to serve as a suitable support for a carbon nanotube – silicate composite matrix with encapsulated extracellular laccase from *Cerrena unicolor.* The mediator capable to shuttle electrons between electrode and protein was adsorbed 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) from aqueous solution. In deareated solution this electrode exhibits peak shaped voltammetric signal corresponding to the one-electron electrooxidation -reduction process of the surface confined mediator. In dioxygen saturated solution bioelectrocatalytic dioxygen reduction is observed with this electrode.

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Enzymatic carbon nanotube based composite electrodes for dioxygen reduction

Katarzyna A. Karnicka, Przemysław Ziaja, Krzysztof Miecznikowski, Paweł J. Kulesza

Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland

e-mail: kkarnicka@chem.uw.edu.pl

One of the most frequently considered enzymes for use as the cathodic biocatalyst in biofuel cells is laccase. It belongs to the multicopper group of oxidases, and drives the four-electron reduction of the co-substrate O_2 to H_2O effectively, while it is quite unspecific with respect to the electron donating substrate. The dianion $ABTS^{2-}$ (2,2' – Azinobis (3 – ethylbenzothiazoline – 6 – sulfonate)) undergoes a reversible oxidation - reduction reaction and is commonly used with oxygen reducing enzymes as a mediator. ABTS was mostly considered as a diffusional mediator but recently attempts have been made to immobilize ABTS together with laccase on the electrode surface. In order to improve the effectiveness of the bioelectrocatalytic system for the electro-reduction of oxygen, we have employed carbon nanotubes (CNTs). Carbon nanotubes exhibit very good mechanical and electronic properties and they facilitate electron transfer in bioelectrocatalytic systems. We have prepared colloidal suspensions of carbon nanotubes modified with ABTS utilizing the procedure proposed by us for the fabrication of phosphomolybdate-stabilized carbon nanotubes [1]. The bioelectrocatalytic film based on CNTs_ABTS and laccase exhibits very good electrocatalytic activity towards oxygen reduction. The combination of CNTs and ABTS gives a highly effective mediation system able to propagate charge between the active center of the enzyme and the electrode surface.

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19:15 Poster 13

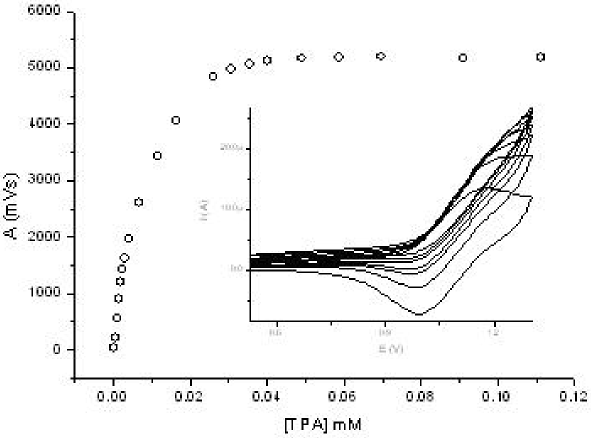
Electrochemiluminescence of Langmuir-Blodgett films of Nafion

Thiago Kohls[1], Ligia M. Moretto[1], Paolo Ugo[1], Denis Badocco[2], Paolo Pastore[2], Neso Sojic[3]

1. *Dipartimento di Chimica Fisica, Università Cà Focari di Venezia, S. Marta 2137, Venezia 30123, Italy* **2.** *Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, Padova 35131, Italy* **3.** *Universitè Bordeaux (ENSCPB), Avenue Pey-Berland 16, Bordeaux 33607, France*

e-mail: abnormtk@yahoo.com.br

The success of Nafion modified electrodes in electroanalytical applications can be ascribed to their unique ion-exchange selectivity and pre-concentration capabilities, good wetting properties, chemical and biological inertness and mechanical robustness. The deposition of Nafion coatings on electrodes surfaces can be easily performed by recasting polymer solutions by microvolume evaporation or spin-coating. In some cases, however, such procedure brings to unsatisfactory reproducibility in the behaviour of the modified electrode. Significant improvements in the reliable use of ionomer-coated electrodes could indeed come from the development of deposition procedures able to achieve a better control of the deposition at a molecular level. Operating in this direction, recently, we developed original methods for preparing ultrathin films of Nafion and other ionomers by using Langmuir-Blodgett (LB) technique [1, 2]. In the present work, we exploited the potentialities of electrochemiluminescence (ECL) to study mechanism and behaviour of an analyte incorporate in a modified electrode where the film is very thin and compact. These characteristics can change dramatically properties such as the diffusion coefficient and the mechanism of charge transfer. Nafion LB coatings were deposited on transparent ITO (indium-tin oxide) electrodes and loaded by ion-exchange with $Ru(bpy)_3^{2+}$, used as electroactive luminescent probe. Such modified electrodes are characterized electrochemically and the luminescence of electrode surface is registered by a photomultiplier tube while changing the applied electrochemical potential. The onset of luminescence occurred near 0.9–1.0V, which was consistent with the oxidation of the immobilized $Ru(bpy)_3^{2+}$, and then the ECL intensity arose steeply. More information on the loading of the redox probe is obtained by ECL measurements; $Ru(bpy)_3^{2+}$ emits a strong luminescence when reacts with TPrA [3]. The experimental evidences that have to be kept in mind to justify the ECL origin in the presence of the Nafion membrane are the following: 1. both oxalate and TPrA are not electro-oxidized (both at neutral and alkaline pH); 2. TPrA is present in the film in its protonated form and is able to displace the ruthenium complex from it; 3. when the complex is in the film, the oxalate/ $Ru(bpy)_3^{3+}$ system does not produce ECL (oxalate cannot be in the film because negatively charged); 4. when the complex is in the film together with the protonated TPrA, the system does not produce ECL. The experimental evidences suggest that ECL process occurs only when $Ru(bpy)_3^{2+}$ is in the film and TPrA is outside. Emission should occurs at the interface and in the most external layer of the polymeric film.



The figure shows the ECL emission area vs. the TPrA concentration obtained from CV experiments (see the inset). The results obtained indicate that linearity is present only at low TPrA concentrations. Signal bends and reaches a plateau because the Ruthenium complex becomes the limiting species. Due to its good affinity for Nafion, $Ru(bpy)_3^{2+}$ remains strongly attached to the film and can be electrochemically recycled many times. This aspect is very attractive for application to sensors development.

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19:15 Poster 14

Multifunctional bio-electrocatalytic systems for reduction of oxygen and hydrogen peroxide

Barbara Kowalewska[1], Krzysztof Miecznikowski[1], Paweł J. Kulesza[1], Anna Belcarz[2], Grażyna Ginalska[2]

1. *Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland* **2.** *Medical University, Faculty of Pharmacy, Department of Biochemistry, Chodźki 1, Lublin 20-093, Poland*

e-mail: bstar@chem.uw.edu.pl

Combination of multi-walled carbon nanotubes, cobalt porphyrin, and peroxidase (horseradish, cabbage) enzyme in the film (deposited onto glassy carbon electrode substrate) produces a bio-electrocatalytic system capable of effective reduction of oxygen in such neutral media as 0.1 mol dm^{-3} KCl and 0.1 mol dm^{-3} KCl + 0.01 citrate buffer (pH = 6).

Carbon nanotubes have been modified with ultra-thin layers of 4-(pyrrole-1-yl) benzoic acid, or phosphododecamolybdate, to form stable colloidal suspensions of carbon nanostructures. The resulting inks have been utilized during sequential deposition of components. Co-existence of cobalt porphyrin, peroxidase enzyme together with dispersed carbon nanotubes leads to synergistic effect that is evident from some positive shift of the oxygen reduction voltammetric potentials (more than 50 mV in citrate buffer) and significant (ca. twice) increase of voltammetric currents (relative to those of the enzyme-free system). The multi-component bio-electrocatalytic film has also exhibited relatively higher activity towards reduction of hydrogen peroxide. It is reasonable to expect that the reduction of oxygen is initiated at cobalt porphyrin redox centers, and the undesirable hydrogen peroxide intermediate is further reduced at the horseradish or cabbage peroxidase enzymatic sites. An important function of carbon nanotubes is to improve transport of electrons within the bio-electrocatalytic multi-component film.

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Covalently bonded ionic liquid modified electrodes

Adam Lesniewski[1], Joanna Niedziolka[1], Barbara J. Palys[2], Cecile Rizzi[3], Laurent Gaillon [3], Marcin Opallo[1]

1. *Polish Academy of Sciences, Institute of Physical Chemistry, Kasprzaka 44/52, Warszawa 01-224, Poland* **2.** *Uniwersytet Warszawski, Wydział Chemii, Warszawa, Poland* **3.** *Universite Pierre et Marie Curie, Place Jussieu, Bat F Boite 39, Paris 75252, France*

e-mail: l_mada@poczta.onet.pl

Recently few attempts of covalent immobilisation of room temperature ionic liquids for catalytic purpose were reported in literature [1]. It employs immobilisation of ionic liquid having sol-gel precursor as cation [2, 3]. Here analogous concept of designing highly dispersed ionic liquid modified electrode will be presented. The thin film preparation employs sol-gel processing of sol composed of ionic liquid with 1,3-alkylimidazolatotrimethoxysilane cation and tetramethoxysilane on ITO electrode surface. In order to increase electrode reaction efficiency for some experiments this step was preceded by deposition of the ITO nanoparticles (21 nm diameter) by subsequent immersion and withdrawal from their suspension [4]. It has been found that the prepared electrodes acts as anion exchanger for inorganic – $Fe(CN)_6^{3-}$ [5] and organic - 2,2'-azino-bis-(3-ethylbenzothiazoline) sulfonate ($ABTS^{2-}$) anions. Silicate confined ionic liquid electrode preconcentration ability and kinetics of this process depends on composition of the film and type of the anion. It is significantly larger than for electrode modified with non-processed precursor. The amount of absorbed $ABTS^{2-}$ anion is substantially increased on the ITO nanoparticles modified electrodes.

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Tailoring polyacrylate based membranes for anion-sensing purposes

Monika Łyczewska[1], Marzena Goławska[1], Józef Mieczkowski[1], Elizabeth Hall[2], Krzysztof Maksymiuk[1], Agata J. Michalska[1]

1. *Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland* **2.** *Institute of Biotechnology, Tennis Court Road, Cambridge CB21QT, United Kingdom*

e-mail: mlyczewska@chem.uw.edu.pl

In recent years considerable progress in construction of potentiometric sensors has been achieved in the area of miniaturization, disposability and internal solution free construction. Among others polyacrylate based membranes are attractive materials to obtain ion-selective membranes of improved analytical parameters. Due to 1000 times lower diffusion coefficient compared to poly(vinyl chloride) counterparts, poly(acrylate) based membranes [1] offer significant advantages when lowering the detection limit of a cation selective sensor is considered [2,3,4]; among anion selective electrodes, to the authors best knowledge so far, only I^--selective electrodes were reported [4]. In this work we were looking at the effect of composition of n-butylacrylate – acrylonitrile based copolymer on the potentiometric responses of anion sensors. To study the effect of liphophilicity of primary ion chloride and salicylate sensors were chosen a as model. The effect of presence of ion-exchanger or above ion-exchanger + ionophore on achievable responses was highlighted. It was found that increasing amount of acrylonitrile in the copolymer is beneficial for improvement of analytical parameters of the chloride sensors. However, in the case of salicylate sensors, the membrane composition influence on sensor properties is less pronounced.

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Application of polyaniline nanoparticles in electrochemical and optical urea biosensors

Paweł Malinowski, Agata J. Michalska, Krzysztof Maksymiuk

Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland

e-mail: pamal@chem.uw.edu.pl

Enzymatic biosensors are intensively investigated and developing group of chemical sensors. Construction of simple, low cost and disposable sensors is one of main directions of recent studies. Conducting polymers are promising materials for application in construction of biosensors and can be a matrix for immobilizing enzymes or mediator transferring the signal from the analyte. The signal can result from changes of the polymer properties. The applied conducting polymer was commercially available polyaniline dispersion which was simply cast on a transparent plastic support. Then, a cellulose acetate membrane containing an enzyme was deposited on the polyaniline layer. As a model system urea sensor with urease was chosen. Urease catalyzes the hydrolysis of urea into carbon dioxide and ammonia:

$CO(NH_2)_2 + 2\ H_2O + H^+ \text{->} 2\ NH_4^+ + HCO_3^-$

Ammonia leads to local pH increase and consequently to deprotonation of polyaniline. Polyaniline deprotonation results in open circuit potential decrease of the polymer layer, conductivity decrease as well as VIS-spectrum changes dependent on pH change. Either can be easily monitored, and their application for urea sensing purposes is demonstrated. Parameters of determination were optimized and an example of calibration plot was shown on Fig. 1.

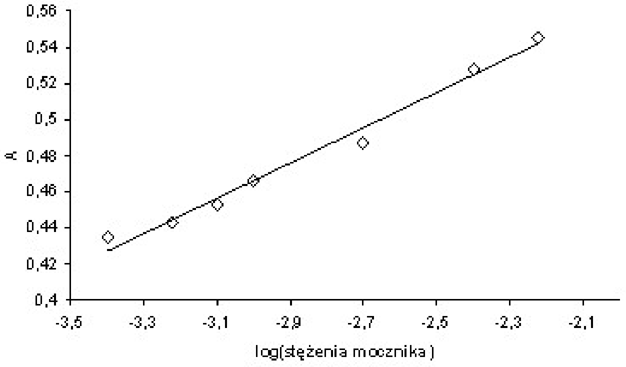

Fig. 1. Analytical characteristic of urea biosensor (absorbance at wavelength 584 nm vs logarithm of urea concentration)

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Visualisation of local catalyst activity towards oxygen reduction in hydrochloric acid solution with RC-SECM

Artjom Maljusch, Kathrin Eckhard, Michael Bron, Wolfgang Schuhmann

Ruhr-Universität Bochum, Anal. Chem. - Elektroanalytik & Sensorik (ELAN), Universitätsstr. 150, Bochum 44780, Germany

e-mail: artjom.maljusch@rub.de

In order to analyse local catalytic activity with high spatial resolution a transient redox competition mode of scanning electrochemical microscopy (RC-SECM) has been developed and described [1]. In a bi-potentiostatic experiment the SECM tip is positioned in close proximity to the surface of sample. Both electrodes are polarised to consume oxygen. If the SECM tip is close enough to an active catalyst, it will start to compete with the sample for the very same analyte in the gap between them. This leads to a noticeable tip current decrease over active sites of the sample. In order to avoid complete O_2 depletion a potential pulse profile is used for electrochemically oxygen generation prior to the competition detection. Highly dispersed electro-deposited spots of gold and platinum on glassy carbon as catalysts for reduction of molecular oxygen were investigated and successfully visualised in chloride free phosphate buffer (pH = 7) using RC-SECM [1]. However, visualisation of local catalytic activity of catalysts for oxygen reduction in chloride containing solutions by high pH has not been reported yet.

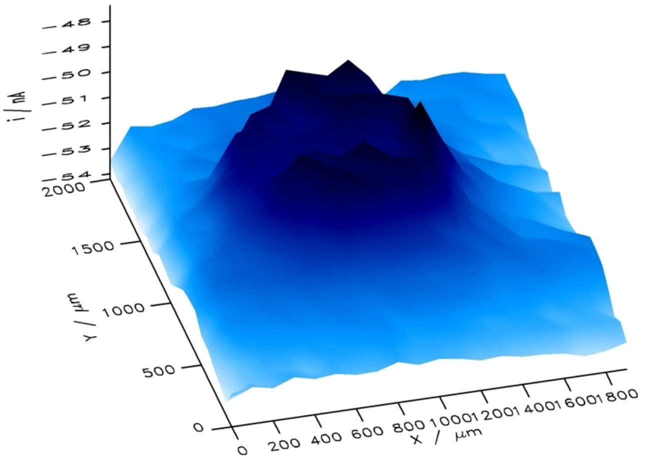

Figure 1. Local catalyst activity visualised by means of RC-SECM

In chloride containing solutions the oxygen generation pulse in RC-SECM leads to chloride oxidation to chlorine, which is very corrosive and can affect the activity of the catalysts. In this contribution, cyclic voltammetry and chronoamperometry were used for investigation of chloride oxidation process in hydrochloric acid solution. To overcome chlorine evolution during the lateral activity measurements the pulsprofile has to be adapted. With this modified RC-SECM the local catalytic activity of catalysts in a hydrochloric acid solution has been studied and successfully visualised (Fig.1). A specifically designed cell allows the investigation of powder catalysts. Development of this approach and first results are presented.

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19:15	Poster	19

Electrochemical Processes at Electrodes in Microwave Fields

Frank Marken

University of Bath, Department of Chemistry, Claverton Down, Bath BA2-7AY, United Kingdom

e-mail: f.marken@bath.ac.uk

In situ microwave activation of electrochemical processes can be achieved at electrodes placed into a microwave cavity [1,2]. In this presentation, effects and applications of microwave radiation for electron transfer in a wide range of solvent systems from aqueous solutions to organic solvents (DMSO, acetonitrile, DMF, formamide) and in an ionic liquid ($BMIM^+PF_6^-$) are reported. Three order of magnitude current increases and considerable temperature enhancements are observed and explained based on the interaction of microwaves with the liquid (electrolyte) and the physical properties of the liquids or solutions. Electrochemical processes in emulsions are shown to be facile in the presence of microwaves with novel applications in electroanalysis [3].

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19:15 Poster 21

Potentiometric response of copper-sensitive sensors based on PEDOT-Arsenazo films.

Barbara Źrałka[1], Teresa Błaż[1], Jan Migdalski[1], Andrzej Lewenstam[1,2]

1. *AGH University of Science and Technology (AGH), al. Mickiewicza 30, Kraków 30-059, Poland* **2.** *Abo Akademi University, Center for Process Analytical Chemistry and Sensor Technology ProSens (PROSENS), Biskopsgatan 8, Turku 00410, Finland*

e-mail: migdal@uci.agh.edu.pl

A new method of preparation of the copper sensitive PEDOT-Arsenazo films is shown. The Arsenazo ligands were introduced to the PEDOT film during electrodeposition. By subsequent soaking in $CdSO_4$ solution Cd(II) ions were introduced. Finally, after conditioning in the $CuSO_4$ solution copper ions were introduced via ion-exchange. In this way the PEDOT-Arsenazo films became sensitive to Cu(II) ions. Described mechanism was fully supported by ESCA spectra which confirmed the presence of arsenic inside film after electrodeposition, presence of cadmium after soaking in $CdSO_4$ solution and exchange of cadmium with copper ions after subsequent soaking with $CuSO_4$ solution. Additionally, potentiometric measurements have shown that cadmium sensitivity induced during soaking in $CdSO_4$ solution disappeared after subsequent soaking in $CuSO_4$ solution and the films became copper sensitive after that.

Chloride influence on the potentiometric response of the copper sensitive PDEOT-Arsenazo films was investigated by potentiometric, voltammetric and ESCA measurements. It has been shown that observed changes of slope and standard potential can be attributed to increasing content of Cu^{+1} or/and Cu^0 inside the film after its contact with chloride ions.

Some practical applications of the copper sensitive films are shown to illustrate behaviour and analytical advantages of presented sensors.

Financial support from KBN, project ***3T08E 085 30*** *is gratefully acknowledged.*

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Ultrathin films derived from lignins as multifunctional electrocatalysts

Grzegorz Milczarek

Poznań Technical University, Institute of Chemistry and Applied Electrochemistry, Piotrowo 3, Poznań 60-965, Poland

e-mail: gregor33@icpnet.pl

Different types of commercially available lignins were adsorbed end/or electropolymerized on glassy carbon (GC) and polycrystalline gold electrodes. Cyclic voltammetric measurements revealed irreversible electrochemical oxidation leading to the development of reversible redox couple(s). Depending on the electrode material and lignin type up to three redox couples could be detected by electrochemical techniques. The formal potentials of these systems were pH dependent with nearly Nerstian slope of -59 mV/pH unit. Some of thus created chemically modified electrodes could be applied for electrocatalytic oxidation of ascorbic acid or electrocatalytic reduction of nitrite in acidic electrolyte. Additionally it was found that some of adsorbed lignins after electrochemical oxidation significantly reduced overvoltage for oxygen reduction on gold electrodes in wide pH range. Mechanisms of electrochemical oxidation of adsorbed lignins and catalytic action of thus formed redox active ultrathin films will be proposed.

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A glucose/O_2 biofuel cell based on electrodes modified with liquid-crystalline cubic phases

Ewa Nazaruk, Sławomir Smoliński, Renata Bilewicz

Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland

e-mail: enaz@chem.uw.edu.pl

The role of biofuel cells is to convert the chemical energy into electrical current using redox enzymes as biocatalysts. The main advantage of this type of fuel cell is the application of natural compounds eg. glucose or ethanol as fuels. To fix the biocatalysts at the electrode surface we applied liquid-crystalline cubic phase. The lipidic cubic phase can be characterized as a curved, non-intersecting bilayer with two unconnected water channels. Monoolein is an example of a lipid forming such a phase. At hydration over 20% the cubic phase is stable in aqueous solutions. Due to the high viscosity and stability in aqueous solutions cubic phases are good matrices for immobilizing enzymes on electrodes, providing electrical contact with electrode surface and protecting them against denaturation. To increase the rate of the electron transfer from the enzyme to the electrode surface several organic and inorganic mediators were tested. As the bioanode, we applied a glassy carbon rod modified with the cubic phase containing glucose oxidase isolated from *Aspergillus niger* and tetrathiafulvalene, methylene green or ferrocenecarboxylic acid as the mediators. The biocathode was glassy carbon electrode modified with the cubic phase containing laccase from *Cerrena unicolor* and 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) as the mediator. Such biofuel cell uses glucose as the anode fuel and dioxygen as the cathode fuel. We determined the main parameters of the presented biofuel cells. The load in the range of 10 kΩ to 10 MΩ was applied to determine the cell current (I_{cell}) and the cell voltage (V_{cell}). When tetrathiafulvalene and ABTS were used as mediators, the biofuel cell has a 0.45 V open circuit potential and 50 mA cm^{-2} circuit current density in phosphate buffer (pH 7.0) containing 15 mM glucose and saturated with dioxygen at room temperature. The maximum power density reached 7 mW cm^{-2} at 0.25 V.

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Investigation of the influence of polymeric membrane composition on the ion transport properties by Electrochemical Impedance Spectroscopy

Beata Paczosa-Bator[1], Witold Kucza[1], Andrzej Lewenstam[1,2]

1. *AGH University of Science and Technology, Faculty of Materials Science and Ceramics (AGH UST), Mickiewicza 30, Kraków 30-059, Poland* **2.** *Abo Akademi University, Center for Process Analytical Chemistry and Sensor Technology ProSens (PROSENS), Biskopsgatan 8, Turku 00410, Finland*

e-mail: paczosa@uci.agh.edu.pl

Electrochemical impedance spectroscopy (EIS) is a powerful technique often used to study the elementary processes during the electrochemical transport. EIS by coupling with potentiometric method has become an effective toll in optimization parameters of ion-selective electrodes (ISE). The conventional construction of ISE with typical composition of polymeric membrane, namely poly(vinyl chloride), plasticizer (bis(2-ethylhexyl) sebacate or *o*-nitrophenyl octyl ether), lipophylic salt - potassium tetrakis(*p*-chlorophenyl) borate and valinomycin with different amount was used during measurements. The influence of the electrochemical properties of ions on the transport properties of the potassium selective membranes was investigated by potentiometric and impedance spectroscopy method. The results were compared with simulated impedances obtained on the ground Nernst-Planck-Poisson (NPP) equations. The NPP model as general allows interpreting the electrodes response without assumptions about steady state.

This work was supported by the Polish Ministry of Science and Higher Education, Grant No. DWM/232/MATERA/2006.

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Electrochemical screen printed graphite sensor in investigation of interactions between methylene blue and DNA

Adriana Palińska[1], Iwona Szpakowska[1], Elżbieta Zwierkowska[2], Selim Achmatowicz[2], Magdalena Maj-Zurawska[1]

1. *Warsaw University, Department of Chemistry, Pasteura 1, Warsaw 02-093, Poland* **2.** *Institute of Electronic Materials Technology (ITME), Wólczyńska 133, Warszawa 01-919, Poland*

e-mail: adusiap@gmail.com

Many molecules show high affinity to nucleic acids as they interact with DNA by several mechanisms [1]. They can join nucleic acids and inhibit basic functions of the living cells. To analytical chemist, nucleic acids offer a powerful tool in recognition and monitoring of many important compounds, e.g. toxic molecules and anticancer agents [2, 3]. Electrochemical techniques are frequently used for the detection. The goal of this work is to investigate the interactions of methylene blue (MB) with dsDNA using home made screen printed three electrode system and various electrochemical techniques: cyclic voltammetry (CV), differential pulse voltammetry (DPV), and square wave voltammetry (SWV). The explanation of the mechanism of interaction between MB and dsDNA is based on the electrochemical behavior of DNA in the absence and in the presence of MB as well as on the electrochemical behavior of MB in the absence and in the presence of DNA. The DNA presence is detected as signals due to oxidation of guanine and adenine and MB presence is detected as signals arising from oxidation or reduction of MB interacting with the DNA. The dsDNA is immobilized on the surface of the electrode by electrostatic attraction enabling very effective electron transfer between the nucleic acid bases and the electrode. After dsDNA immobilization, the electrode is rinsed with deionized water and then immersed into 10 mmol/L KCl in a pH 4.75 acetic acid buffer and electrochemical signals of oxidation of guanine and adenine are measured (blank). Alternatively, after rinsing, the electrode is immersed into a MB solution of given concentration in 10 mmol/L KCl and acetic acid buffer of pH 4.75, and after rinsing electrochemical signals of oxidation of guanine and adenine in buffered KCl solution are measured (sample). The signals obtained using these two procedures are compared and the difference detected proves the presence of MB interactions with DNA. Electrochemical signals of oxidation and reduction of MB intercalated into DNA are measured and compared with measurements of electrode modified only by MB adsorption. The difference detected proves the presence of MB interactions with DNA. Cyclic voltammetry indicates the existence of the interactions between MB and dsDNA. The similar observations of MB oxidation and reduction current using DPV and SWV indicate some difference when either DNA is present or absent. These suggest that MB can play a role of mediator between DNA and electrode surface. The dependence of SWV peak current and peak potential of the guanine oxidation on MB presence indicates strong interaction between this nucleic acid base and MB and kinetic changes in oxidation reaction of guanine. The dependence of peak current of nucleic bases oxidation in DPV and SWV on MB presence indicates strong interaction between guanine and MB facilitating the oxidation of guanine and weak (DPV, SWV) interactions between adenine and MB, proving the DNA and MB interactions in guanine rich DNA regions.

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Galvanostatic polarization of all-solid-state K^+ selective electrodes with polypyrrole ion-to-electron transducer

Paweł Pawłowski, Agata J. Michalska, Krzysztof Maksymiuk

Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland

e-mail: pawpaw@chem.uw.edu.pl

All-solid-state ion selective electrodes (ASS-ISE) are promising sensors for environmental and clinical applications. They benefit from lack of liquid phase (no risk of leakage), relatively low cost, possibility of miniaturization and wide linear response range. These electrodes consist of electronic conductor (electrode support), ion-to-electron transducer (usually conducting polymer) and polymeric ion-selective membrane, usually poly(vinyl chloride) (Fig. 1). In this work glassy carbon (electrode support), conductivity polymer: polypyrrole and K^+-selective membrane with K^+-ionophore (valinomycin) was used.

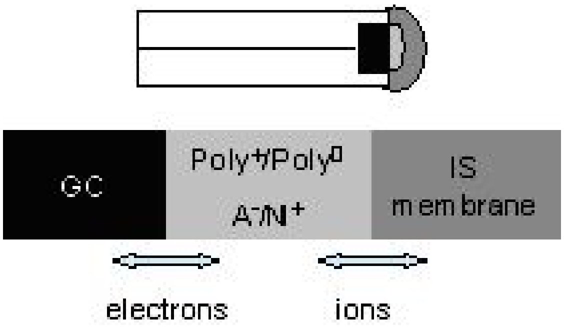

Fig. 1. Structure of ASS-ISE K^+

Under open circuit potential conditions, the detection limit of this sensor is close to 10^{-6} or even 10^{-7}M, depending on kind of lipophilic salt present in the membrane. Because the polymer is covered by a cation-exchanging membrane, K^+ ion spontaneously flow from the conducting polymer to the diluted sample solution. This effect leads to higher K^+ concentration next to membrane surface and thus to detection limit. In this work cathodic galvanostatic polarisation was used to compensate this flow and to lower the detection limit to 10^{-8}M (Fig. 2).

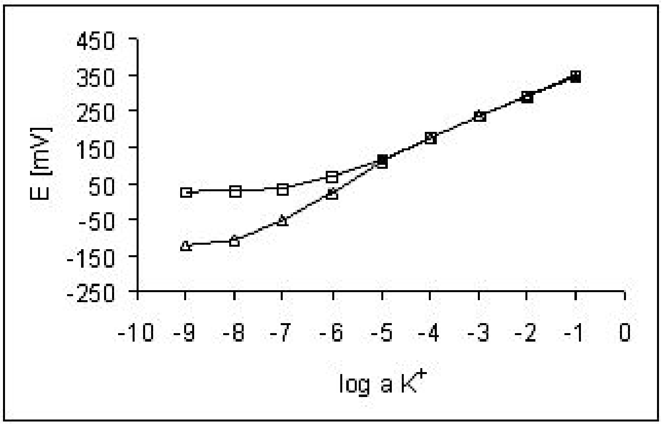

Fig. 2. Potentiometric characteristics of one of the studied electrodes under open cuircut conditions (squares) and for galvanostatically polarized electrode (triangles), I=10 nA.

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Anomalous potentiometric response of the platinum electrode in the oscillatory processes with hydrogen peroxide

Katarzyna Pękala, Rafał Jurczakowski, Barbara J. Palys, Marek Orlik

University of Warsaw, Department of Chemistry, Pasteura 1, Warsaw, Warszawa 02-093, Poland

e-mail: kpekala@chem.uw.edu.pl

The oscillatory oxidation of thiocyanate ions with hydrogen peroxide in alkaline media and in the presence of Cu^{2+} as a catalyst was observed both in the batch reactor and in the flow, continuously stirred tank reactors (CSTR) [1,2]. Luminescent traveling waves were recently reported by us [3]. The main reactions between SCN^- - H_2O_2 - OH^- - Cu^{2+} are:

$4H_2O_2 + SCN^- = HSO_4^- + HOCN + 3H_2O$ (1)

$HOCN + 2H_2O = NH_4^+ + HCO_3^-$ (2)

The complicated mechanism of this reaction involves 30 steps with 23 intermediates. The oscillatory course of this process and other oscillators involving H_2O_2 can be monitored potentiometrically using Pt electrode. We tested also the response of the gold and the glassy carbon electrodes in the SCN^- - H_2O_2 - OH^-- Cu^{2+} system. To our surprise we have found that the oscillatory variations of the Pt electrode potential could not be interpreted as reflecting the changes of the redox potential of the solution, contrary to the responses of the glassy carbon and Au electrodes which both appeared to behave as nearly inert electrodes (Fig. 1).

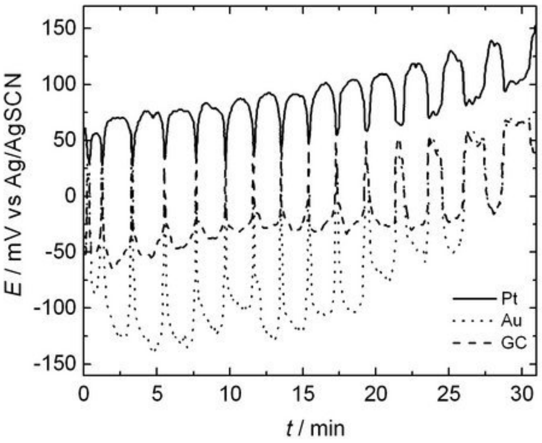

Fig. 1. Comparison of the oscillatory changes of the potential of the Pt, Au and GC electrodes in the NaSCN - $NaOH^-$ - H_2O_2 - $CuSO_4$ system.

The difference between the responses of the various theoretically inert electrodes in the NaSCN - $NaOH^-$ - H_2O_2- $CuSO_4$ system is a novel phenomenon which shows that one has to be very careful with the interpretation of the potential of a given theoretically inert electrode. It is important also because platinum is very often used for the monitoring of the course of various oscillatory processes. If the response of Pt electrode does not reflect directly the bulk redox potential of the solution, it will not be concordant with the theoretical changes of the redox potential predicted by the model of the given process, even if this model is essentially correct. We have found that an anomalous potentiometric response of the platinum electrode is a case also for the $Na_2S_2O_3$ - H_2O_2 - H_2SO_4 - Cu^{2+} system. Since both systems contain hydrogen peroxide, one can suppose that it is the specific interaction of H_2O_2 with platinum surface which makes the response of Pt electrode anomalous. In order to study in more detail this specific state of Pt electrode in both systems we used Raman and SERS spectroscopy. The atypical behavior of the Pt electrode implies further studies of its specific interaction with the studied system which may also reveal unknown details of the mechanism of the investigated oscillatory process.

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Materials with multimodal hierarchical porosity

Wojciech Pudło[1], Veronika Pashkova[2], Wojciech Gawlik[1], Mirosław Derewiński[2], Andrzej B. Jarzębski[1,3]

1. *Silesian University of Technology, Department of Chemical Engineering, M. Strzody 7, Gliwice 44-100, Poland* **2.** *Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences (ICSC), Niezapominajek 8, Kraków 30239, Poland* **3.** *Institute of Chemical Engineering Polish Academy of Sciences, Bałtycka 5, Gliwice 44-100, Poland*

e-mail: wojciech.pudlo@polsl.pl

Silica and silica-alumina thin films and monoliths, both possessing hierarchical multimodal pore structure, were synthesized by inducing a phase separation parallel to the sol-gel transition. It was found that it is also possible to obtain zeolitic layers (MFI type) deposited on parent silica or silica-alumina solid monoliths and such composite preparations retain the initial meso/macroporosity as well as texture of the parent material. The morphology of the obtained materials was observed by SEM (monoliths) and AFM (films) whilst the porosity was determined using adsorption/desorption isotherms. Further development and chemical modification of the pore surface should promote the application of well-defined hierarchically porous material into sensor technology.

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Bi-functional electrocatalytic systems for oxygen reduction in acid medium

Marta Ratter, Iwona A. Rutkowska, Krzysztof Miecznikowski, Beata Baranowska, Adam Lewera, Paweł J. Kulesza

Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland

e-mail: bbaranowska@chem.uw.edu.pl

Modification of carbon-supported $RuSe_x$ nanoparticles or cobalt porphyrin catalytic centers with ultra-thin films of tungsten oxide results in the enhancement of their catalytic properties towards electroreduction of oxygen in acid (0.5 mol dm^{-3} H_2SO_4) medium as evidenced from the positive shift of the O_2 reduction potential and the higher heterogeneous rate constant. An important issue is that the metal oxide support is characterized by good electronic conductivity and proton donating properties. Further, it is reasonable to expect that not only $RuSe_x$ or cobalt porphyrin centers are reactive but also tungsten oxide support is capable of promoting the reduction of the undesirable hydrogen peroxide intermediate. For example, the bi-functional activity of the WO_3-modified $RuSe_x$ system has been the most pronounced at rather low loadings of $RuSe_x$ nanoparticles. An important issue is tolerance of the proposed systems to methanol, ethanol or acetic acid formic acid, i.e. the organic systems that may appear due to crossover in the cathode compartments of methanol or ethanol fuel cells. Further, the WO_3-modified $RuSe_x$ (carbon-free) samples have been immobilized on the gold electrode surface for Synchrotron X-ray Photoelectron Spectroscopy (XPS) examination. The preliminary measurements have been carried out using excitation energies in the range from 90 to 1400 eV. Such experiments allow us to comment on the electronic modification of electron core levels caused by presence of adsorbed WO_3 and to determine the amounts of WO_3 present on the catalyst's surface after contacting with aqueous media. These results show that the WO_3 is not only adsorbed on catalyst's surface but it also tends to interact electronically with RuSex catalytic centers. This phenomenon may also explain the relatively good stability of WO_3 on the RuSex surface.

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Application of Inorganic Redox - Conducting Solids As Charge Relays in Dye-Sensitized Solar Cell

Iwona A. Rutkowska, Krzysztof Miecznikowski, Paweł J. Kulesza

Warsaw University, Department of Chemistry, Pasteura 1, Warsaw 02-093, Poland

e-mail: ilinek@chem.uw.edu.pl

Following the discovery of dye-sensitized solar cell, intensive research has been undertaken in developing semiconductor materials dyes, and the organic solvent or polymer electrolytes to enhance device performance. The sensitizer is typically regenerated by electron transfer from a donor, most commonly iodide ions that are dissolved in the liquid or semi-solid electrolyte present in the pores. The iodide is regenerated in turn by the reduction of triiodide at the counter-electrode. We propose here to utilize mixed-valent polynuclear electronically/ionically conducting inorganic materials, such as nickel(II) hexacyanoferrate(II,III) and Keggin-type heteropolytungstic acids (with and without triiodide/iodide redox couple immobilized in their secondary hydration spheres). The materials are characterized by fast dynamics of electron transfer between mixed-valent metal ion sites. Since the structures are hydrated, they are also good ionic (H^+ or K^+) conductors. Consequently, such redox - conducting materials have been successfully used by us as both electrolytes and charge mediators (relays) in dye-sensitized solar cells. The performance of devices has been evaluated on the basis of their photocurrent density-voltage characteristics and dark current measurements.

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Electrochemical charging of carbon nanotubes modified with polyoxometallates monolayers

Magdalena Skunik, Paweł J. Kulesza, Malgorzata Chojak, Krzysztof Miecznikowski, Beata Baranowska

Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland

e-mail: mskunik@chem.uw.edu.pl

We demonstrate here a novel type of electrode material for electrochemical capacitors (ECs) with improved capacitance properties that is prepared in a form of carbon nanotubes (CNTs) modified with ultra-thin films of a Keggin type polyoxometallate (POM), namely phosphododecamolybdic acid, $H_3PMo_{12}O_{40}$ (PMo_{12}). Such features of POMs as their well-defined structures, the ability to undergo fast and reversible redox reactions, specific photoelectrochemical properties made them model systems not only for nanometric metal (e.g. Mo or W) oxide particles but also for inorganic functional materials of potential utility in electrocatalysis, molecular electronics, sensing and in energy storage applications. Here we refer to such attractive properties of PMo_{12} as its ability to adsorb irreversibly in forms of monolayers on solid surfaces as platinum, gold and carbon. It is notworthy that monolayers of such Keggin type POM's are formed not only on solid electrodes but also on metal (e.g. Pt) nanoparticles, as well as on carbon particles (carbon black) and CNTs. In this communication, we explore the possibility of modification of CNT surfaces through adsorption of the anionic PMo_{12} monolayers. It is apparent from three distinct test experiments (based on cyclic voltammetry, galavanostatic charging-discharging and AC impedance) that capacitors utilizing $H_3PMo_{12}O_{40}$-modified carbon nanotubes are characterized by higher specific capacitances and energy densities than systems built from bare (pristine) carbon nanotubes. It is reasonable to expect that multi-walled CNTs modified through the interfacial adsorption of Keggin-type polyoxometallate (PMo_{12}) monolayers seem to exhibit both double-layer type capacitive effects as well as pseudo-capacitance properties originating from the fast and reversible multi-electron redox reactions of PMo_{12} that significantly contribute to the observed overall capacitance. When it comes to the determination of specific capacitance, a good correlation between such three electrochemical methods as cyclic voltammetry, galvanostatic charging-discharging and AC impedance has been found.

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Photochemistry and photophysics on the metallic surface

Adam Sokołowski, Jacek Waluk

Polish Academy of Sciences, Institute of Physical Chemistry, Kasprzaka 44/52, Warszawa 01-224, Poland

e-mail: adam.sokolowski@gmail.com

Fast developement of analytical techniques allows us to observe even a single molecule on the surface. We need not only excellent detection tools - we also need to enhance the optical response of the molecules. Excellent tools for single molecule investigations are: SERS (**S**urface **E**nhancement **R**aman **S**cattering) and MEF (**M**etal **E**nhanced **F**luorescence). The use of plain, rough or nanostructured metallic surfaces in both methods provides dramatically strong enhancement of Raman or fluorescence signal, respectively. These techniques have been sucessfully used in the study of biomolecules, for example single DNA observations and drug detection. My work is devoted to SERS and MEF investigations of porphyrin isomers - so called porphycenes. The absorption spectra of these molecules overlap with plasmon resonance bands of metals. Most of my work is focused on preparing well-characterized metallic (nanostructured) surface, and attaching molecules to the metal nanostructures.

Depending on surface structure, and, most important, the distance between molecules and the metal (especially - silver or gold), we are able to observe SERS, SERRS or, hopefully soon, MEF effects. At close proximity to the surface, extinguished fluorescence and enhanced Raman signal (SERS, SERRS) dominate. But when polymer spacer (from several up to hundreds of nanometers thick) is present, metal enhanced fluorescence is expected to appear. Single molecule spectroscopy on the metalic surfaces has great potential in modern analytic chemistry, as a base for construction of lab-on-chip devices.

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Surface properties of silicone rubber for sensor applications

Dariusz Szmigiel[1], Krzysztof Domański[1], Piotr Prokaryn[1], Cyrille Hibert[2], Arnaud Bertsch[3], Elzbieta Pamula[4], Anna Ścisłowska-Czarnecka[5], Janusz W. Sobczak[6], Piotr Grabiec[1]

1. *Institute of Electron Technology (ITE), al. Lotników 32/46, Warszawa 02-668, Poland* **2.** *Ecole Polytechnique Fédérale de Lausanne. Microsystems Laboratory STI-LMIS (EPFL), Lausanne CH-1015, Switzerland* **3.** *Ecole Polytechnique Fédérale de Lausanne, Centre of MicroNanoTechnology CMI (EPFL), Lausanne CH-1015, Switzerland* **4.** *AGH University of Science and Technology (AGH), al. Mickiewicza 30, Kraków 30-059, Poland* **5.** *Academy of Physical Education, Faculty of Anatomy (AWF), Al. Jana Pawła II 78, Kraków 31-571, Poland* **6.** *Polish Academy of Sciences, Institute of Physical Chemistry, Kasprzaka 52/56, Warszawa 01-224, Poland*

e-mail: darek@ch.pw.edu.pl

The versatility of silicone polymers, their physical and chemical attributes enable them to be used in a wide band of applications as e.g.: an interconnection between two silicon wafers, a spring material in accelerometers or as the ion selective membranes for ISFETs. Polysiloxanes can also be used in mechanical and chemical decoupling of biomedical micro devices from their environment. Since silicone precursors are viscous it is possible to form substrate or coating films by spin coating method. Polysiloxanes are not photodefinable and cannot be photolithographically treated. Among the possible ways to pattern silicon elastomers is plasma processing. Silicones can be effectively etched and/or permanently modified using fluorine-containing plasma. This treatment, however, may also cause unwanted modification in morphology and surface contamination with fluorine compounds such as C_xF_y or with a mask material e.g. aluminum. Uncontrolled surface changes may turn an initially noncytotoxic material into a cytotoxic one. The chemical composition, roughness and wettability are believed to directly influence the cell viability and adhesion. That is why the surface purity and proper morphology after processing are key factors for biomedical applications. In this work we studied the fluorine-based plasma treatments of a highly popular silicone elastomer based on poly(methylhydrogensiloxane-co-dimethylsiloxane) and their potential effects on BioMEMS devices. Plasma experiments were performed in both RIE and ICP reactors using CF_4, SF_6 and O_2 gases. The surface morphology and wettability were investigated by means of SEM and contact angle measurements, respectively. The chemical composition of post-etch remnants was analysed by XPS. In order to estimate the cytocompatibility of plasma treated elastomer the standard MTT and CV tests were used. The surface morphology was found to be very dependent on the discharge condition (RIE/ICP) and temperature treatment. The polysiloxane surface appeared to preserve or even improve its hydrophobic properties after fluorine containing plasma exposure. The contact angle values varied between 110° and 140°, depending on the treatment temperature and plasma chemistry. The most hydrophobic surface consisted of tiny, irregular pillars covered with conformal fluorocarbon film. The XPS analysis showed that the polysiloxane surface enriched with fluorine. The amount of fluorine found on the surface was three times higher after the treatment in CF_4 plasma than in SF_6 one. Despite some contamination and morphology changes the results of the preliminary cytotoxicity study appeared to be very promising: cell viability on a raw and all plasma treated polysiloxane was very high and comparable to control. Such a result is important if the plasma treated polysiloxanes are considered for use in BioMEMS application.

This work has been partly supported by the European Commission - the Healthy Aims Project IST-2002-1-001837.

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Sporopollenin as a naturally-selected molecular wire

Jay D. Wadhawan, Matthew J. Thomasson

Department of Chemistry, University of Hull, Hull HU67RX, United Kingdom

e-mail: M.J.Thomasson@chem.hull.ac.uk

The electrochemical interrogation of sporopollenin exines extracted from *Lycopodium clavatum* immobilised on graphite electrodes reveal the presence of hydroquinone-type functionalities contained within the carotenoid-like sporopollenin polymer. Electron hopping transport between individual quinol moieties over the retusoid trilete (approximated by a hemisphere) is computed to be highly rapid in acidic media, assuming the concerted proton transfer is not rate-limiting. It is suggested that the biological reason underpinning this form of natural selection is first to provide a physical and UV-shield, and second to confer the sporopollenin particles with a “diffusional protection” of the valuable genetic information contained within each retusoid against reactive oxygen species that would otherwise incur mutations within haploid DNA.

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Redox processes of dithiolated tetraazamacrocyclic complexes of Ni(II) and Cu(II) in solution and immobilized on gold electrodes

Urszula E. Wawrzyniak[1], Bohdan Korybut-Daszkiewicz[2], Sławomir Domagała[1], Krzysztof Woźniak[1], Renata Bilewicz[1]

1. *Warsaw University, Department of Chemistry, Pasteura 1, Warsaw 02-093, Poland* **2.** *Polish Academy of Science, Institute of Organic Chemistry, Kasprzaka 44/52, Warsaw 01-224, Poland*

e-mail: ulamaj@chem.uw.edu.pl

Tetraazamacrocyclic complexes of Cu(II) and Ni(II) designed as building blocks of catenanes and rotaxanes were synthesized and structurally characterized in the solid state using X-ray diffraction techniques. In our present studies, we modify these compounds with organothiol chains to attach them to the surface of the electrode using the self-assembly method. The electrochemical properties of these compounds are studied in the solution and, in the case of Ni-dithiol derivative (Fig. 1), immobilized on the electrode surface. Voltammetric studies of the new cooper complexes dissolved in acetonitrile solutions indicate that macrocyclic architectures based on 2 and 3 tetraazamacrocylic complex units bound by means of two or three (-S-S-) bonds remain stable in nonaqueous solutions and may be useful as building blocks for more complex structures in solution. For the bis and tris macrocyclic compounds studied, the exchange of 1e takes place almost independently at each of the copper centers. The electrochemistry of the Ni macrocycle complex shown below is examined and the electron transfer kinetics are evaluated. The electrochemical experiments reveal reversible one-electron redox processes of the metal center at the +2/+3 oxidation state. The Ni(II)-dithiol derivative can be anchored to the surface by one or two thiol groups. We demonstrate that the thread – like structure is predominant allowing formation of a pseudorotaxane with a p-electron rich compound dissolved in the solution.

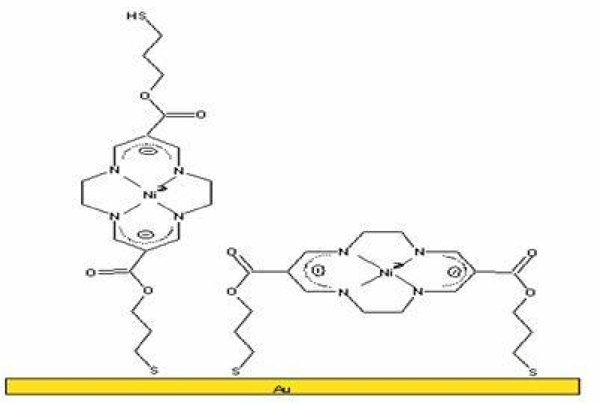

Fig 1. Macrocyclic complexes immobilized on the gold electrode surface

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Non-additivity of faradaic currents associated with the parallel reduction of some metal cations and hydrogen ion at the mercury electrode

Albin Wiśniewski, Wojciech Czerwiński, Marek Orlik

Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland

e-mail: albin@chem.uw.edu.pl

We have found that the parallel reduction of some metal ions (Cd^{2+}, Cu^{2+}, Eu^{3+}) and hydrogen ions at the dropping (DME) and the hanging (HMDE) mercury electrodes reveals interesting non-additivity effects. In the potential range of hydrogen evolution, the current is different from the sum of individual currents for the metal and hydrogen ions, recorded in separate experiments. This effect was diagnosed in double potential step chronocoulometric (DPSC) experiments as the deviations of the anodic charge of the metal from its limiting value, if the anodic oxidation was preceded by the parallel cathodic reduction of the metal and hydrogen ions. The deviations of the anodic charge mean either its anomalous decrease (for relatively small hydrogen evolution rate) or its anomalous increase (for relatively high hydrogen reduction current, at sufficiently negative potentials). In order to explain the origin of these effects we have conducted comparative experiments with the mercury film electrode, deposited on silver. It is noteworthy that for the film Hg electrode those anomalies were *not* observed. The preliminary explanation of non-additivity of the currents at the DME and HMDE assumes the role of convection induced on the surface of these electrodes. This additional convective transport changes the spatial distribution of the Cd^{2+} ions and Cd(Hg) – i.e. on both sides of the Hg|water interface. This affects the anodic current of Cd(Hg) oxidation. These effects manifest themselves differently if both Ox and Red species are on the solution side (as for Eu^{3+}/Eu^{2+}). Various numerical simulations semiquantitatively confirm the above mechanism.

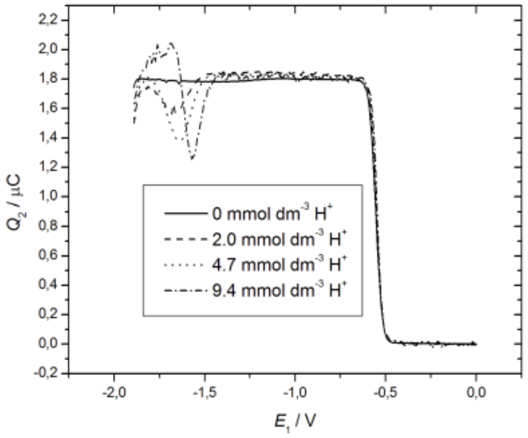

Fig. 1. The pulse chronocoulometric *Q*-*E* characteristics of Cd^{2+}/Cd(Hg) system at dropping mercury electrode, recorded as the faradaic charge of the cadmium amalgam oxidation at the constant potential (E_2 = 0.0 V vs. SCE, t_2 = 100 ms) after prior electroreduction of Cd^{2+} ions (t_1 = 100 ms) at the potential E_1 increasing linearly towards negative values. In the presence of H^+ ions, which start to reduce at -1.50 V, the anodic charge of Cd(Hg) oxidation exhibits substantial deviation from the diffusion limited value.

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Electrochemical oxidation of $[IrX_2(CO)_2]^-$ (X = Cl, Br, and I) complexes

Monika Wysocka-Żołopa, Krzysztof Winkler

University of Białystok, Institute of Chemistry, Hurtowa 1, Białystok 15-399, Poland

e-mail: monia@uwb.edu.pl

Recently, there has been renewed interest in the preparation and properties of compounds that contain one-dimensional chains of metal centers. The unusual properties of these materials make them very attractive for nanotechnology since they offer the possibility of developing electronic devices with very small dimensions. Dihalodicarbonyliridate(I) complexes show a tendency to form linear chains through metal-metal interaction in solid state. One-dimensional crystals of iridium complexes can be prepared by electrochemical oxidation of tetraphenylarsonium dihalodicarbonyliridate(I) in dichloromethane containing tetra(alkyl)ammonium salts as supporting electrolyte. The electrochemical properties of $[Ir(CO)_2X_2]^-$ (X = Cl, Br, and I) complexes have been studied using cyclic voltammetry, chronoamperometry, electrochemical quartz crystal microbalance (EQCM), and scanning electron microscopy (SEM). The cyclic voltammograms of $[IrX_2(CO)_2]^-$ (X=Cl, Br, I) oxidation is shown of Figure 1. The first oxidation step (peak O_1) of $[IrCl_2(CO)_2]^-$ and $[IrBr_2(CO)_2]^-$ is reversible, and responsible for the formation one-dimensional of the long and thin needles on the electrode surface. The needles are about 10 - 15 µm long and 0.2 - 0.4 µm thick. In the case of $[IrI_2(CO)_2]^-$, a broad and irreversible oxidation peak is observed. No reduction current was recorded during the negatively going potential sweep. Deposit formed during oxidation of this complex exhibit different morphology. This deposit exhibit three-dimensional structure.

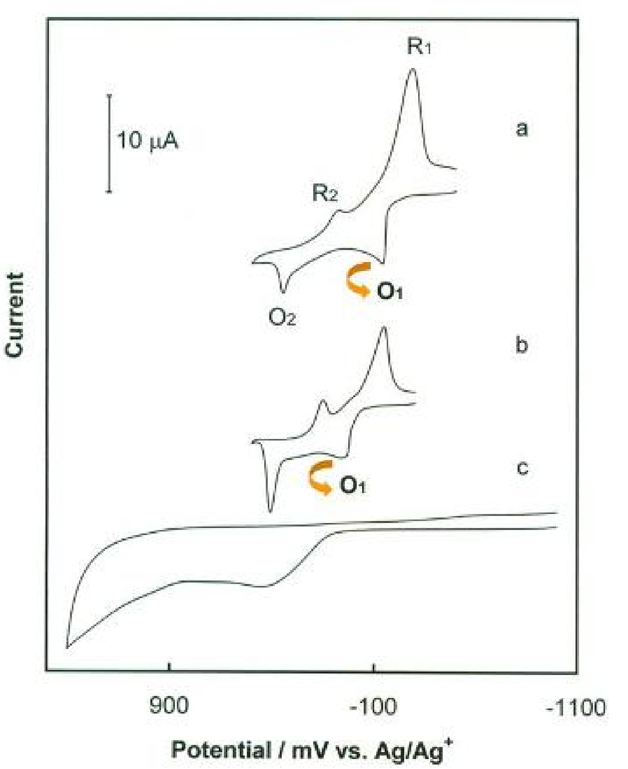

Fig. 1. Cyclic voltammograms recorded in dichloromethane containing 0.05 mol dm^{-3} tetra(ethyl)ammonium percghlorate and: (a) 1.7 mmol dm^{-3} $(Ph_4As)[Ir(CO)_2Cl_2]$, (b) 1.5 mmol dm^{-3} $(Ph_4As)[Ir(CO)2Br_2]$, (c) 1.5 mmol dm^{-3} $(Ph_4As)[Ir(CO)_2I_2]$, at a gold electrode (1.5 mm diameter). The sweep rate was 50 mV s^{-1}.

The process of $[Ir(CO)_2X_2]^-$ (X is Br or Cl) oxidation can be described by the following reaction:

$$[Ir(CO)_2X_2]^- + xTAA^+ \rightleftharpoons (TAA)x[Ir(CO)_2X_2] + (1-x)e^-$$

The stoichiometry of one-dimensional crystals depends on the electrode reactant $(TAA)_{0.6}[IrCl_2(CO)_2]$ and $(TAA)_{0.7}[IrBr_2(CO)_2]$ (TAA is tetra(alkyl)ammonium cation) salts are formed on the electrode surface. In solutions containing high concentration of iridium complexes or upon repeating potential cycling, the formation of electroactive thin film on the electrode surface is observed.

19:15 Poster 38

Prussian Blue based planar biosensor for lactate

Eugene Yashina

Chemistry Department, Moscow State University, Leninskie Gory, 1-3, Moscow 119992, Russian Federation

e-mail: yashinamsu@gmail.com

The construction of sensors is based on the approach for operation of oxidase based biosensors by low potential selective detection of H_2O2 on electrodes modified by electrochemically deposited Prussian Blue (ferric hexacyanoferrate). The approach was first demonstrated by our team in 1994 [1,2] and had been developed in order to achieve the most advantageous H_2O_2 transducer. Electrochemical biosensor for lactate has been made by immobilization of the enzyme lactate oxidase on the top of H_2O_2 transducer (planar sensor for hydrogen peroxide). Immobilization protocol included a formation of the enzyme containing Nafion polyelectrolyte membrane according to procedure developed earlier [2]. Exposure of lactate oxidase to water-organic mixtures with a high (85%) content of the organic sol-vent, resulted in stabilization of the enzyme by membrane-forming polyelectrolyte. The different approaches affecting the immobilization procedure have been studied. Combining the attractive performance of a Prussian-Blue based hydrogen peroxide transducer and optimal immobilization protocol, we have been developing low cost and mass-productive planar sensors for H_2O_2 and biosensors for glucose and lactate based on screen-printed electrodes modified with chemically deposited nano-layers of Prussian Blue. The best results were obtained for lactate oxidase immobilized in siloxans membranes. The corresponding biosensor has following analytical characteristics: improved sensitivity (about 70 mA/M cm^2) and signal-to-noise ratio, low detection limit to compare with known analogs. Lactate may be analyzed in range of 1.10^{-6}-1.10^{-3} M in FIA regime. The biosensor retained the sensitivity within 3 days (for 500 measurements) and could be used for multiuse measurements.

19:15 Poster 39

High sensitivity immunosensors based on nanoelectrode ensembles

Martina Zamuner[1], Stefano Pozzi Mucelli[2], Massimo Tormen[3], Giorgio Stanta[2], Paolo Ugo[1]

1. *Dipartimento di Chimica Fisica, Università Cà Focari di Venezia, S. Marta 2137, Venezia 30123, Italy* **2.** *Università di Trieste, Trieste, Italy* **3.** *Laboratorio TASC (TASC), Basovizza, Trieste 34012, Italy*

e-mail: martina.zamuner@unive.it

In this study we demonstrate the possibility to prepare highly sensitive nanostructured electrochemical immunosensors by immobilizing the biorecognition elements on the polycarbonate (PC) surrounding the gold nanodisks in nanoelectrode ensembles (NEEs). The nanodisk electrodes act as bare electrochemical transducers in close proximity (not in direct contact) with an antigen or antibody-based biorecognition layer. Suitable soluble redox mediators shuttle electrons to/from the biorecognition layer from/to the nanoelectrodes, so exploiting the maximum advantage from the highly improved signal-to-background current ratio, typical of NEEs. In particular, horse radish peroxidase was used as the enzyme label and methylene blue as the redox mediator. Two detection schemes were tested: scheme A, based on the direct immobilization of the target protein on the PC of the NEE, and scheme B, based on the immobilisation on PC of an antibody to capture the target protein. In both case, the biorecognition process was completed by adding a primary antibody and a secondary antibody with the enzyme label. Typical target analytes were Single Chain Fragment Variable antibodies, for scheme A, and Trastuzumab, for scheme B. NEE based tests resulted much more sensitive with respect to western blot tests.

19:15 Poster 40

Electrochemical polymerisation and electrocatalytic properties of structured selected aminophenyl derivatives of some metalloporphyrins

Ievgen Obraztsov[1], Wlodzimierz Kutner[1], Channa A. Wijesinghe[2], Francis D'Souza[2]

1. *Polish Academy of Sciences, Institute of Physical Chemistry, Kasprzaka 44/52, Warszawa 01-224, Poland* **2.** *Wichita State University, Department of Chemistry, 1845, Fairmount, Wichita, KS 67260-0051, United States*

e-mail: e-obraz@ukr.net

Electrochemical polymerisation of zinc and cobalt metalloporphyrins bearing peripheral aminophenyl substituents, vis. tetrakis-*N*,*N*-diphenylaminophenyl-porphyrinazotozinc (diphenyl ZnTPP) and tetrakis-*N*,*N*-diphenylaminophenyl-porphyrinazotocobalt (diphenyl CoTPP) as well as *N*,*N*-diphenylaminophenyl-porphyrin (diphenyl TPP) in the 1,2-dichlorobenzene solutions of different tetraalkylammonium salt supporting electrolytes, was investigated by simultaneous multi-scan cyclic voltammetry (CV) and piezoelectric microgravimetry at an electrochemical quartz crystal microbalance using 10-MHz quartz crystal resonators with gold film electrodes. The electropolymerisation was investigated by simultaneous measurement of CV current, resonance frequency changes, and dynamic resistance changes as a function of potential scanned. Integrity of the resulting polymer films was confirmed ex situ by the reflection mode UV-vis spectroscopy and X-ray photoelectron spectroscopy measurements. The dependence of peak currents of the polymer films in the blank organic solvent supporting electrolyte solutions on the anion size indicated diffusional control of the film conductivity. Electrocatalytic properties of the polymers with respect to the dioxygen electroreduction were investigated. For that purpose, metalloporphyrin monomers were structured with cyclic amine bidentate ligands, such as pyrazine or piperazine, to form sandwich-type stacked complexes and, then, electropolymerised. These ligands served as structuring templates. Subsequently, the templates were extracted from the polymer with an acidic water solution. Then, electrocatalytic properties of the metalloporphyrin polymers in aerated aqueous solutions were examined by CV.

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Preparation and selected properties of composites of the C_{60}-Pd conducting polymer and soluble single-wall carbon nanotubes

Piotr Pieta[1], Emilia Grodzka[2], Krzysztof Winkler[2], Francis D'Souza[3], Wlodzimierz Kutner[1]

1. *Polish Academy of Sciences, Institute of Physical Chemistry, Kasprzaka 44/52, Warszawa 01-224, Poland* **2.** *University of Białystok, Institute of Chemistry, Hurtowa 1, Białystok 15-399, Poland* **3.** *Wichita State University, Department of Chemistry, 1845, Fairmount, Wichita, KS 67260-0051, United States*

e-mail: ppieta@ichf.edu.pl

A composite thin film of the novel electroactive fullerene-palladium (C_{60}-Pd) polymer and single-wall carbon nanotubes, which were non-covalently modified by 1-pyrenebutiric acid (pyr-SWCNTs), was electrochemically prepared under multi-scan cyclic voltammetry (CV) conditions and its conductive, capacitance and visco-elasitic properties investigated. The film was prepared by using a mixed C_{60}, pyr-SWCNTs, and palladium acetate solution of either mixed acetonitrile : toluene (1 : 4, *v* : *v*) or 1,2-dichlorobenzene solvent. A tetrabutylammonium salt, like 0.1 M (TBA)ClO_4 or (TBA)PF_6, was used as a supporting electrolyte. Mass changes of the deposited composite film were measured in situ by piezoelectric microgravimetry with the use of an electrochemical quartz crystal microbalance. The quartz crystal resonators with their electrodes coated by either the C_{60}-Pd or C_{60}-Pd/pyr-SWCNTs composite film were transferred to a blank supporting electrolyte solution, i.e., 0.1 M (TBA)ClO_4 or (TBA)PF_6 in acetonitrile, and current, resonance frequency changes, and dynamic resistance changes vs. scanned potential were simultaneously recorded in different potential ranges. Each polymer revealed electrochemical activity at potentials more negative than ca. -0.7 V. Both cathodic and anodic currents for the C_{60}-Pd/pyr-SWCNTs films were almost twice as high as those for the C_{60}-Pd films. The presence of pyr-SWCNTs in the polymer causes an increase of the electrode capacitance, as manifested by increased CV current. For the potential range 0 to -1.2 V changes of both resonance frequency and dynamic resistance are almost the same for the C_{60}-Pd and C_{60}-Pd/pyr-SWCNTs films. Distinct differences are seen, however, for potentials exceeding -1.2 V. That is, frequency rapidly decreases when the potential reaches the -1.2 V value in the negative excursion. However, this decrease is three times smaller for the C_{60}-Pd/pyr-SWCNTs film than that for the C_{60}-Pd film. This decrease of frequency is accompanied by the increase of dynamic resistance. Changes of dynamic resistance for the C_{60}-Pd film are three times larger than those for the C_{60}-Pd/pyr-SWCNTs film. This behavior suggests that for potentials more negative than -1.2 V the C_{60}-Pd/pyr-SWCNTs film is more rigid than the C_{60}-Pd film. Moreover, redox conductivity of the C_{60}-Pd films doped with pyr-SWCNTs is higher than that of the undoped C_{60}-Pd films. The redox conductivity values, determined from the highest slopes of the rising portions of cathodic CV curves in the range ca. -0.6 to -0.8 V, are 0.92 and 1.48 mS for the film of the C_{60}-Pd and the C_{60}-Pd/pyr-SWCNTs composite, respectively. In the Raman spectrum for the C_{60}-Pd/pyr-SWCNTs film there are peaks characteristic both for pyr-SWCNTs (radial breathing modes, RBM) and C_{60}-Pd indicating that, indeed, pyr-SWCNTs are incorporated into the film during electropolymerization of C_{60}-Pd. Moreover, the RBM peaks for the pyr-SWCNTs film are deconvoluted in the spectrum of the composite due to different extent of aggregation of pyr-SWCNTs.

19:15 Poster 42

Development of a histamine acoustic sensor using film of molecularly imprinted polymer prepared by electrochemical co-polymerisation of bis(bithiophene) derivatives

Agnieszka Pietrzyk[1], Wlodzimierz Kutner[1], Raghu Chitta[2], Francis D'Souza[2]

1. *Polish Academy of Sciences, Institute of Physical Chemistry, Kasprzaka 44/52, Warszawa 01-224, Poland* **2.** *Wichita State University, Department of Chemistry, 1845, Fairmount, Wichita, KS 67260-0051, United States*

e-mail: agapi@ichf.edu.pl

Preliminary results will be presented on application of a selective molecularly imprinted polymer (MIP) film for development of an acoustic histamine sensor. This MIP film and a 10-MHz quartz crystal resonator with Pt film electrodes of an electrochemical quartz crystal microbalance (EQCM) consists the recognition and transduction element of the sensor, respectively. Histamine was imprinted by electrochemical co-polymerisation of self-assembled complexes of this analyte, initially used as a template, and two bis(bithiophene) derivatives each bearing different reception site. The crown ether and dioxaborolane substituents of the bis(bithiophene) polymer subunits served as the respective reception sites. Accordingly, the bis(2,2'-bithienyl)-benzo-[18-crown-6] methane and bis(2,2'-bi-thienyl)-4,4,5,5-tetramethyl-2-phenyl-[1,3,2]dioxaborolane methane monomers were used for electropolymerization in a 0.1 M $(TBA)ClO_4$ solution of 1,2-dichlorobenzene or acetonitrile. Since the histamine molecule contains both a primary aliphatic amine site and an imidazole heteroaromatic ring, in our systematic studies, firstly, two different model analyte compounds were used to probe the histamine imprinting. That is, a phenethylamine model analyte served to test complexation of the protonated aliphatic amine group, $–NH_3^+$, and an imidazole probe to test reception of the nitrogen atom of its ring. In the pH range between pK_{a1} and pK_{a2} of histamine, its amine group is protonated and, therefore, can be complexed by the crown ether moiety. Moreover, the nitrogen atom of the imidazole ring can coordinate at this pH range to the boron atom of the borolane group. The most convenient way to release the histamine template from the polymer was to increase solution basicity to pH=12. Under these solution conditions, the boron atom changes its hybridization from sp^2 to sp^3 and the aliphatic amine group is deprotonated and, therefore, both the phenethylamine and imidazole probe is released. Binding of the imidazole, phenethylamine and histamine template in MIPs was characterized in situ under flow injection analysis (FIA) conditions by the simultaneous piezoelectric microgravimetry and chronoamperometry measurements at EQCM, as well as ex situ by the reflectance mode UV-vis and X-ray photoelectron spectroscopy measurements. Under FIA conditions, EQCM piezoelectric microgravimetry responses [1] of the resonant frequency and dynamic resistance changes after injection of the analyte solution samples were by over an order of magnitude larger for the derivatised bis(bithiophene) polymer films than those for the non-derivatised polymer films, used for comparison, indicating a pronounced analyte preconcentration in case of the former. The frequency change response to the imidazole and phenethylamine probe was linear over at least an order of the concentration magnitude in the range 10 mM to 1.0 M and 25 to 800 mM, respectively. Expectedly, the analyte preconcentration level in film was proportional to the film thicknesses.

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Tuesday, 6 November

Breakfast

Tuesday morning, 6 November, 8:00

Trip

Tuesday morning, 6 November, 9:00

Lunch

Tuesday afternoon, 6 November, 13:00

Session 5

Tuesday afternoon, 6 November, 14:30

14:30 Tutorial lecture

Anode and cathode reactions for biofuel cells based on direct electron transfer reactions between biological components and electrodes

Lo Gorton

Lund University, Department of Analytical Chemistry, Lund SE-221 00, Sweden

e-mail: Lo.Gorton@analykem.lu.se

This presentation will give an overview and discuss a series of anode and cathode reactions based on direct electron transfer between the biological component (enzyme/organelle/whole cell) and various electrodes for possible applications in biofuel cells. Cathode reactions will include those based on direct electron transfer between enzymes able to reduce oxygen directly to water such as the high potential blue multicopper oxidases (laccase and bilirubin oxidase) and electrodes [1]. Anode reactions will cover those based on direct electron transfer between both isolated redox enzymes (e.g., diaphorase, alcohol PQQ dehydrogenase, cellobiose dehydrogenase, hydrogenase [2,3]) and electrodes as well as direct electron transfer between bacteria and electrodes [4,5].

1. S. Shleev, J. Tkac, A. Christenson, T. Ruzgas, A. I. Yaropolov, J. Whittaker, L. Gorton, Biosens. Bioelectron., 20 (2005) 2517-2554.
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3. U. Wollenberger, in Biosensors and Modern Biospecific Analytical Techniques (Ed. L. Gorton), Elsevier, Amsterdam, 2005, pp. 65-130.

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15:10 Keynote lecture

Mediated enzyme reactions: coupling biological electron transfer to electrodes with redox complexes

Donal Leech

National University of Ireland, Galway, Department of Chemistry, University Road, Galway Galway, Ireland

e-mail: Donal.leech@nuigalway.ie

Mediated enzyme reactions form the basis of many applications, ranging from biosensors, through biocatalytic fuel cells, to applications in industrial electrolysis. This presentation will review some of our efforts to date on redox mediation of enzyme reactions for such applications. Our initial research in this area focused on mediated reactions of laccases, a class of copper-based oxidase enzymes that catalyze the four-electron reduction of oxygen to water. Immobilization of the enzyme in a redox mediating hydrogel yields reagentless biosensors, as monitoring of mediated reduction currents for oxygen, present in solution, permits detection of any modulator of enzyme activity. Furthermore, co-immobilization of a redox mediator and an affinity recognition element, such as DNA or antibody, provides a generic platform for the amplified detection of complementary affinity partners (DNA or antigen) that are labelled with redox enzymes. Our studies on laccase biosensors demonstrated, also, that laccases co-immobilized in redox hydrogels can reduce oxygen at relatively high potentials and current densities, suggesting possible applications as cathodes in implantable biofuel cells when combined to oxidation of a fuel, such as glucose, at the anode.

Covalent coupling of enzymes and mediators on the electrode surface can appreciably improve the fuel cell stability. Also, improvements in the design of the redox complexes and polymers (in terms of structure and redox potential) help to increase biosensor and biofuel cell performance. Our approach to improving the stability and the performance of thse devices through tailored surface modification will be presented.

15:30 Short communication

Modification of electrode surfaces with redox complexes for biosensor and biofuel cell applications

Kevin Foster, Susan Boland, Paul Kavanagh, Peter Jenkins, Donal Leech

National University of Ireland, Galway, Department of Chemistry, University Road, Galway Galway, Ireland

e-mail: kevin.foster@nuigalway.ie

Part of our research effort aims to design novel, enzyme-based, high surface area materials capable of efficiently transferring electrons between chemicals and electrodes for application as biosensors and biofuel cells. These bioelectrochemical reactions are enabled by designing novel, efficient, mediated electron transfer processes between selected enzymes and electrode materials. To advance our understanding of integrating immobilisation and function (electron transfer efficiency) we have commenced synthesis of a library of osmium/ruthenium-based redox mediator complexes possessing a range of redox potentials, with each complex in the library amenable to simple immobilisation chemistry. This immobilisation can be achieved either through ligand substitution with a suitable polymer support or through covalent coupling of designed functional groups of the complex to supports. In addition to designing immobilisation for the mediators, we have also commenced research on anchoring redox systems, and enzymes, onto electrode supports, using gold-thiol adsorption and reductive coupling of diazonium salts to carbon to provide functionalised electrode surfaces. This anchoring chemistry can improve the stability of the enzyme/mediator layer and offer improved mediated bioelectrochemical systems for application as biosensors and biofuel cells.

15:45 Short communication

Nanostructured Carbon Electrodes For Oxygen Reduction Catalyzed By Laccase Without any Mediators

Krzysztof Stolarczyk[1], Ewa Nazaruk[1], Krzysztof Biesiada[3], A. Olszyna[3], Jerzy Rogalski[2], Renata Bilewicz[1]

1. *Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland* **2.** *Maria Curie Sklodowska University, Department of Biochemistry, Pl. Sklodowskiej 3, Lublin 20-031, Poland* **3.** *Warsaw University of Technology, Faculty of Materials Science and Engineering (InMat), Wołoska 141, Warszawa 02-507, Poland*

e-mail: kstolar@chem.uw.edu.pl

Laccase is one of the enzymes for which direct electron transfer on macroscopic electrode surface has been demonstrated. However, most approaches to electron conduction from electrode to the enzyme involve mediators, molecular relays which can take electrons from the electrode and deliver them to the redox site of the enzyme. We show the catalytic reduction of oxygen on different carbon materials: boron-doped diamond (BDD), glassy carbon (GC), GC decorated with nanotubes or carbon microparticles in the presence of laccase either remaining in the solution or adsorbed on the electrode. Three different matrices: lecithin, hydrophobin and lipid liquid crystalline cubic phases were used for the immobilization of laccase on the electrode. Significant decrease of overpotential and increase of biocatalytic reduction current is observed without the need of employing additional mediators. These properties of the system studied are very interesting from the viewpoint of applications in electrochemical sensors and microbiofuel cells.

Coffee break

Tuesday afternoon, 6 November, 16:00

Session 6

Tuesday afternoon, 6 November, 16:25

16:25 Tutorial lecture

Biochips and Acoustic Biosensor Arrays Based on Molecularly Imprinted Polymers

Karsten Haupt[1], Fanny Vandevelde[1], Cedric Ayela[2], Liviu Nicu[2]

1. *Compiegne University of Technology, UMR CNRS 6022, Compiegne, France* **2.** *LAAS-CNRS, Toulouse 31077, France*

e-mail: karsten.haupt@utc.fr

The design and synthesis of biomimetic materials that are capable of binding target molecules with high specificity has been a longstanding goal in the analytical chemistry, biomedical and materials science fields. One of the most promising approaches towards producing such materials is molecular imprinting of synthetic polymers. This technique involves using a molecular template, which directs the self-assembly of functional monomers that are subsequently copolymerized in the presence of an excess of cross-linking monomers. The resulting molecularly imprinted polymers (MIPs) possess binding properties that often rival those of antibodies and enzymes, but with far greater stability than their natural counterparts. These properties make MIPs potentially very suitable as recognition elements for chemical sensors, biosensors or biochips [1]. Recent advances in the field will be described, with special emphasis on biochips and biosensors. Biomimetic microchips were produced by depositing MIP microdot arrays on surfaces. MIP precursors with fluorescein as the template were deposited with a microcantilever array. A sacrificial polymeric porogen, poly(vinylacetate), was used to obtain porous dots. Fluorescence microscopy revealed specific binding of fluorescein to the MIP dots. With another MIP selective for the herbicide 2,4-D, competitive binding assays were performed using a coumarin derivative as fluorescent probe [2]. Integrated MIP-based acoustic sensors were developed based on matrices of piezoelectric membranes. Each membrane can be individually actuated by a piezoelectric thin film with two platinum electrodes, allowing for simultaneous actuation and detection of the resonant frequency of the membranes. A MIP precursor solution containing the template 2,4-D and non-imprinted control polymer precursor solution were deposited on the membranes by microspotting. The dots were polymerized under UV light. Polymerization was monitored by following the membrane's resonant frequency in real time. Following polymerization, dip-and-dry experiments were performed in order to validate the MIP's functionality. Elution of the template resulted in an increase of the resonant frequency. This demonstrats the extraction of the template 2,4-D from the dots. After incubation in a 2,4-D solution, frequencies close to the initial values were measured showing that the MIP's binding sites are progressively reoccupied by 2,4-D, a reversible process that could be repeated numerous times. For certain sensor designs, the combination of molecular imprints with nanostructured materials is of particular interest. The creation of polymer surfaces nanostructured at two levels by simultaneous nanomoulding and molecular imprinting is described. Polymer nanomoulding resulted in polymer surfaces carrying nanofilaments or other nanostructures with surface molecular imprints. The number and size of the nanostructures could be fine-tuned by adjusting the morphology of the initial template surface. The molecular imprinting effect was demonstrated using fluorescent ligand or radioligand binding. The usefulness of these molecularly imprinted surfaces as recognition layers in optical sensors was evaluated. The surfaces were also characterised with respect to additional features such as, wetting properties, by contact angle measurements and direct observation of the formation of water microdroplets using environmental scanning electron microscopy. It was found that nanostructuration rendered more hydrophobic a hydrophobic polymer, and more hydrophilic a hydrophilic one [3].

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[3] Fanny Vandevelde, Anne-Sophie Belmont, Jacques Pantigny, Karsten Haupt (2007) Hierarchically nanostructured polymer films based on molecularly imprinted surface-bound nanofilaments. Advanced Materials (in press)

17:05 Keynote lecture

Laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) aided insight into ion-sensing membranes

Agata J. Michalska, Marcin Wojciechowski, Ewa Bulska, Krzysztof Maksymiuk

Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland

e-mail: agatam@chem.uw.edu.pl

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was used to study ions depth profiles across ion–selective membranes. Advantageously, this approach does not require incorporation of additional components (e.g. chromoionophore) in the membrane composition, compared to that used in typical potentiometric applications. Moreover, comparison of ions distribution in differently pretreated membranes is possible. Concentration profiles of primary and interferent (Na^+) ions were recorded, on example of Pb^{2+}-selective poly(vinyl chloride) based membrane. It was found that the contents and the distribution of Pb^{2+} and Na^+ ions across the membrane is strongly dependent on composition of the solutions to which both sides of the membrane were exposed during preconditioning and on the plasticizer included in the membrane formulation. On the basis of concentration profiles, primary ion diffusion coefficients in both membranes were calculated, and the value obtained for o-NPOE containing membrane was found to be about 2 times higher than for DOS plasticized counterpart. Using LA-ICP-MS, ion concentration profiles and their evolution in galvanostatically polarised solvent polymeric poly(vinyl chloride) can visualized. Thus different effects depending on the lipophilic salt cation in the membrane and pre-conditioning solution applied can be followed.

17:25 Short communication

Aligned carbon nanotube thin films for genosensor development

Francesca Berti[1], Giovanna Marrazza[1], Ilaria Palchetti[1], Marco Mascini[1], Luca Lozzi[2], Sandro Santucci[2], Guido Faglia[3], Giorgio Sberveglieri[3]

1. *Dipartimento di Chimica, Università di Firenze (UNIFI), Via della Lastruccia 3, Sesto Fiorentino (Firenze) 50019, Italy* **2.** *Department of Physics, University of L'Aquila (Unita INFM), Coppito, L'Aquila 67020, Italy* **3.** *INFM & UNIVERSITY OF BRESCIA (INFM), VIA VALOTTI 9, Brescia 25133, Italy*

e-mail: francesca.berti@unifi.it

In the last decade, the synthesis of various nanomaterials such as nanowires, nanotubes and nanocrystals has attracted immense attention due to their potential to serve as building blocks for the development of nanoscale biosensor devices. In this work carbon nanotube (CNTs) thin films were designed and tested as working electrode for DNA immobilisation and for the development of an electrochemical genosensor. Carbon nanotubes are promising materials for DNA electrochemical sensing due to their unique electric properties: high surface area, fast heterogeneous electron transfer, electrochemical stability. Self-assembled aligned CNT thin films were prepared by Chemical Vapor Deposition (CVD) onto silicon oxide substrate, using acetylene and ammonia as precursor gases and nickel particles as catalyst. The electrochemical characteristics of these surfaces were obtained studying the electron transfer rates of potassium ferricyanide redox couple under different experimental conditions in Cyclic Voltammetry (CV) experiments. Scanning Electrochemical Microscopy (SECM) has been employed in the feedback mode to increase the information regarding the electrochemical behaviour of the carbon nanostructured materials. The surface was then functionalised with oligonucleotide DNA-probe by covalent immobilisation. The immobilised oligonucleotides are complementary to the sequence of the most common inserts in the GMOs: the Promoter 35S. The biosensor format involves the immobilisation of a probe onto the carbon nanotubes sensor surface, the hybridisation reaction and the square wave voltammetric detection of the duplex formation. Careful attention to the probe immobilisation conditions is crucial for minimizing the signal due to non-specifically adsorbed sequences. Other relevant experimental parameters such as ionic strength, hybridisation time, the use of hybridisation accelerators were examined and optimised.

17:40 Short communication

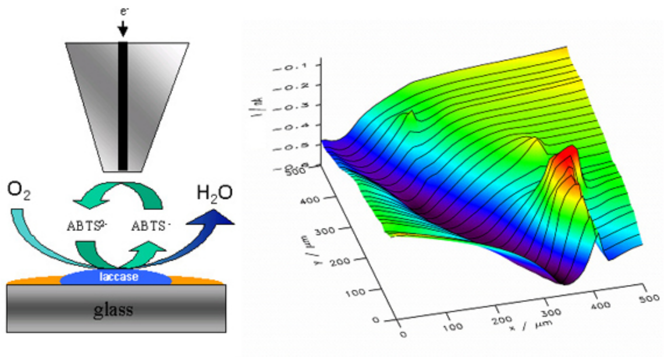
Scanning electrochemical microscopy study of laccase embedded in sol-gel processed silicate film

Wojciech Nogala[1], Malte Burchardt[2], Marcin Opallo[1], Jerzy Rogalski[3], Gunther Wittstock[2]

1. *Polish Academy of Sciences, Institute of Physical Chemistry, Kasprzaka 44/52, Warszawa 01-224, Poland* **2.** *Carl von Ossietzky University Oldenburg, School of Mathematics and Natural Sciences, n/a, Oldenburg D-26111, Germany* **3.** *Maria Curie Sklodowska University, Department of Biochemistry, Pl. Sklodowskiej 3, Lublin 20-031, Poland*

e-mail: nogala@ichf.edu.pl

The safe immobilisation of intact biomolecules plays a crucial role in the construction of enzyme electrodes. Among others the approach based on sol-gel technology seems to be promising. The protein encapsulation into a sol-gel silicate matrix enables to preserve its activity and preventing its leaching to the surrounding solution [1]. The capability to reduce dioxygen directly to water without reactive intermediates formation is one of the most important properties of laccase [2]. In recent years the successful application of electrodes modified by laccase for electrocatalytic reduction of dioxygen was reported. This system can be potentially applied in biofuel cells. Sol-gel process was successfully employed for immobilisation of laccase on the electrode surface. The efficient electron exchange between electrode and encapsulated laccase is achieved. This is because the porous hydrophilic silicate film allows fast redox mediator diffusion between immobilised enzyme and electrode. Among other factors the distribution of laccase immobilised in silicate film affects the efficiency of electrochemical devices employing this enzyme as catalyst. Therefore there is a current interest to estimate this parameter. Here we propose to employ for this purpose scanning electrochemical microscopy (SECM) [3]. This method allows to monitor distribution and activity of enzyme immobilised on flat surface [3]. In this work we present results of the investigation of laccase distribution within sol-gel processed silicate film by SECM. As film support glass plate was used, because of its flat surface, strong affinity to silicate film and lack of electric conductivity. The last property allows to eliminate positive feedback in SECM generation-collection mode experiment. This method was used in combination with confocal laser scanning microscopy. The ability of the enzyme to reduce dioxygen and to generate the oxidised form of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) ($ABTS^{2-}$) was employed for imaging the studied film. The produced anion radical was detected on ultramicroelectrode positioned above laccase encapsulated in the film.



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17:55 Short communication

Polymer film-coated high electron mobility transistors, based on GaN heterostructures, as sensors for benzene derivatives

Krzysztof R. Noworyta[1], Paweł Prystawko[2], Mike Leszczynski[2], Tadeusz Suski[2], Wlodzimierz Kutner[1]

1. *Polish Academy of Sciences, Institute of Physical Chemistry, Kasprzaka 52/56, Warszawa 01-224, Poland* **2.** *Polish Academy of Sciences, Institute of High Pressure Physics (UNIPRESS), Sokolowska 29/37, Warszawa 01-142, Poland*

e-mail: know@ichf.edu.pl

Chemically sensitive field-effect transistors (ChemFETs) have been extensively investigated and widely applied as sensors for various chemical and biological analytes [1] since their invention by Bregveld in 1970 [2]. Main advantages of ChemFETs over conventional ion-selective electrodes (ISE) consist in small dimensions, fast response and possibility of integration in the sensor array or microfluidic and/or electronic systems (a lab-on-chip concept). Moreover, ChemFETs are relatively easy for mass production. Typically, SiO_2/Si heterostructures are used for constructing ChemFET sensors, although organic ChemFETs are extensively investigated as well [1c]. Recently, there is a growing interest in ChemFETs based on wide-bandgap semiconductors, such as diamond, SiC and GaN. The GaN-based ChemFET sensors combine advantages of superior electrical parameters with high thermal and chemical stability. Because a GaN crystal features similar surface chemistry properties as those of metal oxides, its surface can readily be modified resulting in formation of films selectively recognizing analytes of interest. Moreover, the GaN-based ChemFET is transparent to visible light. Therefore, processes occurring on the transistor surface can simultaneously be monitored spectroscopically. Pristine and chemically modified FETs as well as high electron mobility transistors (HEMTs) based on the GaN or the AlGaN heterostructures have already been applied as sensors for determination of pH [3], anions [4] and proteins [5], as well as various gases and vapours [6]. Herein, an overview of operating principles, fabrication procedures and applications of ChemFETs for sensing purposes will be given. Development of cyclodextrin polymer coated high electron mobility transistor, based on AlGaN/GaN/sapphire heterostructure, will be presented and application of the polymer coated heterostructures for detection of benzene derivatives will be discussed. It will be shown that a-cyclodextrin polymer film modified HEMT structure can selectively detect *p*-nitrophenol, especially in its anionic (*p*-nitrophenolate) form. Moreover, attempts to develop a sensor, based on heterostructures coated by molecularly imprinted polymers of functionalised cyclodextrins, for sensing of compounds of biological importance will be described.

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Dinner

Tuesday evening, 6 November, 19:00

Wednesday, 7 November

Breakfast

Wednesday morning, 7 November, 8:00

Session 7

Wednesday morning, 7 November, 9:00

9:00 Tutorial lecture

Chemical and physical functionalization targeting at the application carbon-based materials as chemical sensors

Jerzy P. Lukaszewicz

Nicolaus Copernicus University, Faculty of Chemistry (WChUMk), Gagarina 7, Toruń 87-100, Poland

e-mail: lukaszju@chem.uni.torun.pl

Chemical sensors have become one of the most important branches of contemporary science and technology. Recently there is growing interest in the application of fullerenes and carbon nanotubes in chemical sensors. However, the terms “carbon”, “carbon-based” or “carbon-type” is not limited to fullerenes and nanotubes but also applicable to graphite, carbon black, glassy carbon, or active carbon.

The aim of this paper is to review the basic types of carbon-based materials, selected methods of "carbon" preparation, and the most recent announcements on application of carbon-based materials to chemical sensing. We intend to show how the chemical properties of the carbon surface can be controlled, and how the properties influence possible application of "carbons" to the construction of chemical sensors. The paper describes:

- types of carbon-based materials and the methods of their preparation,
- chemical functionalization of carbon surfaces including CNTs,
- porosity of various carbons as a kind physical functionalization,
- basic electric properties of carbons.

All above mentioned preparative procedures are considered in light of the application of different carbon-based materials to chemical sensors. Special attention is paid to the application of carbon nanotubes to chemical sensing of gases and vapors of relatively strong acceptor and donor properties. The interaction with more (chemically) inert molecules with CNTs is presented, too. Carbon-based sensors of several types are considered: chemoresitors, mass sensitive devices and electrodes. The considered chemical functionalization of carbon-based sensing materials includes: formation of surface oxygen and nitrogen containing functional groups, water solubilization, polymer grafting, inorganic oxide "wrapping", implantation of cations, metallization, fabrication of composite materials incorporating different carbon–based materials and binders, bio-functionalization (DNA-modification, enzyme-modification, protein-modification). Beside CNTs (multi-walled and single-walled), sensing properties of polycrystalline semiconductor carbon films is considered in detail.

9:40 Keynote lecture

Synthesis, size-sorting and surface modification of magnetic nanoparticles

Paweł G. Krysiński, P. Majewski

Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland

e-mail: pakrys@chem.uw.edu.pl

The magnetic ferrite nanoparticles are recently in focus of modern science and biotechnology due to their unique properties, giving them a variety of possible applications, including targeted drug delivery. Colloidal ferrites are usually synthesized in a relatively simple aqueous precipitation reaction, which can be easily adapted for big-scale preparations. However, the main disadvantage of this route is the high polydispersity of the product, unsatisfactory for further practical applications. Here, we propose an efficient way of sorting the particles by size. The colloidal suspension of nanoparticles is centrifuged at increasing rotational speed and the fraction sedimented on the bottom of the tube is collected after each run. The particles' size distribution and the efficiency of the process is estimated by agarose gel electrophoresis. Quantitatively, the mean size in each fraction is measured by Small Angle X-Ray Scattering and Powder X-Ray Diffraction.

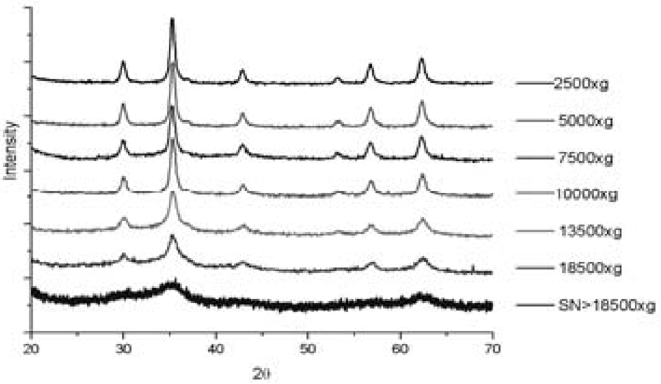

*Fig.1. **Top:** Powder XRD patterns of samples collected at increasing centrifugal forces. Widening of the peaks is observed. Crystallite size calculated from PXRD peak broadening for the unsorted sample: 14 +/- .5 nm.*

Sorted particles are further subjected to chemical modifications of their surface including, in the first step, the adsorption of simple surfactant molecules and/or growth of the colloidal silica layer. Two-dimensional arrays, (on aqueous subphase, Langmuir-type) of particles grafted with oleic acid are transferred onto the solid substrate by Langmuir-Blodgett technique. Subsequently, they were characterized by neutron and X-ray reflectivity as well as IR spectroscopy. The second step includes the covalent attachment of drug molecules (e.g., anthraquinone derivatives) to the particle surface coated with silica. Magnetic properties allow for targeted medicine delivery while silica coating prevents the heavy-metal containing core from direct contact with the organism thus providing higher biocompatibility of these carriers.

10:00 Keynote lecture

All-solid-state ion-selective electrodes with conducting polymer transducer under conditions of galvanostatic polarization

Krzysztof Maksymiuk, Agata J. Michalska

Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland

e-mail: kmaks@chem.uw.edu.pl

All-solid-state potentiometric sensors with a conducting polymer based ion-to-electron transducer have become a promising alternative to well known internal solution ion-selective electrodes (ISEs) with solvent polymeric poly(vinyl chloride) (PVC) based membranes. Recently, considerable progress has been achieved in selectivity enhancement and lowering the detection limit of above mentioned solid-state sensors. Improvement of analytical parameters of ISEs can be also obtained by galvanostatic polarization with small applied currents (usually in the range of nA). Such currents affect ion fluxes, under favourable conditions reducing or eliminating primary ions release from the ion-selective membrane. This method is also a useful tool for studies on fundamental electrochemical properties of ion-selective electrodes, important for their analytical characteristic. This lecture shows limitations and possibilities of potentiometry with ion-selective electrodes under conditions of galvanostatic polarization. Criteria for improved linear response range, related to membrane and transducer composition as well as to magnitude and direction of applied current are discussed. Advantages of chronopotentiometric method to study ion fluxes related to the membrane composition and chemical reactivity of the polymeric transducer are presented. Some diagnostic criteria are proposed, relating the observed potential vs. time dependences with properties of the sensor and transport phenomena in the membrane and sample solution.

10:20 Short communication

Determination of optimum imaging contrast in AC - SECM

Monika Maciejewska[1], Kathrin Eckhard[2], Wolfgang Schuhmann[2]

1. *Wrocław University of Technology, Wybrzeże Wyspiańskiego, Wrocław 50-370, Poland* **2.** *Ruhr-Universität Bochum, Anal. Chem. - Elektroanalytik & Sensorik (ELAN), Universitätsstr. 150, Bochum 44780, Germany*

e-mail: monika.maciejewska@pwr.wroc.pl

It was observed that in alternating current scanning electrochemical microscopy (AC-SECM) the lateral contrast strongly depends on the frequency of the applied AC voltage [1]. Conditions of optimum imaging can be found by generating images for a set of frequencies and choosing the best image. It would be however more elegant to anticipate optimum measurement conditions prior to scanning. The analytical signal in AC-SECM can either be the current magnitude and the phase shift or the real and imaginary part of AC-current. They can be readily transformed into the corresponding impedance values. Each of these parameters reflects the local surface properties and can therefore be used for imaging. As in any kind of scanning probe microscopy the signal is dependent on the tip-to-sample distance. This relationship is represented by an approach curve, which is characteristic for the electrochemical activity of the surface. For this reason a comparison of approach curves to electrochemically different surfaces has to contain information on the optimum imaging contrast. This contrast is a function of the applied perturbation frequency. In this contribution a method is proposed to determine the frequency of interest based on the analysis of approach curves obtained for different frequencies. The optimum frequency may be different for each kind of analytical signal. Calculations allow to obtain a measure of lateral contrast for each analytical signal. Therefore optimum imaging conditions can be predicted prior to the measurement.

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Coffee break

Wednesday morning, 7 November, 10:35

Session 8

Wednesday morning, 7 November, 11:10

11:10 Tutorial lecture

Understanding and Controlling Curvature and Intermolecular Interactions in Biomimetic Membranes

Monique M. Lapinski[1], Angelines Castro-Forero[3], Aaron Greiner[3], Robert Y. Ofoli[3], Paweł G. Krysiński[2], Gary J. Blanchard[1]

1. *Michigan State University, Department of Chemistry (MSU), East Lansing, MI 48824, United States* **2.** *Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland* **3.** *Michigan State University, Department of Chemical Engineering and Materials Science (MSU-CHEMS), East Lansing, MI 48824, United States*

e-mail: blanchard@chemistry.msu.edu

Our research group is interested in creating sensing devices that utilize biomolecules such as enzymes and trans-membrane proteins as the chemically selective agents. In order to locate such molecules in close proximity to a transducing element (e.g. electrode surface, optical window), the interface in which they reside must function as a biomimetic membrane. We discuss in this talk our recent work in creating lipid bilayer systems that may function as biomimetic interfaces. We are interested in both the physical morphology of the bilayers and their fluidity because it is these factors that will determine to a significant extent their utility for our intended application. We consider three aspects of lipid bilayer morphology and dynamics. There are a number of ways to form a lipid bilayer, and among the most widely used methods is the formation of vesicles and their subsequent fusion to a planar substrate. The composition of the vesicles will determine the properties of any resulting planar bilayer, and it is critical to understand whether or not the means by which the vesicles are formed has any bearing on the molecular-scale properties and/or composition of the lipid bilayer. We have studied the translational and rotational motion of chromophores imbedded in bilayers, where the bilayers were formed either by sonication or by extrusion. Our data point to the similarity of the molecular scale environments of the two types of liposomes despite their different morphology. We have also investigated the dynamics of bilayer components, present either in the head group region, or in the acyl chain region. We find that for polar species present in the headgroup region that there can be significant aggregation, a process that leads to molecular-scale heterogeneity in bilayer structures. This finding may have implications on phase segregation phenomena in multi-component lipid bilayer systems. For chromophores imbedded in the nonpolar acyl chain region, our data point to the curvature of the bilayer mediating the local environment of the chromophore, with a sharp break in the organization of the bilayer acyl chain region for vesicles of ca. 1 μm diameter. These results point to the importance of curvature in mediating bilayer dynamics and thus their ability to accommodate different species.

11:50 Keynote lecture

Micro-electrochemistry for enzyme and cellular transport studies

Miklos Gratzl

CWRU, BME Dept. (CASE), Cleveland 44106, United States

e-mail: mxg13@case.edu

Micro-electrochemistry for enzyme and cellular transport studies

Miklós Gratzl

Department of Biomedical Engineering

&

Department of Physiology and Biophysics

CaseWestern Reserve University

Cleveland, OH 44106, USA

Biomedical measurements based on principles of micro-electrochemistry are increasingly used in research as well as in clinical settings. In this talk emerging applications in three areas will be discussed. Activities of certain enzymes can be used as markers for different clinical conditions. Such information is also required in basic research involving small laboratory animals. In both application areas it is desirable, and often necessary to use small quantities of specimen. This problem is addressed here using principles of electrochemistry to realize reagentless pH-stating in microliter volumes of biological samples. Current injection via a Pt mini-electrode generates H^+ or OH^- ions at a rate that is sufficient to maintain pH in the sample during the studied bio-catalytic reaction that may consume or generate OH^- or H^+. In this arrangement enzyme activity directly equals the amount of current required for pH-stating. Results obtained with a total electrochemical pH-stat for 20 microliter biomedical specimens will be discussed. Epithelial cells cover internal organs in tight monolayers that ensure directional mass transport in or out of the organ. Healthy epithelia are crucial to maintain proper organ function. Malfunctioning epithelia cause many diseases including many cancers and genetic disorders. Despite of their importance relatively little direct information is available on ionic secretion from epithelial monolayers and co-secretion of mucus. In this study we adapted ion-selective electrodes and a novel mathematical approach to deconvolution to gain insight in how Cl^-, K^+ and Ca^{2+} are co-secreted with mucins from a model cell line. In spite of many decades of intense basic and clinical research the ultimate failure rate of cancer chemotherapy is still high. This is mainly due to poor selectivity of the available drugs, and inherent or acquired multidrug resistance (MDR) of cancer cells. Significant progress is being made in solving the former problem but new experimental approaches are required to successfully address clinical MDR. We have used carbon fiber based microvoltammetry to monitor variations in extracellular concentration of doxorubicin (DOX), a clinically important cancer drug at sparse monolayers and at single cancer cells. These experiments are complemented with the assessment of uptake dependent efflux by employing a Diffusional Microburet (DMB) to deliver DOX into single cancer cells under a confocal fluorescence microscope. To make such cellular transport studies more comprehensive and controlled, a BioMEMS platform has also been devised and tested. Results from these studies have shed new light on drug transport at cancer cells and its contribution to MDR.

12:10 Keynote lecture

Calixarene - lipid monolayers: towards enzymatic engineering of lipid membranes.

Ewa M. Rogalska[1], Beata Korchowiec[2], Adel Ben Salem[1], Yohann Corvis[1], Jean-Bernard Regnouf de Vains[1], Jacek Korchowiec[3]

1. *Universite Henri Poincare (UHP), Faculté des Sciences, BP 239, Nancy 54506, France* **2.** *Jagiellonian University, Faculty of Chemistry, Department of Chemical Physics, Ingardena 3, Kraków 30-060, Poland* **3.** *Jagiellonian University, Faculty of Chemistry, Ingardena 3, Kraków 30-060, Poland*

e-mail: rogalska@lesoc.uhp-nancy.fr

Three new antimicrobial *p-tert*-butylcalix[4]arene derivatives were studied in a membrane environment, using 1,2-dimyristoyl-*sn*-glycero-3-phosphoethanolamine (DMPE) and 1,2-dilauroyl-*sn*-glycero-3-phosphocholine (DLPC) monolayers; the aim of this study was getting some insight in the relation between the membrane structure and the activity of lipolytic enzymes. The derivatives used have 6-aminopenicillanic acid or benzylpenicillin moieties grafted in alternate positions at the calixarene lower rim. The miscibility of calixarene-antibiotic conjugates with lipid films was studied using surface pressure and surface potential measurements, as well as Brewster angle microscopy. Molecular modeling allowed assessing the lowest energy conformations of the calixarene derivatives and gave more insight in the interactions with the lipid films. The results obtained show that the 6-aminopenicillanic acid derivative decreases the molecule packing in the mixed films compared to the benzylpenicillin derivatives; the decreased molecule packing is accompanied by an increased ordering of the DMPE molecules in the lipid-rich phase. Moreover, the 6-aminopenicillanic acid derivative affects the activity of phospholipase A_2 (PLA_2) catalyzing the hydrolysis of the DLPC monolayer. It may be supposed that the adjustment of the activity of PLA_2 is due to the modifications of the film structure, which influences in turn the process of binding of the enzyme to the substrate surface. The results obtained in this work will be used to develop methods of a controlled enzymatic engineering of selective lipid membranes.

12:30 Short communication

Probing interfacial organization in planar lipid bilayers using tethered pyrene

Monika J. Dominska[1], Gary J. Blanchard[1], Paweł G. Krysiński[2]

1. *Michigan State University, Department of Chemistry (MSU), East Lansing, MI 48824, United States* **2.** *Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland*

e-mail: mdomi@chemistry.msu.edu

Biomolecules such as transmembrane proteins and enzymes are often used as the selective medium in biosensors because of their inherent selectivity. For any sensing device, there is a chemically selective component that is connected to a transducer so that chemical signals can be converted to usable information. For such sensors, the biomolecule used for sensing must be maintained in its active form while in close proximity to the transducer surface. For this reason, we have embarked on a body of work aimed at producing a biomimetic transducer interface that will maintain biomolecule activity, and we have chosen lipid bilayers as the medium. The organization and structure of proteins and lipids in biological membranes is a fluid mosaic, and any interface we design must have similar fluid properties. To understand the fluid properties of bilayer structures and how to control them, we have examined molecular interactions and molecular-scale organization in lipid bilayer structures. With this understanding in place, we will be in a position to introduce biomolecules into the mimic membranes on the transducer surface for sensing applications. We focus on a system where a hydrophilic spacer is placed between the transducer surface and the polar head groups of the bilayer bottom leaflet. The lipid bilayer is composed of phospholipids or fatty acids, with the addition of small amounts of tethered pyrene as a chromophore. Fluorescence spectroscopic data indicate both the polarity of the pyrene immediate environment and the extent to which the chromophore is aggregating within the bilayer structure. Electrochemical data point to the lower leaflet exhibiting limited organization, with a distribution of environments available to pyrene which depend on the identity of the bilayer constituents.

Lunch

Wednesday afternoon, 7 November, 13:00

Session 9

Wednesday afternoon, 7 November, 14:30

14:30 Tutorial lecture

Liquid-Liquid Ion-Transfer Electrochemistry at Stationary and at Flowing Triple Phase Boundaries

Frank Marken

University of Bath, Department of Chemistry, Claverton Down, Bath BA2-7AY, United Kingdom

e-mail: f.marken@bath.ac.uk

Electrochemical processes at liquid-liquid interfaces are of key importance in many extraction and phase transfer catalysis processes and measurements of ion transfer across liquid-liquid interfaces has traditionally been a domain of static experimental systems [1]. In this presentation, the use of both stationary and hydrodynamic liquid-liquid interfaces is compared. Voltammetric studies with immobilised droplets and with flowing liquids are reported. For example, two immiscible liquids, N-octylpyrrolidone (with blue dye) and aqueous 0.1 M $NaClO_4$ are passed through a micro-flow cell with rectangular duct. The resulting flow pattern is dependent on the flow rate and viscosity of each individual phase. Optical micrographs are presented and a plot of flow rate to flow width in the channel flow cell. At the interface of the two flowing liquids a triple phase boundary [2] with the gold electrode is established and electrochemical processes at this dynamic triple phase boundary are monitored. Electrochemically driven anion transfer processes are reported for simple and for more complex anions.

References

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15:10 Short communication

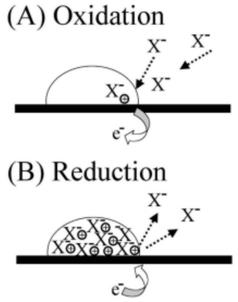
Electrocatalytic Sulphite Detection at a Liquid-Liquid-Solid Three-Phase Boundary Electrode Sensors

Najoua Katif, Tony D. James, Ewan K. Galbraith, Frank Marken

University of Bath, Department of Chemistry, Claverton Down, Bath BA2-7AY, United Kingdom

e-mail: nk227@bath.ac.uk

Electrochemically driven ion transfer processes from aqueous to organic media are readily observed at electrodes modified with an immobilised water immiscible redox liquid [1]. The transfer of ions occurs at a potential determined by the aqueous concentration and aqueous hydration energy.



In this study anion transfer processes are investigated at a 4-(3-phenylpropyl)pyridine | aqueous electrolyte interface and employing the ferrocenylmethyl-dodecyl-dimethylammonium bromide redox system. Facile and reversible anion transfer is observed and in the case of sulphite anions a two-phase electrocatalytic process leading to sulphate is observed. The new method combines anion selectivity and sensitivity due to catalytic currents.

[1] The electrochemical ion-transfer reactivity of porphyrinato metal complexes in 4- (3-phenylpropyl)pyridine vertical bar water systems. M.J. Bonné, C. Reynolds, S. Yates, G. Shul, J. Niedziolka, M. Opallo, F. Marken, New J. Chem. 30 (2006) 327.

15:25 Keynote lecture

On- and off-chip electrochemistry coupled to electrospray mass spectrometry

Leif Nyholm[1], Camilla Zettersten[2], Per Sjöberg[2]

1. *Uppsala University, Department of Materials Chemistry, Angstrom Laboratory, Uppsala, Sweden* **2.** *Uppsala University, Department of Analytical Chemistry, P.O. Box 599, Uppsala, Sweden*

e-mail: Leif.Nyholm@mkem.uu.se

By coupling an electrochemical flow-cell to electrospray mass spectrometry (ESI-MS), a very powerful tool for studies of electrochemical reactions as well as for analyses of electroactive compounds can be obtained. With ESI-MS [1] it is possible to identify and quantitate electrochemically produced oxidation and reduction products and by coupling electrochemistry to ESI-MS it also becomes possible to utilise electrochemical reactions for the preconcentration, ionisation and tagging [2] of selected analytes prior to ESI-MS. The combined approach is, however, complicated by the need to decouple the electrochemical cell from the ESI-MS high voltage and the fact that the electrospray process itself involves electrochemical reactions [1]. Care also needs to be taken to ensure that the electrochemically generated products do not undergo unwanted redox reactions during their transfer to the mass spectrometer [3]. To enable the detection of unstable products it is likewise important to minimise the transfer time between the electrochemical cell and the mass spectrometer. In the present communication, on- and off-chip couplings of electrochemistry to ESI-MS will be discussed with a particular emphasis on the design of the electrochemical flow-cell. It will be demonstrated that the approach can be used to identify electrochemically produced reaction products and that electrochemical ionisation can be used to facilitate studies of compounds immobilised on surfaces. The influence of the design of the electrochemical cell and the flow system in general on the possibilities to detect an electrochemically generated species will also be discussed. A PDMS based device [4] allowing an on-chip coupling of an electrochemical cell to ESI-MS with a subsecond transfer time will likewise be described.

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15:45 Keynote lecture

Analyte capture and desorption/ionization mass spectrometry analysis on porous silicon and silicon nanowires

Rabah Boukherroub[1], Gaëlle Piret[1], Hervé Drobecq[2], Manash Das[1], Vera Praig[2], Yannick Coffinier[1], Sabine Szunerits[3], Oleg Melnyk[2]

1. *Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN), Cité Scientifique Avenue Poincaré, Villeneuve d'Ascq 59652, France* **2.** *Institut de Biologie de Lille (IBL), 1 rue du professeur Calmette, Lille 59021, France* **3.** *Institute National Polytechnique de Grenoble (INPG), 1130, rue de la piscince, Saint Martin d'Hères 38402, France*

e-mail: rabah.boukherroub@iemn.univ-lille1.fr

Desorption/ionization on silicon mass spectrometry (DIOS-MS) is a matrix-free technique that allows for the direct desorption/ionization of low-molecular-weight compounds with little or no fragmentation of analytes. This technique has a relatively high tolerance for contaminants commonly found in biological samples. Desorption/ionization on porous silicon (PSi) or silicon nanowires (SiNWs) mass spectrometry is a technique related to matrix-free laser desorption/ionization. In DIOS, PSi and SiNWs are used as sample support and substrate for the generation of intact gas-phase ions of small molecules upon irradiation with a pulse laser using standard MALDI (matrix-assisted laser desorption/ionization) instrumentation.

In this paper, we report the first use of “click chemistry” to couple functional alkynes to azide-terminated porous silicon and silicon nanowires and the subsequent analysis using DIOS-MS. Porous silicon (PSi)[1] is prepared by electrochemical anodization of crystalline silicon in HF-based solution while silicon nanowires (SiNWs) are obtained by chemical etching[2] of crystalline silicon or using chemical vapor deposition (CVD) techniques.[3,4]

The Cu(I)-catalyzed 1,3-diploar cycloaddition of azides and alkynes, the premier example of “click chemistry” is an efficient route to make a covalent connection among diverse molecules and materials. Azide-terminated monolayers were prepared in a two step procedure starting from oxidized PSi and SiNWs surfaces, involving surface amination followed by subsequent coupling of the terminal NH$_2$ groups with 4-azidobenzoic acid. Amine termination was obtained by the reaction of the oxide with 3-aminopropyltrimethoxysilane at room temperature. The resulting NH$_2$-terminated surfaces were reacted with 4-azidobenzoic acid in the presence of *N,N*-dicyclohexylcarbodiimide to yield azide-modified substrates. The “clicking” between the azide groups and functional terminal alkynes in the presence of Cu(I) catalyst yields 1,2,3,-triazoles via the Huisgen 1,3-dipolar cycloaddition reaction. Terminal acetylene bearing different moieties such as ferrocene and sugar were successfully coupled to the PSi and SiNWs surfaces in high yield. The sequential reactions on the surface leading to alkyne immobilization were monitored using different surface analysis techniques, electrochemical measurements and DIOS-MS.

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16:05 Short communication

Conical recessed gold microelectrode arrays produced during photolithographic methods: Characterisation and causes

Francisco A. Aguiar[1], Andrew J. Gallant[2], Mark C. Rosamond[2], David Wood[2], Ritu Kataky[1]

1. *University of Durham (UDUR), South Rd, Durham DH13LE, United Kingdom* **2.** *School of Engineering, University of Durham, Science Labs, South Road, Durham DH1-3LE, United Kingdom*

e-mail: francisco.aguiar@durham.ac.uk

In this work, surface imaging techniques such as scanning Kelvin nanoprobe (SKN), scanning electron microscopy (SEM) and white light interferometer microscopy show that conical recessed electrodes with gradient potential along the recessed walls are formed during standard photolithographic methods for producing microelectrode arrays. The experimental behaviour of these electrode arrays fits very well with the numerical solution using optimal quasi-conformal mappings proposed recently by Amatore and co-workers [C. Amatore, A. Oleinick, I. Svir, J. Electroanal. Chem. 597 (2006) 69; C. Amatore, A. Oleinick, I. Svir, J. Electroanal. Chem. 597 (2006) 77]. The possible reasons for the formation of conical recesses are discussed.

Coffee break

Wednesday afternoon, 7 November, 16:20

Session 10

Wednesday afternoon, 7 November, 16:45

16:45 Tutorial lecture

Electrochemical sensors based on nano-scaled films and arrays of electroactive polymers. Towards nano-electroanalysis.

Arkady A. Karyakin

e-mail: aak@analyt.chem.msu.ru

Chemistry faculty of M.V. Lomonosov Moscow State University, 119991, Moscow, Russia

Requirements of modern chemical analysis are the high sensitivity and selectivity in combination with the simplicity and low cost. Electrochemical (bio)sensors seem to accomplish these functions most properly, and in addition, allow continuous monitoring of key metabolites. It’s important to note, that modern clinical diagnostics needs improved analytical procedures. In many cases both contactless tomography and traditional biopsy are not enough informative. Due to inherent instability of some key metabolites of interest chemical analysis has to be carried out directly in the damaged organ (tissue). This can be made exclusively with the use of chemical and biological sensors. Accessing limiting performance characteristics of sensors is possible due to their miniaturization. Micro-electrodes demonstrate significantly improved sensitivity and signal-to-noise ratio, the latter being inversely proportional to the electrode radius. Moreover, microelectrodes are characterized by dramatically faster equilibration of diffusion profiles at the electrodes surface. However, a decrease of electrode dimensions limits sensor response to very low current values. To avoid a necessity to measure units of *pico*-Amperes and lower it’s possible to use micro-electrode arrays commonly produced by insulating of macro-electrode surface followed by drilling holes in the insulating layer. The latter behave as individual micro-electrodes, generating cumulative response. The novel branch of electroanalytical chemistry is a formation of nano-electrodes arrays. Being synthesized by simple electrochemical methods, such systems provide record performance characteristics of the corresponding chemical sensors. To form nano-electrode arrays we propose nano-structuring of an advanced electrocatalyst on inert electrode support. Indeed, if background electrode reaction is negligible, analyte fluxes are directed to islands of electrocatalyst, which thus behave as nano-electrodes. Hydrogen peroxide sensor made by deposition of Prussian Blue through different templates (nano-structuring has been confirmed by AFM-investigation) in FIA mode displays: (i) diffusion limited sensitivity (0.7 A L mol^{-1} cm^{-2}), (ii) linear calibration range prolonged over 7 orders of magnitude of H_2O_2 concentration with (iii) its lower limit of 10^{-9} mol L^{-1} (0.03 ppb) H_2O_2; the latter is two orders of magnitude lower compared to the sensor based on conventional (unstructured) Prussian Blue. The 100 times decreased detection limit without loss of sensitivity is the limiting level sensor improvement by forming of micro- or nano-electrode arrays. The analytical characteristics achieved are record in electroanalysis.

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17:25 Keynote lecture

Electrochemical sensing of DNA damage

Miroslav Fojta, Jan Vacek, Petra Brázdilová, Pavel Kostečka, Luděk Havran, Emil Paleček

Institute of Biophysics, v.v.i., Acad. Sci. Czech. Rep. (IBP), Kralovpolska 135, Brno CZ-61265, Czech Republic

e-mail: fojta@ibp.cz

It has been known for decades that nucleic acids are electroactive and surface-active substances yielding at mercury and carbon electrodes redox and/or tensammetric signals. Some of these signals exhibit a remarkable sensitivity to alterations in the DNA structure (such as local unwinding of the DNA double helix, interruptions of the sugar-phosphate backbone or chemical modifications of the nucleobase residues). Hence, electrochemical techniques have proved useful in detecting DNA damage that is usually accompanied by changes in electrochemical activity of particular base residues, changes of the DNA conformation affecting DNA adsorption at the electrode surfaces, and/or may result in appearance of new electrochemical signals specific for the DNA lesions (reviewed in[1]). Behavior of double stranded DNA and mercury and some types of amalgam electrodes is strongly influenced by presence of DNA strand breaks (interruptions of the DNA sugar-phosphate backbone). Based on this finding we proposed a sensor for DNA damage consisting of supercoiled covalently closed circular DNA (scDNA), not containing any strand break, adsorbed at the surface of a mercury or silver amalgam electrode. Upon formation of the strand breaks (due to exposure to a sample containing DNA damaging species), a qualitative change in the sensor AC voltammetric response is observed. By this way, one DNA strand break per 2×10^5 nucleotides can be detected [1]. The technique has been adapted for detecting damage to DNA bases via application of enzymes recognizing specific nucleobase lesions and cleaving the DNA sugar-phosphate backbone at such sites [2]. The most common electrochemical techniques applied in the detection of DNA damage and/or in sensing of potentially genotoxic substances use various types of carbon electrodes and involve measurements of a signal due to electrochemical oxidation of guanine [1]. Guanine is a target for a variety of toxic compounds, including carcinogens and antineoplastic drugs, and its modification usually results in a loss of its electrochemical activity. Other approaches based on guanine signals employ soluble or surface-confined mediators of electrocatalytic guanine oxidation [3]. In addition to the label-free techniques utilizing intrinsic electrochemical activity of DNA, detection principles involving non-covalently bound redox indicators or covalently bound markers. For example, DNA intercalators such as $[Co(bipy)_3]^{2+/3+}$ bind efficiently to duplex (native) DNA adsorbed at surface of a carbon electrode, yielding an intense signal due to oxidation/reduction of the cobalt ion [4]. Upon damage to the DNA, its double-helical structure is disrupted, binding of the indicator is reduced and the signal decreases. Pyrimidine bases in single-stranded regions of damaged (and/or enzymatically pretreated) DNA can be modified by osmium tetroxide complexes followed by electrochemical detection of the osmium markers [5]. Voltammetric techniques can easily be combined with simple magnetoseparation protocols [6] to increase sensitivity and/or specificity of the analysis.

This work was supported by GACR (203/07/1195) and by Ministry of Education, Youth and Sports of the CR (LC06035, FRVS/1468/2007).

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17:45 Keynote lecture

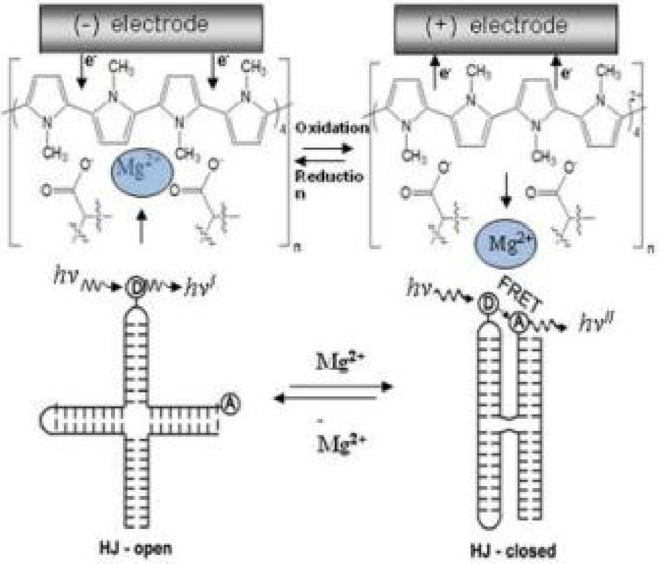
Electrochemical DNA biosensors for label-free detection of nucleic acids exploiting DNA conformational transitions upon hybridization event

Elena E. Ferapontova

University of Aarhus, Chemistry Department, Center for DNA Nanotechnology (CDNA), Langelandsgade 140, Aarhus 8000, Denmark

e-mail: e_ferapontova@chem.au.dk

Several electrochemical DNA biosensors for label-free detection of nucleic acid sequences, based on the molecular beacon principle, are discussed. These systems exploit 1). conformational movements of probe DNA, labelled with a redox active tag, upon hybridization (e.g. shown in the works of A. Heeger, briefly reviewed) and 2). conformational transitions in branched DNA molecules operating as molecular switches, changing between ‘open’ and ‘closed’ conformations in response to the local ionic conditions at the branch point (Figure).



In the first case, electrochemical read-out of the changing signal from the redox tag is used for detection of the hybridization event. In the second case, the switching state of hybridized DNA is read-out optically using the fluorescence resonance energy transfer (FRET) occurring between donor and acceptor dyes located at the termini of the DNA junctions (Figure). In this case, the modulation of the conformational state is performed electrochemically, through electrochemical injection/removal of cations, thus producing change in the conformational state of the DNA. Two electrochemical cation-injection redox systems are shown: Zn/Zn^{2+} and polypyrrol-organic counteranion-Mg^{2+}/ oxidised polypyrrol-organic counteranion (Figure). Chemistries of the electrode modification by DNA and perspectives and drawbacks for application of both methodologies for analysis of multiplexing gene systems “on-chip” are discussed. Current research on electrochemical detection of analytes through their binding to redox-labeled DNA, thus changing DNA conformational states, is also reported.

18:05 Short communication

Electrochemical impedance spectroscopy (EIS) for detection of DNA hybridization in presence of intercalators

Magdalena Gebala, Leonard Stoica, Sebastian Neugebauer, Wolfgang Schuhmann

Ruhr-Universität Bochum, Anal. Chem. - Elektroanalytik & Sensorik (ELAN), Universitätsstr. 150, Bochum 44780, Germany

e-mail: magdalena.gebala@rub.de

Direct, label-free and highly sensitive detection of DNA hybridization is important for the development of DNA chips potentially avoiding initial PCR amplifi-cation. Electrochemical impedance spectroscopy (EIS) was already successfully used for the visualization of DNA hybridization. In EIS, the binding of the target strands to surface-immobilized capture probes is indicated by a shift in the impedance spectrum of the modified electrode [1]. In addition, label-free detection of DNA can be obtained by interaction of DNA with electrochemically active ligands [2]. Actinomycin D is an antitumor antibiotic that contains a 2-aminophenoxazin-3-one chromophore and two cyclic pentapeptide lactones. The chromophore is intercalating with high affinity constant into double-stranded DNA preferentially at GC-Watson-Crick base pairs. In this work, the interactions between ActD and single as well as double stranded DNA is studied by means of EIS. For this purpose, monolayers of thiol-modified ss-DNA in combination with different types of alkanethiols with variable chain length were assembled on gold electrode. The influence of the modified surface on the electron-transfer properties of suitable reversible redox mediators such as $Fe(CN)_6^{3-/4-}$ or $Ru(NH_3)_6^{2+/3+}$ was investigated by means of EIS. The sequence of monolayer formation using thiol-modified single-stranded DNA capture probes, additional surface modification with a thiol derivative, and hybridization with the complementary strand were followed in-situ by means of EIS. Previously, it has been reported [3] that ActD is weakly interacting with ss-DNA, whereas preserves a high binding affinity with immobilised ds-DNA. Intercalation of Actinomycin D into the formed double-stranded DNA could be monitored using EIS, however, a weak non-covalent adsorption onto bare gold or thiolated-gold electrodes was demonstrated. Parameters, such as the nature of the electrolyte, pH value, concentration of the redox mediator, type of thiol used for gold modification were evaluated with respect to their influence on the detection of DNA-hybridization by means of EIS. Based on these results, a new strategy for the detection of DNA hybridization will be proposed.

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18:20 Short communication

Modification of gold microelectrodes for detection of DNA hybridization

Anna M. Nowicka[1], Agata Kowalczyk[1], Zbigniew J. Stojek[1], Donal Leech[2]

1. *Uniwersytet Warszawski, Wydział Chemii, Warszawa, Poland*
2. *National University of Ireland, Galway (NUIG), University Road, Galway none, Ireland*

e-mail: stojek@chem.uw.edu.pl

The development of a suitable electrochemical biosensor for DNA hybridisation is of great interest due to the high sensitivity, low cost, small dimensions, simple design and low power requirements offered by such a device. One of the difficulties that is faced is that that DNA hybridization does not normally produce an adequate electrical signal for the detection. This has been overcome, by e.g. labeling DNA with an enzyme which catalyses the transformation of a specific substrate to a product which may be detected electrochemically [1]. We show in this presentation our strategy to achieve highly sensitive electrochemical assays for enzyme-labeled detection of DNA hybridization. The recognition film in our device is based on a redox polymer that is cross-linked and co-immobilized with a 20 mer oligonucleotide on the gold microelectrode surface either modified or not with colloidal gold. The hybridization process occurrs between the immobilized probe DNA and a biotin-modified target DNA (designed from the ssrA gene of *Listeria Monocytogenes*). The hybridization is followed by addition of an enzyme (glucose oxidase)-avidin conjugate and glucose. As a result bioelectrocatalytic oxidation of glucose takes place. Each hybridization event produces a large number of electrons flowing to the electrode. We have decided to employ the use of microelectrodes since a smaller surface may allow producing more reliable layers and to achieve further progress in improving the analytical performance of the sensor. Modification of the microelectrode surface with colloidal gold increases the true electrode surface area. The biofunctionalized colloidal gold nanoparticles not only reveal extraordinary stability and regeneration properties, but also posses the undisturbed, specific recognition capabilities of the colloid-bound sensing film with DNA probe.

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Dinner

Wednesday evening, 7 November, 19:00

Thursday, 8 November

Breakfast

Thursday morning, 8 November, 7:30

Session 11

Thursday morning, 8 November, 8:25

8:25 Tutorial lecture

Mimicking Photosynthesis by Supramolecular Donor-Acceptor Nanostructures: Design to Devices

Francis D'Souza

Wichita State University, Department of Chemistry, 1845, Fairmount, Wichita, KS 67260-0051, United States

e-mail: francis.dsouza@wichita.edu

Self-assembly governed supramolecular construction of donor-acceptor nanostructures capable of mimicking biological functions is one of the fastest growing areas of research. The potential application of these to the design of molecular systems lies in self-replication, light energy harvesting and nanotechnology. Mimicking the primary events of the reaction centers of photosynthetic bacteria is an important area of research since it directly involves harvesting solar energy. The present tutorial talk will focus on the design and photoinduced electron transfer reactions in supramolecular donor-acceptor nanostructures composed of ferrocene, porphyrin, fullerene and carbon nanotubes. Utilization of metal-ligand axial coordination, crown ether-ammonium cation, hydrogen bonding involving complimentary base-pairing, pi-pi interactions, and a combination of one or more of these binding approaches in the construction of the nanostructures will be discussed. Results of photoinduced charge stabilization, as applicable for light energy harvesting, in the novel supramolecular systems will be shown. Finally, results of the photoelectrochemical cells for light energy conversion build by using some of these supramolecular nanostructures will be presented.

9:05 Keynote lecture

Electro-assisted generation of sol-gel thin films directed to electrochemical sensing

Alain Walcarius, Emilie Sibottier, Mathieu Etienne

Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME), 405, rue de Vandoeuvre, Nancy 54600, France

e-mail: alain.walcarius@lcpme.cnrs-nancy.fr

Sol-gel electrochemistry has gained great popularity in the past decade, mostly because of the ease of formation of silica and organosilica films with tailor-made properties that can be advantageously exploited for several applications when coated on a suitable electrode surface [1-3]. The usual way to get such films involves either dip- or spin-coating a sol-gel medium containing the appropriate (organo)alkoxysilane precursor(s), which are hydrolyzed and (co)condensed on the electrode surface. Some years ago, Shacham and co-workers have developed a new and elegant electrochemically-driven deposition method for getting sol-gel thin films on conducting substrates [4]. The approach is based on altering the surface pH by applying a suitable potential to an electrode immersed in a sol-gel medium, inducing thereby the catalysis of the condensation process thus enhancing the rate of film deposition. The present lecture aims at presenting two extensions of this method: (1) the preparation of organosilica films containing thiol or amine ligands and its combination to the self-assembled monolayers technology to ensure good adhesion to the electrode surface; (2) the formation of well-ordered mesoporous silica films displaying a regular arrangement of mesopore channels oriented normal to the underlying electrode surface. The synthetic pathway involves basically the immersion of an electrode in a silica sol containing the hydrolyzed precursors, alone or in the presence of a surfactant template, where a cathodic potential is applied to increase pH locally at the electrode/solution interface and to induce co-condensation of the precursors. The films were characterized by various physico-chemical techniques (cyclic voltammetry, crystal quartz microbalance, atomic force microscopy, electron microscopy) and special attention was given to highlight the effect of the electro-deposition conditions. It was especially shown that film growth was first linear and then exponential [5], that mesostructuration can be effectively induced by the use of an appropriate surfactant template [6], and that both the amount of organic groups in the final material and its degree or organization greatly affected its permeation properties and the electroanalytical performance of the resulting film electrodes [6-8].

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9:25 Keynote lecture

Adsorption of biomolecules on self-organized nanostructured semiconductor surfaces

Katarzyna Skorupska[1], James R. Smith[2], Sheelagh A. Campbell[2], Daren Mernagh[2], Ferdinand Streicher[1], Hans J. Lewerenz[1]

1. *Hahn-Meitner-Institute (HMI), Glienicker Str. 100, Berlin D-14109, Germany* **2.** *University of Portsmouth, White Swan Road, Portsmouth PO12DT, United Kingdom*

e-mail: skorupska@hmi.de

The layered semiconductor $MoTe_2$ and step bunched silicon surfaces, obtained by electrochemical processing in alkaline solution under cathodic potential are used as substrate for specific adsorption of the protein reverse transcriptase. The experiment is monitored by imaging of the deposite/substrate surfaces using tapping mode atomic force microscope. The RT of the human immunodeficiency virus I was selected due to its medical relevance and its well-defined three-dimensional heterodimer structure that is homologous to the human right hand. In the past, n-$MoTe_2$ was used as a substrate for the RT adsorption and STM imaging [1] because of its surface defects with negatively charged surface states. The step-bunched Si surfaces, exhibiting steps of about 10 atomic bilayers, is known to form an accumulation layer where the surface consists of a high density of negative charge, evidenced by synchrotron radiation photoelectron spectroscopy performed at BESSY [2,3]. Kelvin-Probe atomic force microscopy (AFM) shows an inhomogeneous lateral distribution of the electrostatic potential across the surface. This suggests that specific sites can act for electrostatic and van der Waals binding of the protein at the surface. First AFM data that show adsorption at step edges are presented. Besides protein immobilization, the charge transfer properties between biomolecule and semiconductor substrate are of considerable interest. Future studies will address this and the RT conformation and bonding between silicon and biomolecule.

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Coffee break

Thursday morning, 8 November, 9:45

Session 12

Thursday morning, 8 November, 10:00

10:00 Keynote lecture

Surface modification with polysaccharides for chemical sensing

Caroline L. Schauer

Drexel University, 3141 Chestnut St, Philadelphia 19104, United States

e-mail: caroline.schauer@gmail.com

Because of their catalytic versatility, metals, such as Fe, Mg, Ca and Cu, have been adopted by biological systems, but their reactivity can also make them toxic at low concentrations and classified as poisons. Current means of heavy metal detection has become an increasingly complex process and the sophisticated laboratory analysis of trace levels of heavy metal ions remains unmatched for selectivity and precision. An on-site, over-the-counter detector for heavy metals would simplify the detection and provide a quick and useful means for monitoring contaminant levels in household and remote well waters. Structurally colored thin films offer a promising materials platform for the development of a metal ion sensor due to the rapid, straightforward, field-readable response of the visual color change which occurs upon exposure to metal ions. Our research has focused on cross-linked thin films of chitosan, thiol modified chitosan, and alginate.

Chitin is a colorless biopolymer found in shells of crabs and shrimp and is the second most abundant poly(saccharide) found in nature. Chitosan, the acid soluble form of chitin, is a non-toxic, biodegradable, biopolymer consisting primarily of β(1→4) linked 2-amino-2-deoxy-β-D-glucopyranose units, and is currently used in tissue engineering, antifouling coatings, separation membranes, stent coatings, enzyme immobilization matrices, and as a platform for a taste sensor, optical devices and removal of heavy metals from ground and wastewater.

Chitosan is a commercially interesting compound because of its high nitrogen content (6.89%), making chitosan a useful chelating agent for metal ions. Many factors determine chitosan's capacity for absorption of metal ions including pH, concentration, temperature, percent deacetylation, interaction time, and chain length. For example, if the pH is below the pKa (between 6.2-6.8) of chitosan, then the amines become approximately 90% protonated, resulting in a positively charged chitosan, which is a good adsorbent for anions.

Because chitosan is well known for its metal ion absorbance capabilities, interference-colored, thin single films of chitosan were investigated for their ability to distinguish metal ions using a change in optical properties and thickness. After coating chitosan- hexamethylene 1,6-di(aminocarboxysulfonate) (HDACS) solution onto a polished silicon wafer, the films are measured using reflectance and ellipsometry before and after dipping into a 50 ppm (parts per million) aqueous metal salt solution. Chitosan-HDACS films increased in thickness and red shifted their reflectance spectra in the presence of CrO_3.

Investigations into the modification of chitosan by the addition of thiol groups and their subsequent processing will be discussed. Basically, increasing the amount of thiol added to the chitosan backbone can correlate with an increase in sensitivity, especially for mercury nitrate. Investigation of the 6.67% S thiol glycolic chitosan indicates that the films only red shifted when interacting with the mercury nitrate solution. All other solutions blue shifted, creating a specific sensor for mercury.

Alginates are a family of unbranched binary copolymers of (1à4)-linked b-D-mannuronic acid (M) and a-L-guluronic acid (G) groups. Alginates with various M and G compositions are produced by a number of organisms, and are constituents in the cell walls of brown algae. To demonstrate the repeatability of the spin coating deposition process, twenty-four films were spun from a single solution using identical deposition parameters. Each film was exposed to aerosolized $CaCl_2$ solution for ten seconds before being rinsed and dried. This aerosol application technique allows the calcium to be evenly applied over the film's surface without the problems associated with directly dipping the films into solution. The evenness of cross-linking is evidenced by the films' retained smoothness and virtually constant radial coloration from center to edge. Ellipsometry and reflectance data were gathered for each sample. Film thicknesses and indices of refraction were determined using an M-2000U variable-angle spectroscopic ellipsometer. The Ca^{2+}-alginate films were sensitive to lead and chromium (VI and II).

10:20 Keynote lecture

Immobilization of molecules: From self-assembled monolayers to polymeric hollow structures

Maciej Mazur[1], Paweł G. Krysiński[1], Gary J. Blanchard[2], Jerzy Rogalski[3]

1. *Warsaw University, Faculty of Chemistry, Pasteura 1, Warszawa 02-093, Poland* **2.** *Michigan State University, Department of Chemistry (MSU), East Lansing, MI 48824, United States* **3.** *Maria Curie Sklodowska University, Department of Biochemistry, Pl. Sklodowskiej 3, Lublin 20-031, Poland*

e-mail: mmazur@chem.uw.edu.pl

Immobilization of chemical species onto solid substrates is one of the hottest topics of contemporary surface chemistry. We present two complementary approaches towards molecule immobilization - through coordination to self-assembled monomolecular films or encapsulation within polymeric hollow structures. Monomolecular layers provide an opportunity to define their chemical functionality with molecular precision that can lead - via the appropriate synthetic route - to covalent or electrostatic attachment of desired molecules to the surface. The strategy for molecule immobilization (pyrene, perylene or laccase from *Cerrena unicolor*) reported here relies on ionic coordination of $–COO^-$ terminal groups (present on the immobilized molecule) to zirconated phosphate (ZP) monolayers. As an alternative to this approach we developed a novel method of immobilization through formation of polymeric hollow structures that are capable to entrap the molecules inside the hollow: the polymeric material is deposited onto the liquid droplet containing dissolved chemical species. We used several experimental techniques to confirm that both approaches allow for stable immobilization. The immobilized molecules can be subsequently used as elements of sensor or optical devices, as well as electrodes in fuel electrochemical cells.

10:40 Tutorial lecture

Connecting-up the surface: exploiting molecular wires for sensing

Jay D. Wadhawan

Department of Chemistry, University of Hull, Hull HU67RX, United Kingdom

e-mail: j.wadhawan@hull.ac.uk

An overview of electron transfer in molecular wires is provided briefly. Strategies for surface modification are explored and compared. Last, the use of wires for chemical and biochemical analysis are considered.

Lunch

Thursday morning, 8 November, 11:30

Bus departure to Warszawa

Thursday afternoon, 8 November, 13:00

Unscheduled abstracts

Author alphabetical order

Poster

Ferrocene Liquid Crystals for Electroanalysis

Louise A. Evans, Jay D. Wadhawan

Department of Chemistry, University of Hull, Hull HU67RX, United Kingdom

e-mail: l.a.evans@chem.hull.ac.uk

Two ferrocene liquid crystals, immobilised on an electrode surface in the form of microdroplets are examined in terms of ion-selectivity and ability to act as mediators for bioelectroanalysis.

List of Participants

Wojciech Adamiak
wadamiak@ichf.edu.pl
- Polish Academy of Sciences, Institute of Physical Chemistry
  Kasprzaka 44/52, Warszawa 01-224, Poland

Francisco A. Aguiar
francisco.aguiar@durham.ac.uk
- Department of Chemistry, University of Durham
  Science Labs, South Road, Durham DH1-3LE, United Kingdom
- School of Engineering, University of Durham
  Science Labs, South Road, Durham DH1-3LE, United Kingdom

Mandana Amiri
mandanaamiri@yahoo.com
- Sharif University of Technology
  Azadi Avenue, Tehran 14588, Iran

Beata Baranowska
bbaranowska@chem.uw.edu.pl
- Warsaw University, Faculty of Chemistry
  Pasteura 1, Warszawa 02-093, Poland

Anna Basa
abasa@uwb.edu.pl
- University of Białystok, Institute of Chemistry
  Hurtowa 1, Białystok 15-399, Poland

Francesca Berti
francesca.berti@unifi.it
- Dipartimento di Chimica, Università di Firenze (UNIFI)
  Via della Lastruccia 3, Sesto Fiorentino (Firenze) 50019, Italy

Przemysław Bieganowski
bieganowski@chem.uw.edu.pl
- Warsaw University, Department of Chemistry
  Pasteura 1, Warsaw 02-093, Poland

Aleksander T. Bieguński
abiegunski@nlab.pl
- NLab sp. z o.o.
  Sekwoi 4, Warszawa 05-077, Poland

Renata Bilewicz
bilewicz@chem.uw.edu.pl
- Warsaw University, Faculty of Chemistry
  Pasteura 1, Warszawa 02-093, Poland

Gary J. Blanchard
blanchard@chemistry.msu.edu
- Michigan State University, Department of Chemistry (MSU)
  East Lansing, MI 48824, United States

Johan Bobacka
johan.bobacka@abo.fi
- Abo Akademi University, Process Chemistry Centre, Laboratory of Analytical Chemistry
  Biskopsgatan 8, Turku FIN-20500, Finland

Anastasiya Borisova
avborisova@list.ru
- Chemistry Department, Moscow State University
  Leninskie Gory, 1-3, Moscow 119992, Russian Federation

Rabah Boukherroub
rabah.boukherroub@iemn.univ-lille1.fr
- Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN)
  Cité Scientifique Avenue Poincaré, Villeneuve d'Ascq 59652, France

Michael Bron
michael.bron@rub.de
- Ruhr-Universität Bochum, Anal. Chem. - Elektroanalytik & Sensorik (ELAN)
  Universitätsstr. 150, Bochum 44780, Germany

Sonia Centi
sonia.centi@unifi.it
- Università di Firenze, Dipartimento di chimica (DEPT)
  via della Lastruccia 3, Sesto Fiorentino 50019, Italy

Vasile Coman
Vasile.Coman@analykem.lu.se
- Lund University, Department of Analytical Chemistry
  Lund SE-221 00, Sweden

Bengt Danielsson
bengt.danielsson@tbiokem.lth.se
- Lund University, Pure and Applied Biochemistry Department
  Getingevägen 60, Lund SE-22100, Sweden

Monika J. Dominska
mdomi@chemistry.msu.edu
- Michigan State University (MSU)
  Chemistry Bldg, Lansing 48824, United States

Francis D'Souza
francis.dsouza@wichita.edu
- Wichita State University, Department of Chemistry
  1845, Fairmount, Wichita, KS 67260-0051, United States

Mathieu Etienne
etienne@lcpme.cnrs-nancy.fr
- Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME)
  405, rue de Vandoeuvre, Nancy 54600, France

Louise A. Evans
l.a.evans@chem.hull.ac.uk
- Department of Chemistry
  University of Hull, Hull HU67RX, United Kingdom

Elena E. Ferapontova
e_ferapontova@chem.au.dk
- University of Aarhus, Chemistry Department, Center for DNA Nanotechnology (CDNA)
  Langelandsgade 140, Aarhus 8000, Denmark

Miroslav Fojta
fojta@ibp.cz
- Institute of Biophysics, v.v.i., Acad. Sci. Czech. Rep. (IBP)
  Kralovpolska 135, Brno CZ-61265, Czech Republic

Kevin Foster
kevin.foster@nuigalway.ie
- National University of Ireland, Galway, Department of Chemistry
  University Road, Galway Galway, Ireland

Magdalena Gebala
magdalena.gebala@rub.de
- Ruhr-Universität Bochum, Anal. Chem. - Elektroanalytik & Sensorik (ELAN)
  Universitätsstr. 150, Bochum 44780, Germany

Lo Gorton
Lo.Gorton@analykem.lu.se
- Lund University, Department of Analytical Chemistry
  Lund SE-221 00, Sweden

Maciej T. Gorzkowski
gorzki@chem.uw.edu.pl
- University of Warsaw, Faculty of Chemistry
  Pasteura1, Warsaw 02-093, Poland

Stéphanie Goubert-Renaudin
Stephanie.Renaudin@lcpme.cnrs-nancy.fr
- Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME)
  405, rue de Vandoeuvre, Nancy 54600, France

Miklos Gratzl
mxg13@case.edu
- CWRU, BME Dept. (CASE)
  Cleveland 44106, United States

Karsten Haupt
karsten.haupt@utc.fr
- Compiegne University of Technology, UMR CNRS 6022
  Compiegne, France

Tibor Hianik
hianik@fmph.uniba.sk
- Comenius University, Department of Biophysics and Chemical Physics
  Mlynská dolina F1, Bratislava 842 48, Slovakia (Slovak Rep.)

Martin Jönsson
martinj@ichf.edu.pl
- Polish Academy of Sciences, Institute of Physical Chemistry
  Kasprzaka 44/52, Warszawa 01-224, Poland

Katarzyna A. Karnicka
kkarnicka@chem.uw.edu.pl
- Warsaw University, Faculty of Chemistry
  Pasteura 1, Warszawa 02-093, Poland

Arkady A. Karyakin
aak@analyt.chem.msu.ru
- M.V. Lomonosov Moscow State University
  Vorobyevy gory, Moscow 119992, Russian Federation

Najoua Katif
nk227@bath.ac.uk
- University of Bath, Department of Chemistry
  Claverton Down, Bath BA2-7AY, United Kingdom

Thiago Kohls
abnormtk@yahoo.com.br
- Dipartimento di Chimica Fisica, Università Cà Focari di Venezia
  S. Marta 2137, Venezia 30123, Italy

Agata Kowalczyk
akowalcz@student.chem.uw.edu.pl
- University of Warsaw, Department of Chemistry
  Pasteura 1, Warsaw, Warszawa 02-093, Poland

Barbara Kowalewska
bstar@chem.uw.edu.pl
- Uniwersytet Warszawski, Wydział Chemii
  Warszawa, Poland

Paweł G. Krysiński
pakrys@chem.uw.edu.pl
- Warsaw University, Faculty of Chemistry
  Pasteura 1, Warszawa 02-093, Poland

Paweł J. Kulesza
pkulesza@chem.uw.edu.pl
- Warsaw University, Faculty of Chemistry
  Pasteura 1, Warszawa 02-093, Poland

Wlodzimierz Kutner
wkutner@ichf.edu.pl
- Polish Academy of Sciences, Institute of Physical Chemistry
  Kasprzaka 44/52, Warszawa 01-224, Poland

Jan Labuda
jan.labuda@stuba.sk
- Slovak University of Technology in Bratislava, Institute of Analytical Chemistry (STU)
  Radlinskeho 9, Bratislava 81237, Slovakia (Slovak Rep.)

Donal Leech
Donal.leech@nuigalway.ie
- National University of Ireland, Galway (NUIG)
  University Road, Galway none, Ireland

Adam Lesniewski
l_mada@poczta.onet.pl
- Polish Academy of Sciences, Institute of Physical Chemistry
  Kasprzaka 44/52, Warszawa 01-224, Poland

Andrzej Lewenstam
alewenst@abo.fi
- Abo Akademi University, Center for Process Analytical Chemistry and Sensor Technology ProSens (PROSENS)
  Biskopsgatan 8, Turku 00410, Finland
- AGH University of Science and Technology, Faculty of Materials Science and Ceramics (AGH UST)
  Mickiewicza 30, Kraków 30-059, Poland

Jerzy P. Lukaszewicz
lukaszju@chem.uni.torun.pl
- Nicolaus Copernicus University, Faculty of Chemistry (WChUMk)
  Gagarina 7, Toruń 87-100, Poland

Monika Łyczewska
mlyczewska@chem.uw.edu.pl
- University of Warsaw, Department of Chemistry
  Pasteura 1, Warsaw, Warszawa 02-093, Poland

Monika Maciejewska
monika.maciejewska@pwr.wroc.pl
- Wrocław University of Technology
  Wybrzeże Wyspiańskiego, Wrocław 50-370, Poland

Magdalena Maj-Zurawska
mmajzur@chem.uw.edu.pl
- University of Warsaw, Department of Chemistry
  Pasteura 1, Warsaw, Warszawa 02-093, Poland

Krzysztof Maksymiuk
kmaks@chem.uw.edu.pl
- Warsaw University, Faculty of Chemistry
  Pasteura 1, Warszawa 02-093, Poland

Paweł Malinowski
pamal@chem.uw.edu.pl
- Warsaw University, Faculty of Chemistry
  Pasteura 1, Warszawa 02-093, Poland

Artjom Maljusch
artjom.maljusch@rub.de
- Ruhr-Universität Bochum, Anal. Chem. - Elektroanalytik & Sensorik (ELAN)
  Universitätsstr. 150, Bochum 44780, Germany

Frank Marken
f.marken@bath.ac.uk
- University of Bath, Department of Chemistry
  Claverton Down, Bath BA2-7AY, United Kingdom

Efstathios K. Matsaridis
atlandas@phys.uni-sofia.bg
- Univeristy of Sofia, Faculty of Physics (SU)
  5 James Bourchier Blvd., Sofia 1126, Bulgaria

Ulriika H. Mattinen
umattine@abo.fi
- Abo Akademi University, Process Chemistry Centre, Laboratory of Analytical Chemistry
Biskopsgatan 8, Turku FIN-20500, Finland

Maciej Mazur
mmazur@chem.uw.edu.pl
- Warsaw University, Faculty of Chemistry
Pasteura 1, Warszawa 02-093, Poland

Agata J. Michalska
agatam@chem.uw.edu.pl
- Warsaw University, Faculty of Chemistry
Pasteura 1, Warszawa 02-093, Poland

Jan Migdalski
migdal@uci.agh.edu.pl
- AGH University of Science and Technology (AGH)
al. Mickiewicza 30, Kraków 30-059, Poland

Grzegorz Milczarek
gregor33@icpnet.pl
- Poznań Technical University, Institute of Chemistry and Applied Electrochemistry
Piotrowo 3, Poznań 60-965, Poland

Ligia M. Moretto
moretto@unive.it
- Dipartimento di Chimica Fisica, Università Cà Focari di Venezia
S. Marta 2137, Venezia 30123, Italy

Luc J. Nagels
luc.nagels@ua.ac.be
- University of Antwerp, Department of Physics
Antwerp, Belgium
- University of Antwerp, Department of Chemistry
Groenenborgerlaan 171, Antwerp 2020, Belgium

Renate L. Naumann
naumannr@mpip-mainz.mpg.de
- Max Planck Institute for Polymer Research (MPIP)
Ackermannweg 10, Mainz 55128, Germany

Ewa Nazaruk
enaz@chem.uw.edu.pl
- Warsaw University, Faculty of Chemistry
Pasteura 1, Warszawa 02-093, Poland

Joanna Niedziolka
joaniek@ichf.edu.pl
- Polish Academy of Sciences, Institute of Physical Chemistry
Kasprzaka 44/52, Warszawa 01-224, Poland

Wojciech Nogala
nogala@ichf.edu.pl
- Polish Academy of Sciences, Institute of Physical Chemistry
Kasprzaka 44/52, Warszawa 01-224, Poland

Gilbert Nöll
gilbert.noll@analykem.lu.se
- Lund University, Department of Analytical Chemistry
Lund SE-221 00, Sweden

Anna M. Nowicka
anowicka@chem.uw.edu.pl
- University of Warsaw, Department of Chemistry
Pasteura 1, Warsaw, Warszawa 02-093, Poland

Krzysztof R. Noworyta
know@ichf.edu.pl
- Polish Academy of Sciences, Institute of Physical Chemistry
Kasprzaka 52/56, Warszawa 01-224, Poland

Leif Nyholm
Leif.Nyholm@mkem.uu.se
- Uppsala University, Department of Materials Chemistry, Angstrom Laboratory
Uppsala, Sweden

Ievgen Obraztsov
e-obraz@ukr.net
- Polish Academy of Sciences, Institute of Physical Chemistry
Kasprzaka 44/52, Warszawa 01-224, Poland

Ayodele O. Okunola
ayodele.okunola@ruhr-uni-bochum.de
- Ruhr-Universität Bochum, Anal. Chem. - Elektroanalytik & Sensorik (ELAN)
Universitätsstr. 150, Bochum 44780, Germany

Marcin Opallo
mopallo@ichf.edu.pl
- Polish Academy of Sciences, Institute of Physical Chemistry
Kasprzaka 44/52, Warszawa 01-224, Poland

Beata Paczosa-Bator
paczosa@uci.agh.edu.pl
- AGH University of Science and Technology, Faculty of Materials Science and Ceramics (AGH UST)
  Mickiewicza 30, Kraków 30-059, Poland

Adriana Palińska
adusiap@gmail.com
- Warsaw University, Department of Chemistry
  Pasteura 1, Warsaw 02-093, Poland

Paweł Pawłowski
pawpaw@chem.uw.edu.pl
- Uniwersytet Warszawski, Wydział Chemii
  Warszawa, Poland

Katarzyna Pękala
kpekala@chem.uw.edu.pl
- University of Warsaw, Department of Chemistry
  Pasteura 1, Warsaw, Warszawa 02-093, Poland

Roman Pielaszek
roman@pielaszek.net
- Polish Academy of Sciences, Institute of High Pressure Physics (UNIPRESS)
  Sokolowska 29/37, Warszawa 01-142, Poland

Piotr Pieta
ppieta@ichf.edu.pl
- Polish Academy of Sciences, Institute of Physical Chemistry
  Kasprzaka 44/52, Warszawa 01-224, Poland
- Leibniz-Institute for Solid State and Materials Research
  P.O.Box 270116, Dresden D-01171, Germany

Agnieszka Pietrzyk
agapi@ichf.edu.pl
- Polish Academy of Sciences, Institute of Physical Chemistry
  Kasprzaka 44/52, Warszawa 01-224, Poland

Wojciech Pudło
wojciech.pudlo@polsl.pl
- Silesian University of Technology, Department of Chemical Engineering
  M. Strzody 7, Gliwice 44-100, Poland

Hanna Radecka
hanna.radecka@pan.olsztyn.pl
- Instytut Rozrodu Zwierząt i Badań Żywności PAN (IRZBŻPAN)
  Tuwima 10, Olsztyn 10-747, Poland

Marta Ratter
bbaranowska@chem.uw.edu.pl
- Warsaw University, Faculty of Chemistry
  Pasteura 1, Warszawa 02-093, Poland

Ewa M. Rogalska
rogalska@lesoc.uhp-nancy.fr
- Universite Henri Poincare (UHP)
  Faculté des Sciences, BP 239, Nancy 54506, France

Iwona A. Rutkowska
ilinek@chem.uw.edu.pl
- Warsaw University, Department of Chemistry
  Pasteura 1, Warsaw 02-093, Poland

Gulnara R. Safina
gulnara207@hotmail.com
- Lund University, Pure and Applied Biochemistry Department
  Getingevägen 60, Lund SE-22100, Sweden

Hamid Sarraf
sarraf_20002000@yahoo.com
- RISO NATIONAL LABORATORY
  Roskilde DK-4000, Denmark
- Denmark Technical University, Department of Chemistry
  Lyngby 2800, Denmark
- Institute of Chemical Technology (VSCHT)
  Technicka 5, Prague 16628, Czech Republic

Caroline L. Schauer
caroline.schauer@gmail.com
- Drexel University
  3141 Chestnut St, Philadelphia 19104, United States

Wolfgang Schuhmann
wolfgang.schuhmann@rub.de
- Ruhr-Universität Bochum, Anal. Chem. - Elektroanalytik & Sensorik (ELAN)
  Universitätsstr. 150, Bochum 44780, Germany

Katarzyna Skorupska
skorupska@hmi.de
- Hahn-Meitner-Institute (HMI)
  Glienicker Str. 100, Berlin D-14109, Germany

Magdalena Skunik
mskunik@chem.uw.edu.pl
- Warsaw University, Faculty of Chemistry
  Pasteura 1, Warszawa 02-093, Poland

Andrzej Sobkowiak
asobkow@prz.rzeszow.pl
- Rzeszow University of Technology
  Rzeszów, Poland

Adam Sokołowski
adam.sokolowski@gmail.com
- Polish Academy of Sciences, Institute of Physical Chemistry
  Kasprzaka 44/52, Warszawa 01-224, Poland

Nickolaj F. Starodub
nstarodub@hotmail.com
- Ukrainian National Academy of Sciences, A. V. Palladin Institute of Biochemistry
  9 Leontovicha, Kyiv 01030, Ukraine

Zbigniew J. Stojek
stojek@chem.uw.edu.pl
- Uniwersytet Warszawski, Wydział Chemii
  Warszawa, Poland

Krzysztof Stolarczyk
kstolar@chem.uw.edu.pl
- Uniwersytet Warszawski, Wydział Chemii
  Warszawa, Poland

Dariusz Szmigiel
darek@ch.pw.edu.pl
- Instytut Technologii Elektronowej (ITE)
  al. Lotników 32/46, Warszawa 02-668, Poland

Sabine Szunerits
sabine.szunerits@lepmi.inpg.fr
- Institute National Polytechnique de Grenoble (INPG)
  1130, rue de la piscince, Saint Martin d'Hères 38402, France

Federico Tasca
federico.tasca@analykem.lu.se
- Lund University, Department of Analytical Chemistry
  Lund SE-221 00, Sweden

Matthew J. Thomasson
M.J.Thomasson@chem.hull.ac.uk
- Department of Chemistry
  University of Hull, Hull HU67RX, United Kingdom

Bernadette Tse Sum Bui
tsesum@ccr.jussieu.fr
- Compiegne University of Technology, UMR CNRS 6022
  Compiegne, France

Lilia S. Vladimirova
vladimirova@phys.uni-sofia.bg
- Univeristy of Sofia, Faculty of Physics (SU)
  5 James Bourchier Blvd., Sofia 1126, Bulgaria

Jay D. Wadhawan
j.wadhawan@hull.ac.uk
- Department of Chemistry
  University of Hull, Hull HU67RX, United Kingdom

Alain Walcarius
alain.walcarius@lcpme.cnrs-nancy.fr
- LCPME-CNRS
  Villers-les-Nancy 54600, France

Urszula E. Wawrzyniak
ulamaj@chem.uw.edu.pl
- University of Warsaw, Department of Chemistry
  Pasteura 1, Warsaw, Warszawa 02-093, Poland

Albin Wiśniewski
albin@chem.uw.edu.pl
- Warsaw University, Faculty of Chemistry
  Pasteura 1, Warszawa 02-093, Poland

Scott D. Wolter
woltersd@duke.edu
- Electrical and Computer Engineering, Duke University
  Durham, NC 27708, United States

Monika Wysocka-Żołopa
monia@uwb.edu.pl
- University of Białystok, Institute of Chemistry
  Hurtowa 1, Białystok 15-399, Poland

Eugene Yashina
yashinamsu@gmail.com
- Chemistry Department, Moscow State University
  Leninskie Gory, 1-3, Moscow 119992, Russian Federation

Martina Zamuner
martina.zamuner@unive.it
- Dipartimento di Chimica Fisica, Università Cà Focari di Venezia
  S. Marta 2137, Venezia 30123, Italy

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