

SMCBS 2003  
Surface Modification for Chemical and Biochemical Sensing

International Workshop  
Białowieża, Poland

November 13-16, 2003

**Programme  
and  
Book of Abstracts**



PIELASZEK RESEARCH  
BONIFACEGO 74/94  
02-936 WARSZAWA  
POLAND

TEL: +48(22)8425918  
E-MAIL: BOOKS@PIELASZEK.COM  
E-MAIL: CONFERENCES@SCIENCE24.COM

Copyright ©2003 by *pielaszek research*, all rights reserved

ISBN 83-89585-01-4

Cover designed by Renata Marczak

This book was set automatically by  
*Conference Engine* ©1998-2003 *pielaszek research*, all rights reserved  
Printed in Poland

SMCBS 2003 International Workshop

has been organized by

SURPHARE

'Surface Phenomena and Reactions'  
(Contract No. G5MA-CT-2002-04034)

Centre of Excellence in Competitive and Sustainable Growth  
European Commission Programme  
(Grow-2001-5.2)



# Contents

<b>Introduction</b>	<b>6</b>
Preface . . . . .	6
Organisers . . . . .	7
Honorary Committee . . . . .	7
International Scientific Committee . . . . .	7
Organizing and Programme Committee . . . . .	7
SURPHARE Center of Excellence . . . . .	8
General Information . . . . .	8
Management and administration . . . . .	9
OBJECTIVES . . . . .	10
INNOVATIVE CHARACTER . . . . .	10
WORKPLAN . . . . .	10
INTERNATIONAL ATTRACTION . . . . .	11
<b>Programme of SMCBS 2003 Workshop</b>	<b>12</b>
Thursday, November 13th . . . . .	12
Friday, November 14th . . . . .	12
Saturday, November 15th . . . . .	24
Sunday, November 16th . . . . .	32
<b>Address book</b>	<b>36</b>

# Introduction

## Preface

The present volume contains programme and abstracts of invited tutorial lectures, as well as contributed keynote lectures and short oral communications presented at the International Workshop, entitled 'Surface Modification for Chemical and Biochemical Sensing', SMCBS 2003. We are pleased and feel honored to host twenty distinguished foreign and Polish scientists who have kindly accepted our invitation to present their tutorial lectures.

The workshop is organized as a part of the activity of the Centre of Excellence (CoE) 'Surface Phenomena and Reactions' (SURPHARE) within the Sixth Frame Programme of the European Commission.

Surfaces of solid substrates of chemical or biochemical sensors, operating either in gas or liquid media, are usually modified for selective or, in some cases, even specific sensing. The workshop focuses on the art of chemical as well as non-chemical decorating of surfaces and resulting recognition activity of the sensors toward target analytes.

Main topics of the workshop cover various aspects of surface chemistry related to sensing and biosensing in solutions or gases including

- Chemical surface reactions
- Self-assembled monolayers (SAMs)
- Langmuir and Langmuir-Blodgett films
- Properties of thin films
- Chemically modified electrodes
- Polymer modified electrodes
- Novel techniques and instrumentation for surface examination
- Signal processing and detection techniques

The Organising Committee thanks all those who contributed to the workshop. Our gratitude is particularly due to the authors of the contributions, to the chairpersons and members of the International Scientific Committee. Also, we gratefully acknowledge the European Commission through SURPHARE CoE for financial support of the present scientific event.

On behalf of the Organising Committee, we welcome all workshop participants and readers of the present volume.

*Włodzimierz Kutner*  
Chairman  
Organising and Programme Committee

## Organisers

### Honorary Committee

- Prof. Alexander Jabłoński  
Director of the Institute of Physical Chemistry of the Polish Academy of Sciences Warsaw, Poland
- Prof. Janusz Flis  
Coordinator of the SURPHARE Centre of Excellence at the Institute of Physical Chemistry of the Polish Academy of Sciences, Warsaw, Poland

### International Scientific Committee

- Prof. Tibor Hianik (Comenius University, Bratislava, Slovak Republic)
- Prof. Francis D'Souza (Wichita State Univ., Wichita KS, USA)
- Prof. Paweł Kulesza (Warsaw University, Warsaw, Poland)

### Organizing and Programme Committee

- Chairman: Prof. Włodzimierz Kutner
- Members: M.Sc. Agnieszka Kochman and M.Sc. Renata Marczak

# The Institute of Physical Chemistry Centre of Excellence 'Surface Phenomena and Reactions' SURPHARE

## General Information

The basic aims of the initiation of the SURPHARE were to enhance the network co-operation between different scientific institutions and to strengthen the links between centres working in the field of surface science. The Centre intends to raise competence of its research personnel and become the leading institution attracting top scientists and young researchers.

Surface science and surface engineering have been developed since early sixties of the last century. Fast development of these fields was stimulated by progress in vacuum technology. Surface science and surface engineering include studies on formation of surfaces with defined chemical composition, structure and physical properties as well as studies on phenomena and chemical reactions at surfaces. The research results make it possible to select the technology suitable to obtain materials with well defined surface parameters.

Surface phenomena occurring in the boundaries of solids, liquids and gases play an important role in industrial processes and their recognition can influence engineering projects. The processes important in industry and technology include chemical catalysis, corrosion protection, power industry (fuel and solar cells), processing of plastic materials, modern electronics of integrated circuits, industry of machine design, and systems of selective detection (microsensor membranes using modern selective receptor systems).

Finding out mechanisms of the physicochemical processes, running under known thermodynamic conditions at the phase boundaries, is the way to control the formation or modification of the surface with well defined properties. In order to determine these properties it is necessary to perform studies applying wide range of experimental and theoretical methods that allow characterisation of the surface as well as monitoring and describing the processes occurring on them. The experimental techniques for surface studies available in CoE include Auger electron spectroscopy (AES), photoelectron spectroscopy (UPS and XPS, ESCA), infrared spectroscopy (IR), isotherm desorption spectroscopy (IDS) and thermally stimulated desorption (TDS), atomic force microscopy (AFM), scanning tunnelling microscopy (STM), low energy electron diffraction (LEED), X-ray diffraction (XRD), Langmuir-Blodgett (LB) trough facility.

The Centre is engaged in the following main research activity:

**Heterogenic catalytic reactions** - comprises making new compounds of the required physicochemical properties and controlling elementary steps of surface processes occurring during reaction. Efficiency and selectivity of the catalyst are determined by the formation of expected forms of reagents on the catalyst surface. The following aspects of these studies are emphasized: quantitative description of chemical composition of the surface, definition of the surface structure in atomic and nanometer scale including the vacancies and defects as well as adsorbed molecules, construction of the modern catalysts in which the active particle is introduced to the selected place in the catalyst carrier.

**Metal hydrides** - formation of hydrides by using a high pressure technology and electrochemical methods; adsorption of hydrogen and its ingress into metals.

**Electron spectroscopy** - surface analysis by AES, XPS, and elastic scattering; theory of elastic backscattering of electrons on surfaces.

**Evaporated metal layers** - chemical reactivity.

**Corrosion and protection** - surface modification for enhanced protection against corrosion.

**Thin films for chemical and biochemical sensing** - preparation and property studies of both the molecular-layer-thick and polymer surface films on solid electrodes for electrochemical and piezoelectric microgravimetry sensing of target analytes.



Scientists of CoE collaborate with their partners in industrial enterprises in evaluating, designing the apparatus and working up the technological methods. Establishing of SURPHARE CoE results in bringing together scientists of the Institute engaged in surface science and facilitates collaboration with industry.

The aims of the Centre are to:

- develop a scientific co-operation with other surface science laboratories in Europe
- intensify personal contacts
- exchange information related to recent advances in surface science
- increase the education level and research experience of young scientists.

These objectives are realised by organising international conferences and workshops as well as exchanging scientists. Scientists and PhD students of the Institute are sent to other research institutions for training and for gaining experience in the advanced research techniques. Also, researchers from other institutions are hosted in the Centre for training and for a joint study in surface science.

The conferences and workshops focus on surface phenomena encountered in corrosion, on characterisation and modification of surfaces for enhancement of their catalytic activity and the ability of selective sensing of analytes of interest. A work is also conducted to strengthen the co-operation on standardisation and quantification of the surface science techniques.

## Management and administration

The Centre is managed by Prof. Janusz Flis, head of the Electrochemistry and Corrosion Department of the Institute and the Centre Coordinator, supported by the International Advisory Board, Coordination Board, and Task Leaders. The Centre is also supervised by the authority of the Institute whose part the Centre remains.

### Management structure of the Centre

The International Advisory Board consists of five members, i.e., the Director of the Institute of Physical Chemistry, Prof. Aleksander Jabłoński, and four distinguished scientists from other European research centers.

- Prof. Dr. B. Gruzza, Surfaces and Interfaces Group, Physics Department, Blaise Pascal University, Clermont-Ferrand, France
- Prof. Dr. Waldfried Plieth, Department of Mathematics and Nature Sciences of the Institute of Physical Chemistry and Electrochemistry, Dresden Technical University, Dresden, Germany
- Prof. Dr. Sven Tougaard, Physics Department, University of Southern Denmark, Odense, Denmark
- Prof. Dr. K. Wandelt, Institute of Physical and Theoretical Chemistry, Bonn University, Bonn, Germany.

The Coordination Board comprises all Task Leaders:

- Prof. Janusz Flis (WP1 and WP7)
- Prof. Stanisław Filipek and Prof. Maria Czachor (WP2)
- Dr. Anna Maciołek (WP3)

- Prof. Włodzimierz Kutner (WP4)
- Prof. Aleksander Jabłoński (WP5)
- Dr. Iwona Flis-Kabulska (WP6)

and also other researchers of the Institute.

## OBJECTIVES

The importance of solid surfaces in different areas of technology is growing continuously, including design of catalysts, modern microelectronics, polymers, in corrosion science and engineering, advanced materials for new process technology and for engineering structures. Research in this area requires multidisciplinary approach to problem solving and highly sophisticated instrumentation. Because of relatively high cost of this instrumentation for analysis and modification of surfaces, the surface research should be conducted jointly by the organisations hiring highly qualified personnel and equipped with that instrumentation. Accordingly, the main objective of the CoE activity is to promote scientific collaboration with laboratories, which are well equipped with adequate instrumentation.

## INNOVATIVE CHARACTER

The innovation offered by the Centre consists mainly in the intensive dissemination of knowledge in the field of surface science, and in standardisation of measurement techniques. The emphasis is put on surface analysis, surface modification, characterisation of surface processes, and on presentation of advanced research techniques. These goals are realised by organising scientific symposia and workshops. The work is being performed on standardisation and quantification of surface science techniques. Great effort is put on training of young scientists in using advanced techniques for surface characterisation and modification.

## WORKPLAN

The proposed activities of SURPHARE are presented in seven Work Packages, WP1 through WP7.

Four packages, WP1 through WP4, involve scientific meetings. In total, five conferences and workshops are being organised during three year period of the CoE activity. The aim of these meetings is to provide information on advances in surface science, to share experience in the modern experimental techniques, and to launch joint research proposals for the nearest future. Internationally renown scientists from European and other countries are invited to the conferences and workshops to teach and pass their knowledge to students and young researchers. Particularly, young scientists are strongly encouraged to participate in the meetings.

Work Package WP5 is foreseen to strengthen co-operation on standardisation and quantification of surface science techniques, whereas Work Package WP6 focuses on training of Centre's scientists and PhD students by co-operation with internationally renown laboratories. Work Package WP7 involves the management of the Centre.

**WP1** Conference 'Advances in Corrosion Science and Application' main themes: (i) Surface modification for corrosion protection; (ii) Modern surface analytical techniques in corrosion science, Zakopane, September 2003. Person responsible in the Centre: Prof. Janusz Flis

**WP2** Conference 'New Methods of Modification of Reactivity of Amorphous and Nanocrystalline Materials' Warsaw, Summer 2003. Persons responsible in the Centre: Prof. Stanisław M. Filipek and Prof. Maria Janik-Czachor

**WP3** 'Workshop on Morphology of Surfaces and Interfaces in Soft Matter. Fundamentals and Applications', Jadwisin, Summer 2003 Person responsible in the Centre: Dr. Anna Maciołek.

- WP4** 'International Workshop on Surface Modification for Chemical and Biochemical Sensing', Białowieża, November 13-16, 2003. Person responsible in the Centre: Prof. Włodzimierz Kutner
- WP5** Strengthening of co-operation on standardisation and quantification of surface science techniques. Person responsible in the Centre: Prof. Aleksander Jabłoński
- WP6** Training of scientists and PhD students in surface science methods. Persons responsible in the Centre: Dr. Iwona Flis-Kabulska Prof. Zbigniew Karpiński and Prof. Jerzy Pielaszek Dr. Beata Lesiak-Orłowska Dr. Robert Nowakowski
- WP7** Management and co-ordination of the Centre. Person responsible in the Centre: Prof. Janusz Flis

## INTERNATIONAL ATTRACTION

Research results are presented at different national and international scientific meetings. Then, they are published in scientific specialty journals or as monographs; some results are directly applied in industrial processes. Interdisciplinary attitude of the Institute to science requires a large co-operation between the Departments and other research centres. Active participation of the scientists from the Institute in international events attracts other centres to mutual co-operation.

Every year over a hundred scientists from Europe, America and Asia visit our Institute. Majority of visits is connected with participation of our guests in conferences and symposia. Many scientists from European and other countries collaborate with researchers of the Institute by giving lectures and by being engaged in the join research. Our top quality commercial and unique home-built instrumentation encourages foreign researchers to perform experiments in our laboratories.

SURPHARE is engaged in the long-term co-operation with scientific institutions of Europe and other continents. The researchers of the Centre are involved in eleven international and national research projects. Moreover, they collaborate with industrial enterprises, such as power stations and refineries. Competence of the scientists and fluency in foreign languages (English is spoken by almost all the researchers while German, French and Russian are less popular) enable the researchers from the Institute to co-operate with their peers in partner institutions of other countries.

# Programme of SMCBS 2003 Workshop

---

## Thursday, November 13th

---

12:00 - 13:00

### Lunch

Institute of Physical Chemistry, Kasprzaka 44, 01224 Warsaw

---

13:00 - 14:00

### Registration, Agnieszka Kochman and Renata Marczak

Institute of Physical Chemistry, Kasprzaka 44, 01224 Warsaw

---

14:00 - 18:00

### Departure for Bialowieza

We will arrive in Bialowieza by bus at around 18:00

---

19:00 - 20:00

### Get-together party

---

## Friday, November 14th

---

07:00 - 08:00

### Breakfast

---

08:00 - 10:15

### Session 1, Chairpersons - Francis D Souza, Włodzimierz Kutner

---

8:00 - 8:40

#### Molecularly Imprinted Polymers in Analytical Chemistry

**Karsten Haupt**<sup>1)</sup>

Tutorial  
lecture

*1) Compiègne University of Technology, UMR CNRS 6022, Compiègne, France*

Molecular imprinting of synthetic polymers is a process where functional and cross-linking monomers are copolymerised in the presence of a target molecule (the imprint molecule), which acts as a molecular template. The functional monomers initially form a complex with the imprint molecule, and following polymerisation, their functional groups are held in position by the highly cross-linked polymeric backbone. Subsequent removal of the imprint molecule reveals binding sites that are complementary in size and shape. In that way, a molecular memory is introduced into the polymer, which is now capable of selectively rebinding the target.

Molecularly imprinted polymers can be regarded as antibody or receptor binding site mimics and have been applied in applications where molecular binding events are of interest, including tailor-made separation materials, antibody and receptor mimics in immunoassays and screening systems, and recognition elements in biosensors. These applications benefit from the higher chemical and physical stability of molecularly imprinted polymers compared to their biological counterparts, and their comparatively low cost.

This talk will cover the general principle of the molecular imprinting technique, as well as the main applications of imprinted polymers, with special emphasis on immunoassays and biosensors.

---

8:40 - 9:20

#### The Solution-polymer Interface: PVC ISE-s and MIP-s

**George Horvai**<sup>1)</sup>, **Tímea Pap**<sup>2)</sup>

Tutorial  
lecture

*1) Budapest University of Technology and Economics, Dept. Chem. Inf. Techn., Gellert ter, Budapest H-1111, Hungary*

*2) Techn. Anal. Res. Group of the Hung. Acad. Sci., Gellert ter 4, Budapest H-1111, Hungary*

Polymer-liquid interfaces constitute the sensing area of several sensors. Adsorption at this interface contributes to sensing the analyte and to various types of interferences. In this lecture we show results concerning the structure of two interesting systems:

1. Ion-selective membranes made from plasticized PVC and used in aqueous solutions
2. Molecularly imprinted polymers used in different solvents

Most commercial ion-selective sensors for clinical analysis are made with plasticized PVC membranes. The structure of plasticized PVC is not well understood and the compositional changes in the immediate vicinity of the surface were completely unknown. We have shown by various spectroscopies that concentration gradients of different components penetrate at different depths into the membrane. Interestingly the surface-near region was found to be almost pure liquid plasticizer without much polymer. This result has been used recently by others for different purposes. Plasticized polyurethane sensor membranes were found to behave in the same way and this is important for biocompatibility. Fundamental electrochemical studies to determine ion transfer rates at ITIES could be carried out using the plasticized PVC interface.

Molecular imprinting is an attractive way to create very selective adsorbents. These can be used for example in QCMB sensors. The response and particularly the selectivity of such sensors depends crucially on the adsorption isotherms of individual substances and mixtures. We could recently show that simultaneous adsorption of two substances may not only lead to competition but also to synergy. Selectivity studies have also helped to understand how individual molecules are adsorbed and what can be the structure of the binding sites.

---

## Electron Transfer Reactions of Heme-containing Enzymes at the Electrodes: Bioelectrocatalysis and its Optimisation

9:20 - 9:40

**Elena E. Ferapontova**<sup>1)</sup>

Keynote  
lecture

*1) Centre for Chemistry and Chemical Engineering, Lund University (KC), Lund SE-221 00, Sweden*

Direct electrochemical studies of biological ET reactions with redox enzymes enable the development of highly efficient bioelectrocatalysts of interest. The obligatory condition for these studies is the existence of a direct electronic communication between the electrode and the enzyme redox active sites. When enzyme-electrode interactions provide this, then direct bioelectrocatalysis can be studied under conditions when the electrode replaces the natural redox partner of the enzyme. However, direct ET of the enzymes at the electrodes is sometimes not attained or accompanied by the loss of enzymatic activity, as in the case of multifactor-containing enzymes, which successful operation at the electrode requires internal ET between their active sites in addition to the electrode-enzyme ET reaction. Mimicking the natural environment of these enzymes by the modified electrodes is then of particular interest. Therewith, a simulation of the molecular surfaces of the enzyme biological partners by self-assembled monolayers of alkanethiols may provide the necessary amount/orientation of the enzyme molecules for direct ET reaction with the electrode, as well as a conformation appropriate for efficient intramolecular ET.

It is discussed how the choice of the electrode material/electrode modification and solution composition affect ET reactions of heme-containing enzymes. Direct ET reactions between the electrodes and cytochrome c, a model ET enzyme, as well as direct bioelectrocatalysis of H<sub>2</sub>O<sub>2</sub> reduction based on direct ET from the electrode to the heme active site of horseradish peroxidase, one of the most studied members of the family of the heme enzymes, are covered in detail. It is also reported how the choice of alkanethiols of different polarity/hydrophobicity and charge might provide the surface properties of the electrodes necessary for adsorption and orientation of the multifactor heme-containing enzymes favourable for efficient electrode-assisted biocatalysis.

---

## Studies of New Procedures for Sensors and Biosensors Development Based on Modified Gold and Platinum Supports

9:40 - 10:00

**Simona Carmen Litescu**<sup>1)</sup>, **Camelia Bala**<sup>1)</sup>, **Jean-Louis Marty**<sup>2)</sup>

Keynote  
lecture

*1) Faculty of Chemistry, University of Bucharest, Panduri 90, Bucharest, Romania*

*2) Centre de Phytopharmacie, Université Perpignan, Perpignan, France*

Possible new procedures devoted to sensor and biosensors development using deposited layers on solid supports were studied, the characteristics of the resulted systems and their potential applications being presented.

Solution casting, spin coating and electrochemical treatments were studied and compared as possible deposition procedures. Advantages and drawbacks of each used method were pointed out as result of the carried out studies oriented to two different aims: enzyme immobilisation, respectively the development of a potential electrochemical model for antioxidants properties evaluation.

Studies dedicated to enzymes immobilisation initiated with the study of self-assembly structuring of several well-known mercapto-derivatives (glutathion, cysteamine, 16-mercaptodecanoic acid) on solid supports, and, as result of the obtained data, reached to the deposition of mercapto-silane derivatives (3-aminopropyl triethoxy silane-3APTS, and 3-mercapto-trimethoxy silane-3 MTMSy) on the same kind of supports. Electrochemical, spectrochemical (Fourier Transform Infrared) and Scanning Electron Microscopy characterisations were performed. An optimum procedure, able to ensure a good degree of deposition reproducibility for 3-amino-propyltriethoxysilane

and 3-mercaptopropyl trimethoxysilane was established. The deposited layer was electrochemical, FTIR and SEM characterised proving homogenous distribution of functional groups on layer surface.

Potential applications of the developed system to acetylcholinesterase immobilisation were considered.

A LDL- gold modified electrode was developed and was used as lipidic model for the properties assessment of two of the most commonly used phenol-like preservatives, the deposited surface being characterised. The resulted tool was applied to antioxidative potentiality monitoring of investigated compounds in bulk system using two sources of free radical attack, other possible applications being envisaged.

10:00 - 10:15

## Effect of Support Material and Conditioning on Wettability of PAH/PSS Multilayer Films

Short communication

**Marta Kolasińska<sup>1)</sup>, Piotr Warszyński<sup>1)</sup>**

*1) Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences, 9 Niezapominajek, Krakow, Poland*

The technique of layer-by-layer (lbl) deposition of polyelectrolytes allows to control the total thickness of multilayer film and its structure on a molecular level. Due to versatility of this technique, such self-assembled polyelectrolyte films have a great application potential. That is, they can be used for chemical and biochemical sensing, as separation membranes for gases or dissolved species and for modification of surface properties, which is of special importance in biomaterial area. It is often assumed that the properties of the polyelectrolyte multilayer films are independent of the underlying substrates. However, there should exist a minimal number of layers above which the properties of the system are governed by the choice of polycation/polyanion pair. The structure of the multilayer films is also strongly dependent on the deposition conditions and the most frequently used control parameters are ionic strength and pH of the solution. Also the long-time exposure to the conditions different than those encountered during deposition usually leads to the change of the polyelectrolyte multilayer structure.

We developed efficient method for characterizing wettability of heterogeneous surfaces produced by 'layer-by-layer' adsorption of polyelectrolytes. Three types of polyelectrolytes were used in our studies: polyallylamine hydrochloride (PAH) of a cationic type, polysodium 4-styrenesulfonate (PSS) of an anionic type, both having molecular weight of about 70 000 and polyethyleneimine (PEI) of about 75 000. As the support materials for deposition a natural ruby mica, glass, titanium foils and unpolished silicon wafers were used. Adsorption of polyelectrolytes was performed from NaCl solutions of various concentrations under natural pH and from Tris buffer at pH=7.4. The contact angle of substrates covered by polyelectrolyte multilayers was determined by using direct image analyzing technique of sessile drops. Periodic oscillations in contact angle values were observed for multilayers terminated by PAH and PSS, respectively, PAH being more hydrophobic. However, amplitude of the contact angle variations depended on the electrolyte used for deposition and was the smallest for low electrolyte concentration suggesting significant interpenetration of oppositely charged layers of polyelectrolytes. It was also observed that starting from the third PAH/PSS layer deposited from 0.15 M NaCl, the contact angle of water on consecutive polyelectrolyte layers was practically independent of the substrate. When examining the effect of long time conditioning in solution of various pH on wettability of films, we found that the film becomes more hydrophilic after conditioning in pH=3 and pH=11 but in neutral pH the wetting of the film does not change. However, while after acidic treatment of the multilayer film the periodic oscillations in contact angle values were still observed, there were practically no oscillations between consecutive layers when they were treated with basic solution. This behavior suggests either the partial removal of the film or some major structural changes within the film together with OH<sup>-</sup> incorporation.

10:15 - 10:35

## Cofee break

10:35 - 12:50

## Session 2, Chairpersons - George Horvai, Krzysztof Maksymiuk

10:35 - 11:15

## Conjugated Polymers to Build up Biosensors: Implementation of Biochips

**Gerard M. Bidan<sup>1)</sup>**

Tutorial lecture

*1) CEA-Grenoble, DRFMC/SI3M, UMR 5819 SPrAM, 17 rue des Martyrs, Grenoble 38054, France*

Implementation of electroconducting conjugated polymer, ECP, based sensitive layers to build up (bio)sensors, appears to offer a number of advantages over other technologies: (i) ease of construction, (ii) various routes of functionalisation of surfaces, (iii) chemoelectronic properties, i.e. ability to transduce a (bio)chemical recognition event into an electrical signal.

1. ECPs as a matrix for specific immobilisation of receptors

(i) The synthesis of films onto electrode surfaces by electropolymerization of monomers in solution is easily obtained. The thickness of the deposit is directly related to the amount of electricity passed during the electropolymerization reaction. This easy electrodeposition on an electrode surface opens the route to miniaturization since the deposit cover exactly the surface of the metallic dot; (ii) a versatile functionalization by biological moieties either by grafting or doping, that allows the assembly of a myriad of (bio)receptors at the surface of electrodes enabling one to perform selective recognition.

2. ECPs as sensitive components

The redox state (doping level), ionic transport and electronic transfer properties of ECP films are collective properties, which are sensitive to minor (bio)chemical interactions. These (bio)chemical perturbations result in transducible responses such as changes in electronic conductivity, UV-vis absorption spectrum, voltamperometric curve or photocurrent signal.

The potentialities of ECPs as passive supports or structural materials to provide a stable environment to the receptor have been exploited in the construction of various electrochemical biosensors such as enzymatic sensors and immunosensors. The electrochemical addressing is a key point for constructing sensor arrays and allows an easy miniaturisation since semiconductor microfabrication techniques can be easily used to create multielectrode devices. This will be illustrated by the presentation of our methodology for the preparation of addressed DNA matrices (DNAchips) [1]. Electrospotting involving a moving electrochemical cell tip has been proven to be fruitful for the creation of an ECP pattern on a unique gold electrode and allows multiparametric imaging by Surface Plasmon Resonance technique [2].

Enzyme, single stranded DNA sequence or peptide [3] immobilisation's onto or into ECP films will illustrate one-step functionalisation or post-functionalisation. The need for versatile processes for the immobilisation of biological species onto surface led us to develop a more general grafting based on affinity interactions between a biotinylated polypyrrole substrate and the biological probe. A surface renewable DNA sensor [4] has been developed. Taking into account the availability of a wide variety of avidin or biotin conjugates, this new approach enables the study of biosensing behaviour of many commercial biomolecules.

The ECP matrix may act as a mediator for the electrical wiring of enzymes. Literature results and our recent data on electrochemiluminescence detection on polypyrrole will be presented

Interfacing ECP materials with biology appears to be a very promising area leading to miniaturised and multiparametric sensors based on a wide panel range of analyte-receptor interactions.

#### REFERENCES

1. G. Bidan, M. Billon, K. Galasso, L. Livache, G. Mathis, A. Roget, L. M. Torres-Rodriguez, and E. Vieil, *Appl. Biochem.*, 89 (2000) 183.
2. P. Guedon, T. Livache, F. Martin, F. Lesbre, A. Roget, G. Bidan, and Y. Levy, *Anal. Chem.* 72 (2000) 6003.
3. T. Livache, H. Bazin, P. Caillat, and A. Roget, *Biosensors and Bioelectronics*, 13 (1998) 629.
4. A. Dupont-Fillard, A. Roget, T. Livache, M. Billon, *Anal. Chim. Acta*, 449 (2001) 45.

---

## Modified Electrodes Based on Lipidic Cubic Phases

Renata Bilewicz<sup>1)</sup>

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

Retaining enzymes in functionally-active forms on the electrode surface is a challenging and difficult task. Liquid crystalline phases formed by polar lipids in aqueous media are widely used as model matrices to mimic biological processes. The lipidic cubic phase can be characterized as a curved bilayer forming a three-dimensional crystallographically well-ordered structure that is interwoven by aqueous channels. It provides a stable, well-organized environment in which diffusion of both water-soluble and lipid-soluble compounds can take place. The phases are isotropic and optically transparent and, therefore, they are ideal matrices also for spectroscopic investigations by which the functionality of any active site present in the matrix can be probed. Small solutes and water-soluble proteins diffuse within the network of aqueous channels allowing crystallization from this compartment.

Cubic phases based on monoacylglycerols form readily and have attracted large interest due to their ability to incorporate and stabilize membrane proteins. Their lyotropic and thermotropic phase behaviour have been thoroughly investigated. Phase diagram of monoolein (monooleoyl-rac-glycerol, MO), water mixtures will be described. At hydration over 20% lipidic cubic phases Ia3d and Pn3m are formed. The latter are stable in the presence of excess of water. The cubic phase is a gel-like material which upon introduction of some compounds or large concentrations of supporting electrolyte, may undergo phase transition, so the phase should be monitored, preferably by polarized light microscope. Deterioration of cubic phase is reflected by turbidity. Cubic phases Pn3m can be stored for days without any phase transitions even at temperatures as low as 5°C. Due to high viscosity and stability in the presence of water these cubic phases can be simply smeared over solid substrates such as electrodes and used to host enzymes and synthetic catalysts leading to new types of catalytically active modified electrodes. We have shown earlier that cubic phase modified electrodes are useful for the determination of cholesterol and CO<sub>2</sub> (Ropers et al. 2001, Rowiński et al. 2002, 2003).

In order to describe the efficiency of transport of small hydrophilic molecules within the film we determined loading times, diffusion coefficients and concentrations of selected redox mediators in the layer by voltammetry and chronocoulometry. Two types of electrodes were used: a normal size electrode working in the linear diffusion regime and an ultramicroelectrode working under spherical diffusion conditions. This allowed to determine together concentration and the diffusion coefficient in the medium in direct contact with the electrode surface

The monoolein-based cubic phase matrix was used for immobilizing laccases from *Trametes sp.* and *Rhus vernicifera* on the electrode surface. The contact between the electrode and the enzyme was maintained using suitable electroactive probes. Using the probe in its oxidized form allowed turning the reaction on or off, by applying an adequate potential to the electrode and generating the probe in the form undergoing the enzymatic transformation. The electrodes modified with cubic phases containing laccase and the hydroquinone/quinone couple were used for reducing dioxygen in aqueous solutions.

11:15 - 11:55

Tutorial  
lecture

## References

1. M.-H. Ropers, R. Bilewicz, M.-J. Stebe, A. Hamidic, A. Micloc, E. Rogalska, *PhysChemChemPhys.*, 3 (2001) 240.
2. P. Rowinski, R. Bilewicz, M. J. Stebe, E. Rogalska, *Anal. Chem.*, 74 (2002) 1554.
3. P. Rowinski, A. Korytkowska, R. Bilewicz, *Chem. Phys. Lipids.*, 124 (2003) 147.

11:55 - 12:15

Keynote  
lecture**Surface Potentials: The Unexplored Way to Develop Sensors for Small Organic Ions and Large Biomolecules****Luc J. Nagels<sup>1)</sup>***1) Chemistry Department, Antwerp University, Groenenborgerlaan 171, Antwerpen B-2020, Poland*

Many surfaces develop potentials when they contact solutions containing ionized substances. Very often, intermolecular attractions between the surface materials and the ionized substances are the basis of these "non-Faradaic" potentiometric phenomena. Until now, potentiometric sensing has made little use of the phenomenon to determine small organic ions and large biomolecules. Some reasons for this slow evolution are the lack of good theoretical models, and the lack of synthetic receptor molecules to attract small organics and large biomolecules to the specific surfaces used in potentiometry. Our group developed equipment to screen potentiometric electrode coatings for the determination of ionizable organics, using HPLC and CE. This equipment speeds up coating testing and allows one to perform measurements on less available but important (bio-)organics. Organic acids, oligonucleotides, amines, aminoalcohols, pharmaceutical drugs, analgesic drugs, and proteins have been dealt with so far. The electrode coatings that are most successful are the so-called "liquid membrane" types, based on PVC. When macrocyclic or podant host molecules are incorporated, the best recognized organic substances can be determined with extremely low detection limits. These host molecules are very efficient for the determination of a very important class of hydrophilic compounds. This approach is shown to work also for large biomolecules such as oligonucleotides. Another way of decreasing detection limits for the hydrophilic compounds is to increase the hydrophilicity of the electrode coating surface. For proteins, we used antibodies linked to the surface of conductive polymers as a recognition strategy. Applications of the electrode coatings will be shown in application for detection in HPLC and CE, as well as links will be given to DNA- and proteome chip technology.

12:15 - 12:35

Keynote  
lecture**Solid Amalgam Electrodes and Alloy Electrodes for Electroanalysis****Oyvind Mikkelsen<sup>1)</sup>, Silje M. Skogvold<sup>1)</sup>, Knut H. Schroder<sup>1)</sup>***1) Department of Chemistry, Norwegian University of Science and Technology (NTNU), Trondheim N - 7491, Norway*

Liquid mercury is a unique material for the working electrode in voltammetry because of its high negative potential of hydrogen evolution, its ability to form liquid amalgams and the possibility to regenerate continuously a new electrode surface simply by dripping out a new mercury drop from a glass capillary. However, mercury is considered as a toxic heavy metal and, therefore, should be avoided in online apparatuses for use in field.

Because voltammetry is very suitable for field and remote monitoring, issues concerning the use of mercury electrodes in environmental analyses have led to considerable research effort aimed at finding alternative to mercury electrode materials with comparable or better performance.

In this presentation an overview of several compact (non-film) solid amalgam and alloy electrodes will be given, including the dental amalgam electrode [1, 2], silver electrodes alloyed with only a few percent of mercury, silver-bismuth electrode, gold-bismuth electrode, silver-copper electrodes, etc.

The accessible potential windows in different electrolyte solutions for these electrodes will be systematically presented and discussed as well as their possibility for use in detection of several different metals including cobalt, nickel, zinc, cadmium, iron, lead, copper, mercury, and silver in low ppb and sub ppb level in real samples will be given. In particular, solid amalgam electrodes are very promising, with acceptable low toxicity, for use in field measurements. Assessment of the toxicity risk and the long-time stability for remote and unattended monitoring will be discussed.

The differences between homogeneous amalgam electrodes, prepared by using techniques known from dental clinical practice, and mercury film or mercury layer electrodes on solid substrates will be reviewed as well. Analogous comparisons will be presented for compact (non-film) alloy electrodes.

Key words: Anodic stripping voltammetry, Solid electrodes, Dental amalgam, Mercury electrode, Heavy metals, Alloy.

## REFERENCES

1. O. Mikkelsen and K. H. Schroder, *Electroanalysis* 15 (2003) 679.
2. O. Mikkelsen and K. H. Schroder, *Electroanalysis* (2003) in press.

12:35 - 12:50

Short com-  
munication**Determination of Silver and Copper at Low ppb and sub-ppb Concentration Ranges in Mixture in Natural Water by Using Anodic Stripping Voltammetry at a Gold-bismuth Alloy Electrode**



**Oyvind Mikkelsen<sup>1)</sup>, Silje M. Skogvold<sup>1)</sup>, Knut H. Schroder<sup>1)</sup>**

1) Department of Chemistry, Norwegian University of Science and Technology (NTNU), Trondheim N - 7491, Norway

A procedure of detecting copper and silver at low ppb and sub-ppb concentration ranges in mixtures in natural water was developed. Both these metals influence significantly biological life in natural water and are considered to be highly toxic even if present in trace amounts.

Our procedure involves the use of differential pulse anodic stripping voltammetry (DPASV) along with the working electrode of a gold alloy containing 4% bismuth. The procedure has been tested and found appropriate for determination of artificial samples prepared by using distilled water as well as for real samples, like spring-, river- and seawater. In the river and seawater samples, copper and silver present in a sub-ppb range was detected with a standard deviation close to 5% by the use of a standard addition method.

The gold alloy electrode containing small amount of bismuth was found to be stable for several weeks, and having a stable baseline making baseline subtraction possible and thereby improving detectability. The copper and silver DPASV peak in 0.05 M NH<sub>4</sub>Cl was observed at +275 mV and +800 mV, respectively. Moreover, potential of hydrogen evolution was more negative and time stability was higher of the gold-bismuth alloy electrode than those of the genuine gold electrode.

The results show that this electrode can be used over a long period of time without any maintenance, which is important for online determination of pollutants in soil and groundwater.

Key words: Differential pulse anodic stripping voltammetry, Gold-bismuth electrode, Seawater, Copper, Silver, Alloy.

**Lunch**

12:50 - 13:50

**Session 3, Chairpersons - Francesco Paolucci, Wolfgang Schuhmann**

13:50 - 16:05

**Design, Synthesis and Characterization of Monomolecular Interfacial Layers**

13:50 - 14:30

**Gary J. Blanchard<sup>1)</sup>**

1) Michigan State University, Department of Chemistry (MSU), East Lansing 48824, United States

Tutorial lecture

Chemical sensing poses a challenge because it requires both sensitivity and selectivity for success. For many measurement schemes, sensitivity occurs at the expense of selectivity. To overcome this limitation, a sensitive detection technique is usually coupled to a highly selective screening system. We use monomolecular films to induce selectivity because they afford high permeability and excellent control over chemical identity. Following an overview of interfacial binding chemistry we use, we will focus on two different applications of monomolecular films to underscore the versatility of this structural motif.

We have designed ultrathin polymer layers to achieve differential control over adsorption and desorption kinetics of selected vapor phase molecules. We synthesize and deposit maleimide-vinyl ether alternating copolymer layers, where each polymer layer contains different pendant side group functionalities, and the order of layer deposition is controlled. The adsorption isotherm behavior of these interfacial structures, when exposed to methanol and hexane vapor, shows that the identity of the adsorbates and the order of polymer adlayer deposition both influence the interfacial adsorption characteristics.

We will also cover the growth and characterization of amphiphilic biomimetic assemblies grown on gold and ITO substrates. One assembly possesses a moiety capable of forming an intermediate hydrophilic region with amides that can participate in a hydrogen-bonding network within the monolayer (C<sub>6</sub>-A-C<sub>12</sub>), and the other is a tetradecane structure (C<sub>14</sub>). These structures present hydrophobic aliphatic chains to an adsorbate and are useful for subsequent deposition of a lipid monolayer, to form a hybrid bilayer membrane (HBM). Examination of the capacitance, cyclic voltammetry and FTIR data for the C<sub>6</sub>-A-C<sub>12</sub> and C<sub>14</sub> systems demonstrates their stability and organization, while preserving some fluid-like behavior, essential for biomimetic applications.

**Spectroscopic and Electrochemical Characterization of Interfacial Biomimetic Assemblies for Biosensors**

14:30 - 15:10

**Paweł G. Krysiński<sup>1)</sup>, Gary J. Blanchard<sup>2)</sup>**

Tutorial lecture

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

2) Michigan State University (MSU), East Lansing 48824-1322, United States

We have synthesized several novel biomimetic interfacial structures through the covalent growth of individual layers on oxide-based, electrochemically active substrates (e.g. gold oxide, ITO, boron-doped diamond). Our goal is to deposit selected biomolecules on conductive substrates in such a manner as to retain their biological activity. We have constructed model hybrid bilayer membrane structures, approximating a lipid bilayer structure. The covalently bound self assembled monolayers (SAMs) we report here are characterized by a hydrophilic region adjacent to the electrode surface, with hydrophobic structure beyond the hydrophilic region. Next there is a second hydrophilic

region comprised of amide bonds, that are terminated with aliphatic chains. The route we describe is general; the adlayer moieties can be controlled synthetically and the properties of the substrate can be controlled by choice of material. Our aim is to control the adlayer structure, thickness and spacing of hydrophilic and hydrophobic regions to produce interfacial films that can function as hybrid bilayer matrices (HBMs). We characterize these systems using picosecond time-resolved and steady-state fluorescence and infrared spectroscopies in conjunction with electrochemical measurements. We have studied the role and importance of molecular motion within the layers and evaluated the dipolar coupling between imbedded chromophores and the substrate. While the dominant interactions in SAMs are thought to be the bond between the adlayer molecule head group and the substrate, and between the layer constituent molecules, longer range dipolar interactions between the substrate and any distant adlayer functionalities are often neglected. Such interactions are likely to be important in the formation of hybrid bilayer lipid membrane structures that represent a biomimetic interface capable of hosting and maintaining activity of biomolecules in a non-biological, electronically addressable environment.

15:10 - 15:30

Keynote  
lecture

## Electrochemical Sample Pretreatment and Detection Techniques for Lab-on-a-Chip Applications

**Leif Nyholm<sup>1)</sup>, Gustav Liljegren<sup>1)</sup>, Oliver Klett<sup>2)</sup>**

1) *Uppsala University, Department of Analytical Chemistry, P.O. Box 599, Uppsala, Sweden*

2) *Uppsala University, Department of Materials Science, P. O. Box 534, Uppsala SE 751 21, Sweden*

As a result of the rapid development within the field of lab-on-a-chip systems, there is currently a growing interest in miniaturised electrochemical devices. This can be explained by the fact that electrochemical devices can be readily miniaturised and that the required electrodes can be manufactured with standard microfabrication techniques. Electrochemically controlled solid-phase microextraction, employing electronically conducting polymers, is a new promising sample pretreatment technique [1-3]. As the extraction and desorption of analytes is controlled merely by the potential of the conducting polymer, this technique is highly suitable for inclusion in miniaturised chip-based systems. By use of electrochemical detection in capillary electrophoresis, employing e.g. arrays of microfabricated electrodes [4, 5], both efficient chip-based separations and low detection limits can be obtained even for complex samples.

This presentation will focus on our recent research aiming at the development of electrochemical techniques for chip-based sample preparation and detection. It will be demonstrated that electrochemically controlled solid phase extraction can be used for straightforward sample preparation and significant sample preconcentration. It will also be shown that electrochemical detection in capillary electrophoresis can be performed without interferences from the capillary electrophoretic electric field. A novel potentiostatless electrochemical detection technique based on the utilisation of the capillary electrophoretic electric field will likewise be described.

1. T. P. Gbatu, O. Ceylan, K. L. Sutton, J. F. Rubinson, A. Galal, J. A. Caruso and H. B. Mark Jr., *Anal. Commun.*, (1999), 36, 203.
2. G. Liljegren, J. Pettersson, K. E. Markides and L. Nyholm, *Analyst*, (2002), 127, 591.
3. G. Liljegren and L. Nyholm, *Analyst*, (2003), 128, 232.
4. O. Klett, F. Bjorefors and L. Nyholm, *Anal. Chem.*, (2001), 73, 1909.
5. O. Klett and L. Nyholm, *Anal. Chem.*, (2003), 75, 124.

15:30 - 15:50

Keynote  
lecture

## Thick, Oriented and Selective Antibody Immobilization on the Surface of Optical Transducers with the Use of Self-assembled Layer and Specific Receptors

**Nickolaj F. Starodub<sup>1)</sup>**

1) *A. V. Palladin Institute of Biochemistry, Ukrainian National Academy of Sciences, 9 Leontovicha, Kiev-30 01030, Ukraine*

In the report some theoretical aspects and the experimental results about treatment of transducer surface and the use of self-assembled layer and specific receptors for immobilization of Ab are presented. It was shown that the layer of polyelectrolytes self-assembled (PESA) provides higher (~10 times) specific signal of SPR and planar polarization interferometry immune sensors in comparison with that when their surfaces were not treated (bare gold) or treated by glutaraldehyde (silicon nitride) or by dodecanthiol. It is result of increase of the density of recognizing elements on the surface. Staphylococcal protein A and lectins allow to structure and to orient Ab toward solution due to the presence of specific binding site for them in second C-domain of Ig. Different types of Ab have an unequal affinity to the individual lectins. The effective thickness of immobilized Ab increases in series: bare surface, treated by or PESA and contained PESA with protein A or some lectins. The higher layer is observed at the formation of IgG-anti-IgG complex since IgG surface has a great number of Ag determinants. The thickness of anti-IgG-IgG layer is near to that observed for IgG-anti-IgG if protein A or lectins were introduced into PESA. It testifies that F(ab)<sub>2</sub> fragments are oriented towards solution. The use of some lectins instead of protein A as intermediate layer for the Ab immobilization allows us to obtain more high sensitivity of the determination of such low weight toxins as 2,4-D, simasine and nonylphenol. This phenomenon is analysed in term of density of recognising sites on the surface and their free orientation. The glycosylated protein of jp51 may be selective immobilized from mixture of

retroviral proteins (p24 and gp51) if it is necessary to discriminate ill animals and preliminary immunized ones by vaccines with p24 protein. The overall scheme of effective Ab immobilisation on the optical transducer surface is given on the basis of obtained result summation.

---

## The Study of the Interaction of a Model $\alpha$ -Helical Peptide with Lipid Bilayers and Monolayers

15:50 - 16:05

**P. Vitovic<sup>1)</sup>, R.N.A.H. Lewis<sup>2)</sup>, R.N. McElhane<sup>2)</sup>, Tibor Hianik<sup>1)</sup>**

Short communication

*1) Department of Biophysics and Chemical Physics, Comenius University, Mlynská dolina F1, Bratislava 842 48, Slovakia (Slovak Republic)*

*2) Department of Biochemistry, University of Alberta, Edmonton T6G 2H7, Canada*

We studied the interaction of the  $\alpha$ -helical peptide acetyl-Lys<sub>2</sub>-Leu<sub>24</sub>-Lys<sub>2</sub>-amide (L<sub>24</sub>) with tethered bilayer lipid membranes (tBLM) and lipid monolayers formed at an air-water interface. The interaction of L<sub>24</sub> with tBLM resulted in strong adsorption of the peptide to the surface of the bilayer, characterized by a binding constant of  $40 \pm 8 \text{ nM}^{-1}$ . This binding constant was similar to that characteristic of the specific interaction of some hormonal peptides with their receptors. The peptide induced an increase in the compressibility of the tBLM in a direction perpendicular to the membrane surface. The pure peptide formed a stable monolayer at the air/water interface. The pressure-area isotherms were characterized by a transition of the peptide monolayer, which probably corresponds to the partial intercalation of the  $\alpha$ -helices at higher surface pressure. Interaction of the peptide molecules with lipid monolayers resulted in an increase of the mean molecular area of phospholipids both in the gel and liquid-crystalline states. With increasing peptide concentration, the temperature of the phase transition of the monolayer shifted toward lower temperatures. The analysis showed that the peptide-lipid monolayer is not an ideally miscible system and that the peptide molecules form aggregates in the monolayer.

---

## Coffee break

16:05 - 16:25

---

## Session 4, Chairpersons - Karsten Haupt, Marcin Opallo

16:25 - 18:50

---

### Detection of Surface-active Compounds at Au and Pt Ultramicroelectrodes

16:25 - 17:05

**Andrzej S. Baranski<sup>1)</sup>**

Tutorial lecture

*1) University of Saskatchewan, 110 Science Pl., Saskatoon S7N5C9, Canada*

In recent years in my laboratory a new detection method was developed, which takes advantage of changes in voltammograms (recorded with either Pt or Au electrodes) caused by the adsorption of inorganic and organic molecules. These changes may include reduction or oxidation of the adsorbate, inhibition of oxygen adsorption, inhibition of hydrogen adsorption and also changes in the charging current. Cyclic or square-wave voltammograms are periodically recorded (usually, 1 to 20 curves per second). The detection is carried out in a stripping mode after the accumulation of analyte on the electrode surface for 10 to 1000 ms. Typical scan rates are between 10 and 1000 V/s. Removal of oxygen from the studied solutions is unnecessary. Electrochemical conditioning of the working electrode is sufficient to ensure a stable response for a period of several hours. For strongly adsorbing molecules the linear dynamic range extends over two orders of magnitude from about  $10^{-7} \text{ M}$  to  $10^{-5} \text{ M}$  with the relative standard deviation for replicate determinations lower than 5%. The smallest discernable signal is associated with about 0.1 % surface coverage, which corresponds to the adsorption of about  $10^{-18} \text{ mol}$  of analyte on an electrode  $5\text{-}\mu\text{m}$  in radius. The method was extensively tested under flow-injection and capillary electrophoresis conditions and HPLC. We also tested the usefulness of cyclic chronopotentiometry and the Cyclic Reciprocal Derivative Chronopotentiometry for the detection of surface-active compounds. The detection limits were similar to those obtained using square-wave voltammetry, however, the new techniques were particularly useful for end-column detection in capillary electrophoresis, because under controlled current conditions the detector response is unaffected by the offset voltage caused by the separation potential.

---

### Conducting polymer based electrochemical ion sensors

17:05 - 17:45

**Krzysztof Maksymiuk<sup>1)</sup>**

Tutorial lecture

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

Thin films of conducting polymers (CP) due to coupled electronic and ionic conductivity as well as capability of reversible oxidation / reduction and membrane properties seem to be optimal materials for electrochemical sensors construction with facile chemical to electrical signal transduction.

Electrodes modified with stable CP films, as e.g. polypyrrole, polianiline and poly(3,4-ethylenedioxythiophene) are characterized by either anion- or cation-exchange properties and can be utilized to construct potentiometric ion-sensors [1]. The accessible concentration range from  $10^{-5} \text{ M}$  to  $1 \text{ M}$  is similar to that of classical ion-selective electrodes, the properties can be easily tailored by the choice of dopant ion and low-cost sensors can be obtained by a simple electropolymerization.

However, these simple sensors suffer from low selectivity and high susceptibility toward pH and redox interferences. Therefore, the most promising application of CP in potentiometric ion sensors is to use them as ion to electron

transducer for ion-selective plastic membrane electrodes [1,2], where the above mentioned disadvantages are eliminated. All-solid-state and single-piece constructions of these electrodes will be characterized.

The capability of reversible oxidation / reduction of CP films, coupled with counter-ions release or incorporation can be utilized in amperometric ion-sensors [3]. Pulse- and ac-techniques applied with polypyrrole coated electrodes enable ion concentration determination within the range comparable to that typical for potentiometric method, but with significant elimination of redox interferences. A method of sensitivity and selectivity enhancement by appropriate choice of signal recording and time-scale of the experiment will be presented.

1.J. Bobacka, A. Ivaska, A. Lewenstam, *Electroanalysis*, 15 (2003) 366.

2.E. Bakker, M. Telting-Diaz, *Anal.Chem.*, 74 (2002) 2781.

3.A. Michalska, S. Walkiewicz, K. Maksymiuk, *Electroanalysis*, 15 (2003) 509.

17:45 - 18:05

Keynote  
lecture

## All-solid-state Conducting Polymer Based Potentiometric Sensors for Low Activity Measurements

**Agata J. Michalska<sup>1)</sup>**

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

The possibility of shifting the detection limit of traditional, i.e. internal solution ion-selective electrodes (IS-ISE), down to picomolar levels has reached much attention in recent years[1]. The primary ions leakage from the plastic membrane phase into the sample solution is the origin of the detection limits observed for IS-ISE being in order of mM at the most. Thus, the control of ions transport through the membrane is the key to extend the linear responses range of ion-selective electrodes.

The ions leakage is also affecting the responses of other potentiometric sensors, in this number also those in which conducting polymer (CP) films are used as alternative membranes or all-solid-state ion-selective electrodes (ASS-ISE, where the internal solution was replaced by CP film). Due to the nature of the solid state electrodes the selection of remedies available to control (or reduce) the ion leakage is limited compared to their internal solution counterparts.

One of the possible approaches to prevent the leakage of ions from the ASS-ISE is to surface modify the CP transducer part of the sensor with complexing ligand[2].

The other attitude takes into consideration the nature of CP which affects the detection limits of both ASS-IS and CP membrane based sensors. This approach relates the local elevation of ions concentration at the CP surface to spontaneous processes of polymer charging/discharging. Taking into account the advantage of the electron and ion conductivity of CP, ion fluxes at the interface can be precisely adjusted by means of current control[3]. Thus, lower detection limits can be obtained both for ASS-IS and CP based sensors. The results obtained experimentally are in good accordance with those theoretically predicted.

### References

1. T. Sokalski, A. Ceresa, T. Zwickl, E. Pretsch. *J. Am. Chem. Soc.* 119 (1997) 11347.

2. A. Michalska, A. Konopka, M. Maj-Zurawska, *Anal. Chem.* 75 (2003) 141.

3. A. Michalska, J. Dumanska, K. Maksymiuk, *Anal. Chem.* in press.

18:05 - 18:25

Keynote  
lecture

## Microsystem Technology as a Road from Macro to Nano-world. New Opportunities Created by National Centre of Silicon Micro- and Nanotechnology.

**Piotr Grabcic<sup>1)</sup>, Krzysztof Domański<sup>1)</sup>, Paweł Janus<sup>1)</sup>, Michał Zaborowski<sup>1)</sup>**

*1) Institute of Electron Technology (ITE), Lotników 32/46, Warsaw 02-668, Poland*

Tremendous progress of microelectronic technology observed within last 40 years is closely related to even more remarkable progress of technological tools. It is important to note however, that these new tools may be used for fabrication of diverse multifunctional microstructures as well. Such devices, called MEMS and MOEMS microsystems integrate microelectronic and micromechanical structures in one system enabling interdisciplinary application, with most interesting and prospective being bio-medical investigations. Development of these applications requires however co-operation of multidisciplinary team of specialists, covering broad range of physics, (bio) chemistry and electronics, not mentioning medical doctors and other medical specialists. Thus, dissemination of knowledge about existing processing capabilities is of key importance. In this paper examples of various applications of microelectronic technology for fabrication of Microsystems which may be used for medicine, will be presented. Besides, information concerning a National Silicon Micro- and Nanotechnology centre being created in Institute of Electron Technology in Warsaw and new, emerging opportunities will be given. Emphasize will be put on areas of possible cooperation with focus on surface chemistry.

18:25 - 18:40

Short com-  
munication

## Transformations of Surface-bound Pyrene and Anthracene

**Maciej Mazur<sup>1)</sup>, Gary J. Blanchard<sup>2)</sup>**

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

*2) Michigan State University, Department of Chemistry, East Lansing 48824, United States*

We have studied surface transformations of two polycyclic aromatic hydrocarbons (pyrene and anthracene) covalently attached to the surfaces of modified quartz, indium tin-oxide (ITO) and gold. We applied two immobilization

strategies. For quartz and ITO we prepared acid chloride terminated monolayers and reacted the acid chloride moieties with the amino groups of aminopyrene or aminoanthracene. For gold substrates, we self-assembled monolayers of 11-mercaptoundecanoic acid, transformed the carboxylic groups into interchain anhydrides, and then attached aminopyrene (or aminoanthracene) through the amide bonds.

We investigated the surface bound molecules using steady-state emission spectroscopy and cyclic voltammetry. It was shown that the immobilized polycyclic aromatic hydrocarbons can be electrochemically or photochemically oxidized into reactive radical cations. These radicals react with water molecules and are transformed into intermediate monohydroxy derivatives. The further oxidation of monohydroxy compounds results in the formation of dihydroxy/dione systems. It was found that the final products of pyrene oxidation are 1,6 and 1,8 pyrene-diones/dihydroxypyrenes. The oxidation of anthracene results in formation of 1,4-anthracenedione/dihydroxyanthracene couple.

---

## Social event and panel discussion

---

19:00 - 21:30

### Modification of Macroporous Electrodes: A Spectroscopic and Bioelectrochemical Study

19:00 -

**Samia Ben Ali<sup>1</sup>, Bernard Desbat<sup>3</sup>, D. A. Cook<sup>2</sup>, P. N. Bartlett<sup>2</sup>, Alexander Kuhn<sup>1</sup>**

Short communication

1) *Laboratoire d'Analyse Chimique par Reconnaissance Moléculaire, Ecole Nationale Supérieure de Chimie et de Physique de Bordeaux (LACReM), 16 Avenue Pey Berland, Pessac 33607, France*

2) *Department of Chemistry, University of Southampton, SO17 1BJ, Southampton, United Kingdom*

3) *Laboratoire de Physicochimie Moléculaire - Université Bordeaux I, 351 Cours de la Libération, Talence 33405, France*

The performance of the enzyme based biosensors depends on many parameters, in particular on the enzyme activity. Our approach consists in layer-by-layer building of a dehydrogenase biosensor using electrostatic interactions in order to prevent damaging of the enzyme by direct interactions with the electrode. In order to increase the sensitivity and stability of the sensors, organised porous metal structures has been used as electrode substrates [1]. Our attention is focused on one particular mediator family based on a skeleton of nitrofluorenone, i.e., (2,4,7-trinitro-9-fluorenylidene)-malonitrile, (TNFM), which adsorbs on the surface of gold electrodes and exhibits appreciable electrocatalytic activity towards NADH (nicotinamide adenine dinucleotide) oxidation [2, 3]. The adsorption of this molecule has been studied by cyclic voltammetry and surface infrared spectroscopy in order to elucidate the detailed mechanism of the molecule-surface and mediator-NADH interactions. These studies suggest that the monolayer of redox mediator is irreversibly bound to the gold surface via the CN groups when the electrode is exposed to negative potentials in order to transform one ore more nitro groups into the catalytically active NO/NHOH couple. Electrochemical results show that macroporous electrodes can be modified with the redox mediator on their entire inner surface. Therefore, the amount of the adsorbed mediator directly depends on the surface area of the electrode and the total inner surface is also accessible for the catalytic NADH oxidation. The currents can be further enhanced by adding  $\text{Ca}^{2+}$  ions to the solution and the produced  $\text{NAD}^+$  seems to be enzymatically active [4].

#### References

[1] S.A.G. Evans, J.M.Elliott, L. M. Andrews, P.N. Bartlett, P. J. Doyle, and G. Denault, *Anal. Chem.* 74, 1322-1326, (2002).

[2] N. Mano and A. Kuhn, *Electroanal. Chem.*, 477, 79-88, (1999).

[3] N. Mano and A. Kuhn, *Biosensors & Bioelectronics*, 16, 653-660, (2001).

[4] S. Ben Ali, D.A. Cook, A. Thienpont, P.N. Bartlett and A. Kuhn, *Electrochem. Commun.*, 5, 747-751, (2003).

---

### Integrated Circuits Protection with the Langmuir-Blodgett Films

19:00 -

**Wojciech R. Fabianowski<sup>1</sup>, Aleksandra Karpinska<sup>1</sup>**

Keynote lecture

1) *Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, Warsaw 00-664, Poland*

One of the problems in the modern microelectronics is the environmental protection of Integrated Circuits (IC). Especially, Chip-on-the-Board systems are sensitive to the temperature and relative humidity changes. Currently, IC can be protected as flip-chip with epoxy underfill; hermetic or semihermetic housing or polymer resin encapsulation. The last method offers simplicity, good environmental protection and can be applied directly to the chip without cavities, ceramic packages. Environmental protection of used glob-top encapsulation can be improved when the IC surface is modified by deposition of a coupling monolayer or multilayer system prior to the polymer resin coating.

Molecules forming the coupling monolayer or multilayer system can be applied for the IC encapsulation by using two methods. In the first one, molecules can be applied to form a separate film deposited by the Langmuir-Blodgett transfer or self-assembly (S.A.) technique. In this case crucial role is played by the chemical nature of coupling molecules and thickness of the deposited film. In the second method, coupling molecules can be added directly to the encapsulating resin and the coupling film is formed due to their diffusion to the interface region and surface enrichment. Two sets of experiments were performed. In the first one, special electronic testers "PW-ITE 5" with

resistors lines of different widths and spacings were modified with LBT deposited 1, 10, 20 or 50 stearic acid monolayers. Therefore, testers were modified with thin organic films with the thicknesses equal to respectively 1.5, 4.5, 10 or 23 nm. In the second set of experiments, "PW-ITE 5" testers were modified with different compounds forming S.A. monolayers like 9,10-dialkylanthracene-di(15-crown-5 ethers) or such simple molecules as anthranilic acid added in the 1% w/w amount directly to the epoxy encapsulating resin. Next, all modified "PW-ITE 5" testers were subjected to the highly accelerated aging procedure (100% RH; 85 °C). Then, resistivity changes of both testers and number of "living" structures were measured. The best results, i.e., the highest number of "living" structures after accelerated aging test, were obtained for the anthranilic acid molecules added directly to the encapsulating epoxy resin. The lowest values of resistivity changes were obtained for ICs protected only with 20 monolayers of stearic acid molecules (film thickness about 10 nm). Both for thinner and thicker films, poorer environmental protection was observed (faster raise of the resistivity changes in the electronic tester structures). The results obtained suggest the best environmental protection with the film only about 10 nm thick.

19:00 -

Keynote  
lecture

## Surfactants-containing Aggregations in Effectively Two-dimensional Space in View of a Non-equilibrium Statistical-mechanical Model

**Adam Gadomski<sup>1)</sup>**

1) *University of Technology & Agriculture, Institute of Mathematics & Physics, al. Kaliskiego 7, Bydgoszcz 85-796, Poland*

Systems comprising of entities with well-developed and electrically-active surfaces, like polymers, surfactants and colloids, are rich in entropically driven reactions. They may be not only between charged parts of the (bio)molecules but also they can be amongst the molecules, and even appear to be present amidst their clusters. Typically, they are of dipole-dipole type, induced dipolar and even quadrupolar (having an origin in the surface tension effect), to list but a few. Because of water ubiquitous character and role in such systems, a formation of hydrogen-bonding is to be mentioned here too. Due to merely amphiphilic character of the surfactants some specific additional reactions, rather slow or very instantaneous, can also be noticed [1].

All the reactions mentioned above readily help to cause emergence of aggregation phenomena, frequently mentioned in a phase-transition context, and quite extensively studied recently, mostly by means of experimental 2D Langmuir-like set-ups [2].

Mesoscopic nonequilibrium thermodynamics, starting from the well-known Gibbs equation, and making use of the concept of Onsager's reciprocity relations, and coefficients, looks capable of proposing a systematic description of the aggregation process in terms of surfactants' and surfactants clusters' sizes, size- and time-dependent diffusion-migration coefficient as well as by enabling a proper as well as unambiguous selection of the interaction potential governing the formation of the effectively two-dimensional system [3].

Such a choice can be proposed for the effectively two-dimensional interacting surfactants-containing assemblies, with the often applied under such physical circumstances screening Coulomb (DLVO) potential but in a limit of either the adequately chosen (high) temperature or when the conception of diluted-regime approximation really applies [4].

### References

- [1] A. Plonka, Dispersive kinetics, *Prog. React. Kinetics & Mechanism* 94, 89-175 (1998).
- [2] V.M. Kaganer, H. Mouhwald, and P.Dutta, Structure and phase transitions in Langmuir monolayers, *Rev. Mod. Phys.* 71, 779-819 (1999).
- [3] J.C. Earnshaw and D.J. Robinson, Scale invariance in two-dimensional reaction-limited colloidal aggregation, *J. Phys.: Condensed Matter* 7, L397-L403 (1995).
- [4] A. Gadomski and J.M. Rubi, On the two principal curvatures as potential barriers in a model of complex matter agglomeration, *Chem. Phys.* 293, 169-177 (2003).

19:00 -

Keynote  
lecture

## Screen-printed Voltammetric Genosensors for Detection of *Listeria Monocytogenes* in Food

**Tomasz M. Oczkowski<sup>1)</sup>, Selim Achmatowicz<sup>2)</sup>, Marian Filipiak<sup>1)</sup>**

1) *Faculty of Commodity Sciences, Poznań University of Economics, al. Niepodległości, Poznań 60-967, Poland*

2) *Institute of Electronic Materials Technology (ITME), Wólczańska, Warsaw 01-919, Poland*

The authors report here a preliminary evaluation of genosensor for detection of *Listeria monocytogenes* in food. Over the past decade, there has been an interest in electrochemical DNA biosensors for converting the hybridisation events into an analytical signal. Attractive features of this technology include simple approach, low-cost and single use sensor. Some of these approaches are based on screen-printed electrodes as electrochemical transducers. The purpose of the present study of DNA biosensors is to investigate the application of screen-printed electrochemical sensors for coupling with methods of amplification of the nucleic acid signal. A sequence of listeriosis O gene (hlyA) has been used as the probe. During the measurements, we used different kind of thick-film electrodes as disposable voltammetric sensors, based on various conventional and modified inks. The DNA probes were successfully adsorbed at controlled potential around 500 mV vs. Ag/AgCl on the surfaces of carbon electrodes. The DNA mod-

ified electrodes were electrochemically characterised with some of electroactive DNA binding complex  $\text{Co}(\text{bpy})_3^{3+}$ , daunomycin, ethidium bromide and methylene blue. The reaction on the electrode surface was monitored by cyclic and square-wave voltametry. The DNA hybridization has been observed in dependence of different concentration of oligonucleotides (in the range between  $1 \mu\text{g ml}^{-1}$  -  $20 \mu\text{g ml}^{-1}$ ). The hybridization reaction was performed using real samples of *Listeria monocytogenes* amplified by PCR. The new single-use genosensors, if combined with some of DNA amplification methods, allows determination of the genotype of the *Listeria monocytogenes* in shorter time than traditional phenotypic and biochemical testing.

Financial support by KBN 3P06T00522 is acknowledged.

## Simulation of the Double Hemicylinder Electrode System Through Conformal Mapping. Application to Steady-state and Transient Electrogenerated Chemiluminescence

19:00 -

Short communication

**Alexander Oleinick<sup>2)</sup>, Irina B. Svir<sup>2)</sup>, Christian Amatore<sup>1)</sup>**

1) *Ecole Normale Supérieure, Département de Chimie, UMR CNRS-ENS-UPMC 8640 "PASTEUR", 24 rue Lhomond, Paris Cedex 05 75231, France*

2) *Mathematical and Computer Modelling Laboratory, Biomedical Electronics Department, Kharkov National University of Radioelectronics, 14 Lenin Avenue, Kharkov 61166, Ukraine*

Paired microelectrodes or arrays of mikroelectrodes are often used in modern electrochemistry because they offer a possibility to generate different species at different microelectrodes, including anion and cation radicals, which allows to investigate electrogenerated chemiluminescence (ECL). Recently, we used the conformal transformation for the simulation of the double hemicylinder generator-collector microelectrode assembly [1], which is applied here for investigation of ECL in a cell with two parallel-hemicylindrical microelectrodes. Employment of the conformal mapping techniques for the simulation of two-dimensional electrochemical problems at microelectrodes represents the most efficient and easiest way of obtaining an accurate numerical solution for diffusion at microelectrodes or microelectrode assemblies. Conformal transforms allow mapping of a two-dimensional real space, where the flux lines may be extremely curved or present singularities onto a space in which the flux lines become (almost) parallel [2]. It is probably the best numerical approach for the symmetrical electrode problems.

Furthermore, conformal mappings have the important own properties and often allow obtaining the exact solution of the problem. There are a few analytical solutions for the steady-state current in the double-band and channel-double-band microelectrode generator-collector systems using the conformal mapping [3-6] and ECL steady state intensity for the double-band microelectrode system [3, 4]. The analytical expressions for the steady-state current and ECL intensity in a cell with two microelectrode hemicylinders are presented here. Our next aim is to compare the efficiency of ECL emission in two different microelectrode systems: with two bands [3,4] and two hemicylinders, where the equal conditions have been created for: the ECL excitation (the same reaction scheme), equal electrode surface areas (with the corresponding radii, widths and length of the electrodes) and common numerical approach for the simulations (i.e., the conformal mappings and the ADI method) in both cases.

### References

1. C. Amatore, A. I. Oleinick, I.B. Svir, J. Electroanal. Chem. 553 (2003) 49.
2. C. Amatore, in I. Rubinstein (Ed.), Physical Electrochemistry: Principles, Methods and Applications, M. Dekker, New York. (Ch. 4) 1995.
3. B. Fosset, C. A. Amatore, J. E. Bartelt, A.C. Michael, R. M. Wightman, Anal. Chem. 63 (1991) 306.
4. C. A. Amatore, B. Fosset, K. M. Maness, R. M. Wightman, Anal. Chem. 65 (1993) 2311.
5. I. A. Arkoub, C. Amatore, C. Sella, L. Thouin, J.-S. Warkocz, J. Phys. Chem. B 105 (2001) 8694.
6. C. Amatore, C. Sella, L. Thouin, J. Phys. Chem. B 106 (2002) 11565.

## Simulation of the Droplet Interior Problem

19:00 -

**Irina B. Svir<sup>1)</sup>, Alexander I. Oleinick<sup>1)</sup>, Richard Compton<sup>2)</sup>**

Keynote lecture

1) *Mathematical and Computer Modelling Laboratory, Biomedical Electronics Department, Kharkov National University of Radioelectronics, 14 Lenin Avenue, Kharkov 61166, Ukraine*

2) *Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom*

Recent work [1-3] has shown that electrodes, often made of platinum or basal plane graphite, can be usefully modified with random arrays of microdroplets of insoluble oils such that oxidation or reduction of redox groups within the oil molecules is accompanied by counter ion insertion into the droplet to maintain electroneutrality. Thus, for example, the reduction of 4-nitrophenyl nonyl ether droplets was shown [2] to induce proton and alkali metal insertion from the aqueous electrolyte bathing the droplet array. Similarly [3], anion insertion is observed in the case of oxidation of droplets of tetra-alkylphenylene diamines. A variety of evidences [1-3] has been presented to suggest that these charge transfer reactions take place exclusively at the three phase boundary formed between the droplet, the electrode surface and the electrolyte solution. Accordingly, it is of interest to examine the voltammetric response of a single droplet under such conditions. Early calculations using the dual reciprocity finite element method showed that charge insertion at the three phase boundary could be distinguished voltammetrically from

other mechanisms of charge insertion [4] but these calculations were not readily extended beyond the case of simple charge transfer, notably for the case of coupled chemical reaction kinetics inside the droplet. Nor was the coupling of transport processes outside the droplet. Accordingly, we propose in this paper a new numerical approach based on the use of the conformal mapping technique. For the simulation of 2D electrochemical problems at microelectrodes this approach represents the most efficient and easiest way of obtaining accurate solution of diffusion problems and allows transformation back to real space where the flux lines may be extremely curved from the transformed space in which the flux lines are almost parallel [5]. Although we consider here only the simulation of the droplet interior problem ( $\omega_{in}$  area), the suggested conformal mapping also allows to solve the droplet problem considering additionally the exterior electrolyte ( $\omega_{out}$  area) as well.

## References

1. J. D. Wadhawan, R. G. Compton et al., J Amer. Chem. Soc., (2003) in press.
2. A. J. Wain, N. S. Lawrence, P. R. Greene, J. D. Wadhawan, R. G. Compton, PhysChemChemPhys., 5 (2003) 1867.
3. J. D. Wadhawan, R. G. Evans, C. E. Banks, S. J. Wilkins, R. R. France, N. J. Oldham, A. J. Fairbanks, B. Wood, D. J. Walton, U. Schroeder, R. G. Compton, J. Phys. Chem. B, 106 (2002) 9619.
4. Q. Fulian, J. C. Ball, F. Marken, R. G. Compton, A. C. Fisher, Electroanalysis, 12 (2000) 1012.
5. C. Amatore, in I. Rubinstein (Ed.), Physical Electrochemistry: Principles, Methods and Applications, Marcel Dekker, New York. 1995. (Ch. 4).

19:00 -

## Formation, Properties and Potential Applications of Fullerene-based Solid Films

Keynote  
lecture**Krzysztof Winkler<sup>1)</sup>***1) Institute of Chemistry, University of Bialystok, Hurtowa 1, Bialystok 15-399, Poland*

Results of investigation into the electrochemical properties of fullerene and their derivatives in solid state will be reviewed. These systems can be divided into three groups:

- (i) polycrystalline thin layers
- (ii) non-crystalline films
- (iii) fullerene based polymers.

Special emphasis will be placed on the electrochemistry of fullerene-based polymers. Several methods for the electrochemical polymerization of fullerene systems will be described. The properties of fullerene containing polymers will be discussed. Recent results of fullerene-based double cables; formation and the properties of these systems will be presented

## Saturday, November 15th

07:00 - 08:00

### Breakfast

08:00 - 12:00

### Excursion

12:00 - 13:00

### Lunch

13:00 - 15:15

## Session 5, Chairpersons - Paweł J. Kulesza, Gunther Wittstock

13:00 - 13:40

### Electron Transfer in Complex Two-cofactor-containing Enzymes at Alkanethiol-modified Gold Electrodes

Tutorial  
lecture**Lo Gorton<sup>1)</sup>, Elena Ferapontova<sup>1)</sup>, Tautgirdas Ruzgas<sup>1)</sup>, Leonard Stoica<sup>1)</sup>***1) Centre for Chemistry and Chemical Engineering, Lund University (KC), Lund SE-221 00, Sweden*

In biological redox catalysis, energy transduction, and many aspects of regulation, electron transfer (ET) is linked directly to conformational change, ligand/substrate binding, ion/proton transfer etc., and the ways in which these events occur and how the system as a whole is optimised and harmonised are still not well understood. Studies of biological electron transfer (ET) within multi-cofactor redox enzymes under conditions when the electrode replaces the natural redox partner of the enzyme can contribute to understanding intramolecular ET within the biomolecules followed by ET coupling of the active sites. The obligatory condition for the bioelectrocatalytic event in this case is the existence of a direct communication between the electrode and at least one of the active sites present in the enzyme, which is difficult to attain in some cases. Mimicking the natural partner/environment of protein by



the modified electrode is then of particular interest to achieve an efficient ET reaction through the enzyme. To provide a biomembrane-like microenvironment of the membrane/intermembrane enzymes at the electrode surface self-assembled monolayers (SAM) of synthetic terminally functionalised alkanethiols can be used. Therewith, a successful simulation of the molecular surfaces of enzyme biological partners, e.g. cytochrome c, by the SAM of alkanethiols on gold may provide the necessary amount/orientation of the enzyme molecules for direct ET reaction with the electrode, as well as a conformation appropriate for efficient intramolecular ET, including electrostatic compatibility of the docking sites and the aspect of mobility in achieving a proper orientation for fast ET. We report how the choice of alkanethiols of different polarity/hydrophobicity and charge provides the surface properties of the Au electrode necessary for the proper adsorption/orientation of sulphite oxidase, theophylline oxidase, or fructose dehydrogenase.

## Chemical Sensors Based on Conducting Polymers

13:40 - 14:20

**Johan B. Bobacka**<sup>1)</sup>

Tutorial  
lecture

*1) Abo Akademi University, Process Chemistry Centre, Laboratory of Analytical Chemistry, Biskopsgatan 8, Turku FIN-20500, Finland*

Conducting polymers such as polypyrrole (PPy), polythiophene (PT), polyaniline (PANI), and their derivatives, are truly multifunctional materials. The unique electrical, electrochemical and optical properties of conjugated polymers can be used to convert chemical information (concentration, activity, partial pressure) into electrical or optical signals in the solid state. Therefore, conjugated polymers are useful as transducers in chemical sensors. One of the key issues is to combine conjugated polymer transducers with selective molecular recognition in order to obtain durable chemical sensors.

Conducting polymer modified electrodes can be obtained by electrochemical polymerization of various monomers with different substituents and counterions. Alternatively, soluble conjugated polymers may be cast on the electrode surface from solution. Since conducting polymers are electroactive materials with mixed ionic and electronic conductivity, they can interact with various ions and redox species in the surrounding medium in a relatively non-selective manner. Therefore the goal is often to immobilize specific recognition sites (receptors) in the conducting polymer film in order to achieve selectivity to a certain target species. Such recognition sites can be immobilized as counterions or the recognition sites can be covalently bound to the conjugated polymer backbone.

Interactions between the target species and the conducting polymer film may influence the:

- optical properties of the polymer film
- electrical conductivity of the polymer film
- oxidation/reduction current at the polymer modified electrode
- equilibrium potential of the polymer modified electrode

The basic principles of chemical sensors based on conducting polymers will be illustrated in this tutorial lecture by considering the following three types of electrochemical sensors:

1. Conductimetric gas sensors
2. Amperometric biosensors
3. Potentiometric ion sensors

## Electrochemical Processes in Mesoporous TiO<sub>2</sub> Phytate Films

14:20 - 14:40

**Frank Marken**<sup>1)</sup>, **Katy J. McKenzie**<sup>1)</sup>

Keynote  
lecture

*1) Department of Chemistry, Loughborough University, Epinal Way, Loughborough LE11 3TU, United Kingdom*

The formation of nanofilm deposits of TiO<sub>2</sub> nanoparticle phytates based on the directed assembly methodology [1] is demonstrated. Alternant exposure of a tin-doped indium oxide (ITO) or gold electrode surface to aqueous solutions of TiO<sub>2</sub> nanoparticles (3-4 % in HNO<sub>3</sub>, ca. 6 nm diameter) and phytic acid (40 mM, at pH=3) causes layer-by-layer growth of a three dimensional mesoporous structure.

Cytochrome c in aqueous phosphate buffer (pH=7) is readily accumulated into the mesoporous TiO<sub>2</sub> phytate film predominantly due to electrostatic binding of the positively charged protein to the negatively charged interfacial phytic acid [2]. Voltammetric data for the reversible reduction and re-oxidation of cytochrome c suggest strong adsorption and ideal thin film behaviour over a wide range of conditions. Voltammetric and quartz crystal microbalance data are presented for accumulation and electrochemically driven desorption of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> [3].

1. K. J. McKenzie, F. Marken, M. Hyde, R.G. Compton, *New J. Chem.*, 26, (2002), 625.
2. K. J. McKenzie, F. Marken, *Langmuir*, 19, (2003), 4327.
3. K. J. McKenzie, F. Marken, X. Gao, S. C. Tsang, K.Y. Tam, *Electrochem.*

Commun., 5, (2003), 286.

14:40 - 15:00

Keynote  
lecture

## Photocatalytic and Photoelectrochemical Properties of the Pt(IV)-Chloride Surface Modified TiO<sub>2</sub>

**Wojciech Macyk**<sup>1)</sup>

1) *Faculty of Chemistry, Jagiellonian University, Ingardena 3, Kraków 30-060, Poland*

Recently it was found that amorphous microporous titanium dioxide doped in the bulk with [PtCl<sub>4</sub>] can catalyse photodegradation of 4-chlorophenol (4-CP) with visible light [1-3]. Even higher degradation rates and significant photocurrent generation were achieved when the platinum complex was chemisorbed onto the surface of the anatase [4, 5]. Upon visible light irradiation an oxidising weakly bound chlorine atom (E = 1.3-2.4 V) and a reducing Pt(III) species (ca. -0.7 V) are formed. The transient Pt(III) is capable of electron injection into the conduction band of TiO<sub>2</sub>. The Cl atoms oxidise the adsorbed 4-CP molecules. Another important oxidising agent, the hydroxyl radical (ca. 2.4 V), is formed in the reductive pathway as a product of superoxide transformations, as proven in experiments of salicylic acid formation from benzoic acid.

Electrochemical and photoelectrochemical studies enabled to estimate potential levels and to clarify several mechanistic details. The anatase modification of titania gave the best results both in 4-CP photocatalytic degradation and photocurrent generation. The behaviour of various [PtCl<sub>4</sub>]/TiO<sub>2</sub> materials, based on different crystalline forms of TiO<sub>2</sub> was parallel to the activity of unmodified TiO<sub>2</sub> upon UV irradiation. Flatband potential determinations [6] have proven that the difference between rutile and anatase photosensitisation does not originate from the positions of the CB and VB edges, but is caused rather by adsorption properties and charge carrier mobilities.

### References:

1. Zang, L.; Lange, C.; Maier, W.F.; Abraham, I.; Storck, S.; Kisch, H. J. Phys. Chem. B (1998), 102, 10765.
2. Kisch, H.; Zang, L.; Lange, C.; Maier, W.F.; Antonius, C.; Meissner, D. Angew. Chem. (1998), 110, 3201.
3. Zang, L.; Macyk, W.; Lange, C.; Maier, W.F.; Antonius, C.; Meissner, D.; Kisch, H. Chem. Eur. J. (2000), 6, 379.
4. Macyk, W.; Kisch, H. Chem. Eur. J. (2001), 7, 1862.
5. Burgeth, G.; Kisch, H. Coord. Chem. Rev. (2002), 230, 40.
6. Macyk, W.; Burgeth, G.; Kisch, H. Photochem. Photobiol. Sci. (2003), 2, 322.

15:00 - 15:15

Short com-  
munication

## Ionophoric Properties of Different Derivatives of p-tert-butyl-Calix[4]arens Containing Phosphonate Functional Groups

**Urszula Lesinska**<sup>1)</sup>, **Maria Bochenska**<sup>1)</sup>, **Maria Hoffmann**<sup>1)</sup>

1) *Faculty of Chemistry, Gdańsk University of Technology, Narutowicza 11/12, Gdańsk 80-952, Poland*

Calix[4]arens derivatives are of great interest as ionophores for chemical sensors: ion-selective electrodes (ISE) or optodes. Rather rigid and lipophilic macrocyclic structure of p-tert-butyl-calix[4]arens, in which four hydroxy groups can be modified by introducing variety substituents leads to new derivatives. Among them compounds with phosphonic acid or esters groups are so far relatively less studied [1].

We present here structures and complexing properties of p-tert-butyl-calix[4]arens new derivatives bearing different phosphonate functional groups [2, 3]. The potentiometric selectivity coefficients were determined and the complex formation constants were calculated. Complexing properties towards alkali and alkali earth cations, transitional metal ions and ammonium and guanidium ions of ionophores 1-5 are strongly dependent on the rearrangement of the substituents in p-tert-butyl-calix[4]aren skeleton. Different factors such as the nature of the binding sites, their position on calixarene backbone and the role of different plasticizers in the membrane are discussed.

### References

1. S. Kunsagi-Mate, G. Nagy, P. Jurecka and L. Kollar, Tetrahedron 58, 5119- 5124, 2002
2. M. Hoffmann, A. Konitz, A. Sikorski, U. Lesinska, M. Bochenska, J. Incl. Phenomena and Macrocyclic Chemistry, (2003) in press.
3. M. Bochenska, M. Hoffmann, U. Lesinska, J. Incl. Phenomena and Macrocyclic Chemistry, submitted (2003).

15:15 - 15:35

## Coffee break

15:35 - 17:50

## Session 6, Chairpersons - Renata O. Bilewicz, Lo Gorton

15:35 - 16:15

Tutorial  
lecture

## Patterned Organic Thin Films: Reactivity Imaging from Micrometer towards Nanometer Size Regimes with Scanning Electrochemical Microscopy

**Gunther Wittstock**<sup>1)</sup>

1) *Carl von Ossietzky University Oldenburg, School of Mathematics and Natural Sciences, n/a, Oldenburg D-26111, Germany*

Scanning electrochemical microscopy (SECM) has become an indispensable tool for the characterization of reactivities at interfaces such as reactions of immobilized enzymes and other biomolecules [1]. The analysis is based on the detection of redox active species generated by an immobilized enzyme through conversion at the scanning ultramicroelectrode (UME).

In addition to localized analysis SECM instruments can be used as tools for microstructuring [2]. By switching between microstructuring and reactivity imaging the success of individual preparation steps can be analysed forming the basis for the rational optimization of such processes.

By patterning self-assembled monolayers (SAM) of alkanethiolates on gold, a surface template can be formed into which enzymatically active layers can be immobilized. Patterned SAMs have been prepared by microcontact printing [3] and localized electrochemical desorption using SECM. By combination of both approaches patterns become available that contain two or more enzymes. Reaction chains and cofactor recycling between different active regions can be studied as a function of the pattern layout at such specimens [4].

Experiments with higher resolution were enabled by production of smaller electrodes and the usage of topographic information of an tunneling microscopic experiment (ECSTM) for positioning the UME in the SECM experiment [5]. Quantitative evaluation of image data is enabled by the use of the boundary element method for simulating coupled transport processes and heterogeneous reactions in systems of arbitrary geometry [6].

- 1.G. Wittstock, *Fresenius J. Anal. Chem.* (2001), 370, 303.
- 2.T. Wilhelm, G. Wittstock; *Electrochim. Acta* (2001), 47, 275.
- 3.T. Wilhelm, G. Wittstock, *Langmuir* (2002), 18, 9486.
- 4.T. Wilhelm, G. Wittstock, *Angew. Chem. Int. Ed. Engl.* (2003), 42, 2247.
- 5.T. Treutler, G. Wittstock, *Electrochim. Acta* (2003), 48, 2932.
- 6.O. Sklyar, G. Wittstock, *J. Phys. Chem. B* (2002), 106, 7499.

---

## Network Films of Conducting Polymer Linked and Polymeatallate Stabilized Platinum Nanoparticles

16:15 - 16:55

**Paweł J. Kulesza<sup>1)</sup>, Krzysztof Miecznikowski<sup>1)</sup>, Malgorzata Chojak<sup>1)</sup>, Katarzyna Karnicka<sup>1)</sup>**

Tutorial  
lecture

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

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 pursue here 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. By repeated and alternated treatments in the appropriate solution, the amount of material on the electrode surface can be increased systematically in a controlled fashion leading to stable three-dimensional multilayered assemblies [1].

Monolayers of alkanothiols are capable of passivating gold nanoparticles and producing alkanethiolate monolayer protected clusters of gold [2]. 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. In the present work, we explore the ability of polyoxometallates (phosphotungstate, phosphomolybdate) to form self-assembled monolayers on metal (platinum) nanoparticles (ca. 7-10 nm). Such polyoxometallate covered (protected) particles can be linked together by ultra thin conducting polymer (polyaniline, polypyrrole) 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, microgravimetry, FTIR spectroscopy, STM and scanning electrochemical microscopy. The films produce molecular systems capable of charge storage in bilayer type coatings as well as organized monolayer and multilayer assemblies with specific electrocatalytic properties.

### References

1. P. J. Kulesza, M. Chojak, K. Miecznikowski, A. Lewera, M. A. Malik, A. Kuhn, *Electrochem. Comm.*, 4 (2002) 510.
2. F. P. Zamborini, M. C. Leopold, J. F. Hicks, P. J. Kulesza, M. A. Malik, R. W. Murray, *J. Am. Chem. Soc.*, 124 (2002) 8958.

---

## Silicate Modified Electrodes for Chemical Sensing

16:55 - 17:35

**Marcin Opallo<sup>1)</sup>**

Tutorial  
lecture

*1) Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland*

Although silica sol-gel derived glass is an insulator and does not participate in redox reactions, it can be used for

modification of the electrode surface [1] or can be applied as a inert support for bulk modified electrode, most frequently carbon ceramic composite electrode (CCE) [2]. The use of silicate matrix opens numerous possibilities for electrode modification. This is because of relatively simple chemistry of silicates and availability of organically modified precursors of sol-gel process. One can tune the electrode properties as hydrophobicity/hydrophilicity or incorporate redox activity by modification of silicate matrix pore walls by functional groups Also the porosity of this material can be adjusted by selection of the sol-gel process conditions. Finally, the native enzymes or tissue cells can be easily incorporated into silicate matrix without losing their activity, opening the many possibilities of amperometric biosensor preparation [3].

The preparation of silicate modified electrodes and their application as amperometric sensors will be reviewed. These will include pH sensing, gas sensing, stripping analysis and biosensing. The advantages, disadvantages, capabilities and promises of silicate modified electrodes will be discussed.

#### References

1. O. Lev, J. Wu, S. Bharathi, V. Glezer, A. Modestov, J. Gun, L. Rabinovich, S. Sampath, Chem. Mater. 9 (1997) 2354.
2. L. Rabinovich, O. Lev, Electroanalysis 13 (2001) 265.
3. J. Wang, Anal. Chim. Acta, 399 (1999) 21.

17:35 - 17:50

Short communication

## Gold Electrode Modified with Hydrophobic Silicate Thin Film and Redox Liquid

**Joanna Niedziółka<sup>1)</sup>, Marcin Opałło<sup>1)</sup>**

*1) Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland*

Despite the strong development of polymer modified electrodes since 1976 there is still a need for new modification methods. The deposition of redox liquid droplets on the electrode surface is one of the recent examples [1]. Recently, we have reported immobilisation of redox liquid in carbon ceramic composite electrode [2]. Here, the silicate thin film modified electrode with redox liquid will be presented.

The gold electrode modified with thin hydrophobic silicate film and impregnated with redox liquid - t-butylferrocene (t-BuFc) has been prepared and studied. Two types of electrode: disc and wire were used. The film was prepared from sol based on methyltrimethoxysilane. The disc electrode was modified by evaporation of the sol drop. The wire was covered by dip coating and after drying silicate layer was removed from the tip. These electrodes and bare gold electrodes were modified with t-BuFc by immersion (wire) in pure redox liquid or deposition of droplet of redox liquid diluted in hexane (disc). Their electrochemical properties were investigated by cyclic voltammetry and chronoamperometry in aqueous nitrate solution. The slow scan peak shaped voltammogram due to the redox process of t-BuFc was obtained. The decrease of the current magnitude during the subsequent scans is observed and this effect is smaller for silicate modified electrodes than for the bare ones.

It has been concluded that the electrode process occurs at the three phase junction formed by gold and liquid organic|aqueous interface supported by hydrophobic silicate. The current decrease is probably caused by the expulsion of t-BuFc<sup>+</sup> to the aqueous phase [3]. Thin film of hydrophobic silicate acts as the reservoir for the liquid redox probe and it decreases the rate of the above mentioned process.

#### References

- 1.F. Marken et al., J. Electroanal. Chem. 437 (1997) 209.
- 2.M. Opałło, M. Sączek-Maj, Chem. Commun. (2002) 448.
- 3.R. G. Compton et al., J. Electroanal. Chem. 533 (2002) 71.

18:00 - 19:00

## Dinner

19:00 - 21:30

## Session 7, Chairpersons - Gérard M. BIDAN, Ana Maria C. Oliveira Brett

19:00 - 19:40

Tutorial lecture

## Piezoelectric Microgravimetry for Determination of Some Biologically Important Compounds

**Włodzimierz Kutner<sup>1)</sup>, Agnieszka Kochman<sup>1)</sup>, Tibor Hianik<sup>2)</sup>, Victor Gajdos<sup>2)</sup>, Pankaj Vadgama<sup>3)</sup>, Giosio Farace<sup>3)</sup>, Karsten Haupt<sup>4)</sup>**

*1) Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland*

*2) Department of Biophysics and Chemical Physics, Comenius University, Mlynská dolina F1, Bratislava 842 48, Slovakia (Slovak Republic)*

*3) Queen Mary University, Mile End Road, London E1 4NS, United Kingdom*

*4) Lund University, Lund S-221, Sweden*

Adsorption of some biologically significant compounds, such as a pirimicarb (PIR) pesticide, avidine (AV) protein, and 7-N nucleotide, at a chemically modified Au electrode of a quartz crystal piezoelectric transducer (QCPT) was investigated by using piezoelectric microgravimetry with an electrochemical quartz crystal microbalance (EQCM). This adsorption was utilized for determination of the compounds under the batch or flow injection analysis (FIA) conditions.

PIR was determined by using QCPT modified with a molecularly imprinted polymer (MIP) thin film. The MIP film was prepared by a UV light polymerization of a mixture of suitable functional and cross-linking monomers, polymerization initiator, and PIR template. Next, the template was washed out leaving molecular cavities in the MIP film of the size and shape of the template molecule. Then, PIR was determined (limit of detection 0.22 mM and linear concentration range 0.36 to 1.5 mM) by measuring the frequency change,  $\Delta f$ . FIA peaks rather than steps of  $\Delta f$  vs. time were formed indicating lack of chemical interactions between PIR and MIP.

AV was determined by using QCPT coated with a polypyrrole-biotin film prepared by electropolymerization of pyrrole under cyclic voltammetry conditions (CV) in the presence of biotin. The growth of the biotin-modified poly(pyrrole) film was monitored by simultaneous measurement of the CV and piezoelectric microgravimetry curves with the use of an electrochemical quartz crystal microbalance (EQCM) under quiescent solution conditions. Steps rather than peaks were present in the FIA curve due to consecutive injections of the AV samples. These steps were smaller the larger was the injection number indicating that AV interacted chemically with the biotin sites of the poly(pyrrole) film and that these sites were gradually saturated.

A 7-N nucleotide was determined by virtue of hybridization with a single strand of complementary deoxyribonucleic acid (ssDNA). For that purpose QCPT was modified with self-assembled monolayers (SAMs) of ssDNA. Two modification procedures were adopted, i.e., (i) a direct procedure using  $\omega$ -thiolated DNAs to form SAMs and (ii) an indirect procedure using  $\omega$ -thiolated mercaptoundecanoic acid (MUA) esterified with AV for SAMs; then, ssDNA modified with biotin was attached to the immobilized MUA by the AV-biotin non-covalent bonds. The FIA steps and peaks were obtained for ssDNA immobilized according to the (i) and (ii) procedure, respectively, after injecting samples of 7-N nucleotide.

---

## Fluorescent Polymer Biosensor for Nucleotides

**Alina K. Mielniczak<sup>1)</sup>, Barbara J. Wandelt<sup>1)</sup>**

*1) Department of Molecular Physics, Technical University of Lodz (TUL), Zeromskiego 116, Lodz 90 924, Poland*

19:40 - 19:55

Short communication

Progress of industrial processes and medical diagnostics increases need for reliable and cheap instrumentation for continuous recording of data in real time, without complicated sampling. Optical sensor technology can provide low-cost devices that can be tuned to a wide field of applications by coating a fibre optic with a chemically sensitive thin-layer polymer [1].

The molecular imprinting is a technology which produce a polymer with selectively binding sites. This polymer has the ability to recognize a molecule by selective adsorption on a microporous matrix. This technology involves polymerisation of functional monomers together with template molecule. Than the template molecule is removed leaving behind functionalised sites that are able to recognize the template [2].

We developed imprinted polymer with both the recognition element together with transducer element, which generates fluorescence of which intensity depends upon the template binding. A fluorescent functional monomer, trans-4-(p,N,N-dimethylaminostyryl)-N-vinylbenzylpyridinium chloride (vbDMASP), has been used together with a conventional functional monomers to prepare the polymer using imprinting technology [3], the recognition sites were prepared against the nucleotides.

We report here our studies on a thin-layer fluorescent imprinted polymer. Both the steady-states and time-resolved fluorescence spectroscopy shown quenching of fluorescence of the imprinted polymer when it was incubated in presence of nucleotides.

This project was supported by the KBN grant No. 4 T09B 101 24.

### References

1. R. C. Hughes, A. J. Ricco, M. A. Butler, S. J. Martin, *Science* 254 (1991) 74.
2. A. Mayes, K. Mosbach, *Trends in Analytical Chemistry*, vol. 16, No. 6, 1997, 321.
3. B. Wandelt, P. Turkewitsch, S. Wysocki, G. D. Darling, *Polymer* 43 (2002) 2777.

---

## Carbon Ceramic Electrode Modified with Redox Probe Solution in Hydrophobic Polar Solvents

**Galyna Shul<sup>1)</sup>, Marcin Opallo<sup>1)</sup>**

*1) Institute of Physical Chemistry Polish Academy of Sciences, Kasprzaka 44/52, Warsaw 01-224, Poland*

19:55 - 20:10

Short communication

The evolution of sol-gel technology and organically modified ceramic materials created new possibilities for electro-analytical sensors. Lev and coworkers introduced a new class of sol-gel derived composite carbon ceramic electrodes (CCE). One of the ways of modification of CCE with large number of redox groups is impregnation with redox probe solution in hydrophobic polar solvent.

The CCE modified with redox probe (ferrocene, t-butylferrocene or decamethylferrocene) solution in hydrophobic polar solvent (nitrobenzene, 2-nitrophenyloctylether or 2-nitrodiphenylether) was prepared and studied. The electrode material was obtained by sol-gel process. It consists of the graphite powder homogeneously dispersed in hydrophobic silica matrix based on methyltrimethoxysilane. After drying and gelation, the electrode was immersed in modifier solution. The electrochemical properties of the electrode were investigated in aqueous salt solution. The features of cyclic voltammetry curves: stability, peak current magnitude, shape and midpeak potential corresponding to the redox reaction depend on the redox probe, organic solvent and the salt present in aqueous phase. The redox probe is easier to oxidize in the presence of less hydrated anions. The magnitude of peak current is proportional to concentration of salt in aqueous phase.

The electrooxidation of redox probe dissolved in hydrophobic solvent present within pores hydrophobic silicate matrix is followed by anion transfer from aqueous phase, with simultaneous redox active cation transfer to the aqueous phase. The contribution of both reactions phase depends on the type of redox probe, the type of electrolyte and its concentration. The electrode process occurs at the three phase junction formed by graphite particle and liquid organic-aqueous interface supported by hydrophobic silicate matrix. The studied electrode may become attractive sensors on the redox inactive anion present in aqueous phase.

20:10 - 20:25

## Direct Immobilisation of DNA Probes for the Development of Affinity Biosensors

Short communication

**Ilaria Mannelli<sup>1)</sup>, Sara Tombelli<sup>1)</sup>, Maria Minunni<sup>1)</sup>, Ronghui Wang<sup>1,2)</sup>, Marco Mascini<sup>1)</sup>**

*1) Dipartimento di Chimica, Università degli Studi di Firenze (UNIFI), Via della Lastruccia 3, Sesto Fiorentino (Firenze) 50019, Italy*

*2) Chemistry & Chemical Engineering College, Central South University, Changsha, Hunan 410082, China*

An immobilisation procedure based on the direct coupling of thiol-derivatised oligonucleotide probes (Probe-C6-SH) to bare gold sensor surfaces has been optimised for DNA sensing applications. The instrumentation used were the commercially available instruments BIACORE X<sup>TM</sup> and SPREETA<sup>TM</sup> based on surface plasmon resonance (SPR) and a quartz crystal microbalance (QCM).

The performances of the DNA-based sensors resulting from direct coupling of thiol-derivatised DNA probes onto gold SPR-chips or electrodes of quartz crystals, have been studied in terms of the main analytical parameters, i.e. selectivity, sensitivity, reproducibility, analysis time, etc.

A comparison between the thiol-derivatised immobilisation approach and a reference immobilisation method, based on the coupling of biotinylated oligonucleotide probes onto a streptavidin coated dextran sensor surface, using synthetic complementary oligonucleotides has been discussed in detail.

The DNA biosensors developed have been also used to test DNA samples amplified by polymerase chain reaction (PCR).

20:25 - 20:40

Short communication

## Electrochemical Properties and Range of Application of Silver-bismuth Alloy Electrodes. Detection of Zinc, Cadmium and Lead in Real Samples at Sub-ppb Concentration Levels

**Silje M. Skogvold<sup>1)</sup>, oyvind Mikkelsen<sup>1)</sup>, Knut H. Schroder<sup>1)</sup>**

*1) Department of Chemistry, Norwegian University of Science and Technology (NTNU), Trondheim N - 7491, Norway*

As a continuation of our work with alloy electrodes [1, 2], silver alloy electrodes containing different amount of bismuth, ranging from 2 to 15 %, have been studied for use as working electrodes in anodic stripping voltammetry. The electrochemical properties, like the working potential window and potential of hydrogen evolution reaction (HER), are reported. The electrodes have been tested in different solutions. In result, optimal conditions have been found for detection of zinc, cadmium and lead in a sub ppb concentration range in real samples by using differential pulse anodic stripping voltammetry.

Real samples of river and seawater have been examined and concentrations in the ppt range have been detected. With a pre-deposition time of 600 s, the detection limit has been found to be down to 100 ppt for zinc, cadmium and lead, with a standard deviation within 5%.

The use of this non-toxic electrode together featuring outstanding detectability makes the reported system suitable for implementation in continuous monitoring systems for online use.

**Key Words:** Anodic stripping voltammetry, Silver-bismuth electrode, Hydrogen evolution reaction, Heavy metals, Alloy.

### References

1. O. Mikkelsen and K. H. Schroder, *Analyst* (2000) 125, 2163-2165.
2. O. Mikkelsen, S. M. Skogvold, K. H. Schroder, M. I. Gjerde, and T. A. Aarhaug, *Anal. Bioanal. Chem.*, (2003) in press.

20:40 - 20:55

Short communication

**Novel Polymer Modified Electrodes for Sensitive and Selective Detection of Dopamine and Uric Acid****Grzegorz Milczarek<sup>1)</sup>, Aleksander Ciszewski<sup>1)</sup>***1) Institute of Chemistry and Applied Electrochemistry, Poznan University of Technology, Piotrowo 3, Poznan 60-965, Poland*

2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (BAHHFP) was electropolymerized oxidatively on a glassy carbon electrode by cyclic voltammetry. Activity of the polymer modified electrode towards ascorbic acid (AA), uric acid (UA) and dopamine (DA) was characterized by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The response of AA was drastically suppressed and shifted towards more negative potentials at the electrodes modified by the electropolymerized films. Simultaneously, reversibility of both the DA and UA electrode reaction was enhanced. Unusual, selective preconcentration features were observed for DA when the polymer modified electrode was polarized at negative potentials. In a ternary mixture containing the three analytes studied, three baseline resolved DPV peaks are observed. At physiological pH=7.4, after 5 min of preconcentration at -300 mV, peak positions were -0.073, 0.131 and 0.280 V vs. Ag/AgCl for AA, DA and UA, respectively. Relative selectivities, DA/AA and UA/AA, exceeded 4000:1 and 700:1, respectively. The DA response was linear in the range 0.05-3  $\mu\text{M}$  with sensitivity of  $138 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$  and detection limit (3 s) of 5 nM. Sensitive quantification of UA was possible in acidic solution (pH=1.8). Under these conditions a very sharp DPV peak appeared at 630 mV. The response was linear in the range 0.5-100  $\mu\text{M}$  with sensitivity of  $4.67 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$  and detection limit (3 s) of 0.1  $\mu\text{M}$ . Practical utility was illustrated by selective determination of UA in human urine.

**Synthesis and Anion Binding by Phosphonium Calix[4]arenes****R. Pomecko<sup>1,2)</sup>, Z. Asfari<sup>1)</sup>, V. Hubscher<sup>1)</sup>, F. Amaid-Neu<sup>1)</sup>, J. Vicens<sup>1)</sup>, M. Bochenska<sup>2)</sup>***1) UMR 7512 (CNRS-ULP), ECPM, 25 rue Becquerel, Strasbourg 67087, France**2) Department of Chemical Technology, Gdansk University of Technology, Narutowicza 11/12, Gdansk 80-264, Poland*

Anion binding can be achieved by neutral receptors through hydrogen bonding or by positively charged ligands through electrostatic interaction.<sup>1</sup> Some examples of both types of receptors based on calixarene structures have already been published.<sup>2</sup>

We report here the synthesis of two new positively charged calix[4]arene derivatives substituted at the lower rim by two and four triphenylphosphonium butyl groups, respectively. The first results of UV and NMR experiments concerning their ability to complex tetrahedral oxyanions ( $\text{ClO}_4^-$ ) and iodide will also be presented.

## References

1.P. D. Beer and P. A. Gale, *Angew. Chem. Int. Ed. Engl.* 2001, 40, 486.

2.S. E. Matthews, P. D. Beer, in "Calixarenes 2001", Z. Asfari, V. Bohmer, J. Harrowfield, J. Vicens Eds., Kluwer Academic Publishers, Dordrecht, 2001, p. 421-439.

**Molecular Logic Gates****Konrad Szacilowski<sup>1)</sup>***1) Faculty of Chemistry, Jagiellonian University, Ingardena 3, Kraków 30-060, Poland*

Rapid development of different electronic devices was initiated by the discovery of semiconductor-based switch - a transistor in 1948 by J. Bardeen, W.H. Brattain and W.B. Shockley. All electronic devices are based on semiconductor components ever since. Growing demand for bigger memories and faster processors requires smaller and smaller transistors and other components. Soon the integration scale of electronic components will reach the physical limits and further speeding up will not be possible. The only solution of the crisis is application of single molecules and molecular systems for data acquisition, storage, transfer and processing.

There are many chemical systems capable of digital data processing. The most important are: fullerenes, carbon nanotubes, DNA processing systems and Aviram-Ratner type devices. All these systems, except of DNA, use however classical electronics approach. Logic gates and switches are in principle based on the same phenomena as semiconductor devices. Chemical logic gates present other approach. These systems consist of molecules, which can exist in at least two different states (isomers, rotamers etc.) and there are defined physical or chemical stimuli capable of switching the system from one state to the other (for example light, redox potential, temperature, pressure, pH, metal ions etc.).

Usually the chemical logic systems are based on extremely complicated supramolecular complexes, like Balzani's "molecular meccano" systems (rotaxanes, catenanes and dendrimers) or large organic ligands encompassing receptor sites and chromo- or fluorophores, like de Silva's systems.

There are, however, other systems, much simpler from chemical point of view, but their logic structure is even more complicated as compared with previously mentioned systems. One of the simplest chemical systems capable of performing complex logical operations consists of two pentacyanoferrates in equilibrium. Reactivity and photoreactivity of the system strongly depends on different chemical and physical stimuli and perfectly mimics the behaviour of different logic gates.

20:55 - 21:10

Short communication

21:10 - 21:30

Keynote lecture

---

## Sunday, November 16th

---

07:00 - 08:00

### Breakfast

---

08:00 - 10:15

### Session 8, Chairpersons - Andrzej S. Baranski, Johan B. Bobacka

---

8:00 - 8:40

### Porphyrin and Fullerene Modified Electrodes for Electrochemical Catalytic and Sensor Applications

Tutorial  
lectureFrancis D Souza<sup>1)</sup>

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

Metalloporphyrins and fullerenes have been extensively used for modification of electrode surfaces and subsequent applications in the fields of sensors and catalysis.<sup>1,2</sup> Metalloporphyrins as electrode surface modifying agents are very attractive because of their redox tuning by the choice of metal ion in the macrocycle cavity and peripheral substituents on the ring.<sup>1</sup> Recently, fullerenes have also shown promise as materials for electrode surface modification.<sup>2</sup> The present contribution deals with the porphyrin and fullerene surface modified electrodes developed for sensor and catalytic purposes in our laboratory. Specific examples to be discussed include: electrocatalysts for a direct four-electron reduction of dioxygen to water at elevated pH conditions by using ion-pair metalloporphyrin dimer modified electrodes;<sup>3</sup> electrochemical sensors for dioxygen detection in solution by using electrodes modified with condensation polymer film of  $\beta$ -cyclodextrin hosting cobalt porphyrin redox centers;<sup>4</sup> electrocatalytic reaction of  $\alpha,\omega$ -dihaloalkanes by fullerene, C<sub>60</sub>, modified electrodes;<sup>5</sup> modification and electrochemical characterization of electrode surfaces by self-assembled monolayers of functionalized fullerene-ferrocene dyads,<sup>6</sup> and, recognition and catalytic reduction of Cytochrome c by fullerene-palladium modified electrodes.<sup>7</sup>

#### References

1. Biesaga, M.; Pyrzynska, K.; Trojanowicz, M. *Talanta* (2000), 51, 209-224.
2. Sherigara, B. S.; Kutner, W.; D'Souza, F. *Electroanalysis* (2003), 15, 753-772.
3. D'Souza, F.; Hsieh, Y-Y.; Deviprasad, G. R. *Chem. Commun.* (1998), 1027-1028.
4. D'Souza, F.; Choi, J-p.; Hsieh, Y-Y.; Shriver, K.; Kutner, W. J. *Phys. Chem. B* (1998), 102, 212-217.
5. D'Souza, F.; Hsieh, Y-Y.; Wickman, H.; Kutner, W. *Chem. Commun.* (1997), 1191-1192.
6. Hoang, Vu T.; Rogers, Lisa M.; D'Souza, Francis. *Electrochemistry Communications* (2002), 4(1), 50-53.
7. D'Souza, F. et. al. Manuscript in preparation, (2003).

8:40 - 9:20

### Atomic Force Microscopy of DNA Immobilized onto a Highly Oriented Pyrolytic Graphite Electrode Surface

Tutorial  
lectureAna Maria Oliveira Brett<sup>1)</sup>, Ana-Maria Chiorcea<sup>2)</sup>

1) Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra (UC), Rua Larga, COIMBRA 3004-535, Portugal

2) Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra (UC), Rua Larga, Coimbra 3004-535, Portugal

Magnetic AC mode atomic force microscopy (MAC Mode AFM) was used to characterize adsorption of DNA on a highly oriented pyrolytic graphite (HOPG) electrode surface using different concentrations of DNA and adsorption procedures. AFM of DNA immobilized on the HOPG showed that both single-stranded DNA and double-stranded DNA molecules have the tendency to spontaneously self assemble from solution onto the solid support and that this process is very fast. DNA condensed on the substrate in a tight and well spread two-dimensional lattice covering the entire surface uniformly. The interaction of DNA with the hydrophobic HOPG surface induced DNA superposition, overlapping, intra- and intermolecular interactions. Controlling the electrode potential offers the possibility to enlarge the capability of AFM imaging of DNA immobilised onto conducting substrates, such as HOPG. The effect of application of a positive potential of 300 mV (vs. Ag wire) to the HOPG electrode during adsorption was studied. The applied potential considerably enhanced the robustness and stability to mechanical stress of the DNA films, through multiple electrostatic interactions between the negatively charged hydrophilic sugar-phosphate backbone and positively charged carbon surface. The characteristics of the DNA films and the apparent height of the network wires were dependent on DNA concentration and immobilization procedure. The DNA lattices were held together on the substrate surface only by non-covalent interactions, such as hydrogen bonding, base stacking, electrostatic, van der Waals and hydrophobic interactions.



**Molecular and Supramolecular Architectures for Functional Devices**

9:20 - 10:00

**Francesco Paolucci<sup>1)</sup>, Massimo Marcaccio<sup>1)</sup>, Maurizio Prato<sup>2)</sup>, Demis Paolucci<sup>1)</sup>***1) Dipartimento di Chimica "G. Ciamician", University of Bologna (UNIBO), via Selmi 2, Bologna 40126, Italy*Tutorial  
lecture*2) Università di Trieste, Italy*

Organised architectures at a molecular level are attracting increasing attention in materials science for their vital role in emerging technologies related to environmental, energy conversion and catalytic applications, for the development of novel sensors and biosensors and in molecular electronics. The organic functionalization of fullerenes is one of the most intensively investigated areas of fullerene chemistry. Fullerenes are able to accept up to six electrons and their curved surface and small reorganisation energy upon reduction make them attractive candidates for artificial photosynthetic systems. More recently carbon nanotubes are also emerging as important active components of molecular devices. Single walled carbon nanotubes, to which photo and electroactive were covalently tethered, were successfully used for generating photo-induced intramolecular charge separation and as electronic transducers for sensors and biosensors.

**Photoactive Liquid Crystalline Hybrid**

10:00 - 10:15

**Demis Paolucci<sup>2)</sup>, Francesco Paolucci<sup>2)</sup>, Massimo Marcaccio<sup>2)</sup>, Philip Moriarty<sup>1)</sup>, Peter H. Beton<sup>1)</sup>, Robert Deschenaux<sup>3)</sup>, Maurizio Prato<sup>4)</sup>***1) University of Nottingham, Nottingham, United Kingdom*Short com-  
munication*2) Dipartimento di Chimica "G. Ciamician", University of Bologna (UNIBO), via Selmi 2, Bologna 40126, Italy**3) Université de Neuchâtel, Switzerland**4) Università di Trieste, Italy*

The search for liquid crystals (LCs) displaying novel and specific properties is a crucial point for the development of new technologies. Electroactive or photoactive LCs are of high interest because of the possibility to tune the mesomorphic and physical properties. Combination of an electron acceptor subunit (fullerene) and an electron donor subunit (ferrocene) within the same molecular framework could allow to design new switchable materials.

The electrochemical behaviour of this compound was investigated under strictly aprotic conditions by cyclic voltammetry and displays either fullerene- or ferrocene-centered reduction or oxidation process, respectively. The stability of the different mixed ferrocene-fullerene LC under reduction conditions was studied in view of the application of such species as photoactive molecular devices. In fact, photophysical studies revealed that intramolecular electron transfer between the ferrocene and fullerene units represents the major deactivation pathway of the corresponding electronically excited LCs.

In principle, the photoinduced electron transfer could be used to control the liquid-crystalline properties due to the presence of either the ferrocene (light off) or ferrocenium (light on) species.

Furthermore, SPM studies, currently in progress, show that the dynamics of the molecular layer, tuneable by the temperature, is controlled by intermolecular forces.

**Coffee break**

10:15 - 10:35

**Session 9, Chairpersons - Gary J. Blanchard, Paweł G. Krysiński**

10:35 - 12:50

**DNA Modified Screen-printed Carbon Electrodes as Chemical Sensors**

10:35 - 11:15

**Jan Labuda<sup>1)</sup>***1) Department of Analytical Chemistry, Slovak University of Technology, Bratislava, SK-81237, Slovakia (Slovak Republic)*Tutorial  
lecture

Electrochemical DNA biosensors have found their permanent place among chemical sensors. The aim of this work is a development of simple (single-use) electrochemical sensors based on chemical interactions of the surface bound double stranded (ds) DNA. Carbon paste based screen-printed electrodes have been modified with the DNA layer and applied to the determination of various chemicals such as drugs and pollutants that bind to DNA, the detection of species leading to degradation of DNA and the investigation of antioxidants that prevent DNA towards its oxidative damage.

Binding of biologically active quinazoline derivatives to DNA was investigated and a procedure for their determination was described. Significant association of derivatives of polycyclic aromatic hydrocarbons with DNA was observed and used for their analytical determination. The results were compared with those obtained at cyclodextrin based sensors. An reversible association of some local anaesthetics based on the chiral derivatives of alkoxyphenyl-carbamic acids with DNA was found, particularly in weak acidic and neutral solution where the protonated forms of the drug molecules bind electrostatically to the negatively charged DNA backbone. The method for their differential pulse voltammetric determination has been developed and applied to the analysis in spiked serum.

Simple procedure for the detection of a deep DNA degradation by reactive oxygen species has been developed and used for the estimation of antioxidant activity of yeast polysaccharides, phenolic acids, natural flavonoids and plant extracts. Conventional methods were used for the validation. Experimental conditions can be tuned up according to the concentration level of the active substances to be evaluated. Simple solid DNA biosensors are promising for special purposes, particularly for analysis in small labs and in field.

11:15 - 11:55

Tutorial  
lecture

## Ionomer-coated Electrodes and Nanoelectrode Ensembles for Electrochemical Sensing Purposes

**Paolo Ugo**<sup>1)</sup>

1) *Dipartimento di Chimica Fisica, Università Ca' Foscari di Venezia, S. Marta 2137, Venezia 30123, Italy*

This paper focuses on recent advances in the use of ionomer-coated electrodes and nanoelectrode ensembles for the determination of redox ions at trace concentration level.

In the first part, stress is put on recent developments concerning the deposition and electroanalytical uses of electrodes coated with ultrathin films of ionomers (Nafion, Tosflex, Eastman AQ) obtained by using Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) techniques. Problems and achievements for obtaining LB- and LS-films of these polymers are described.

Morphological characteristics of these coatings are obtained by atomic force microscopy and quartz crystal microbalance. Voltammetry allows the ion-exchange and electrochemical characterization of these ultrathin films. Advantages and limits with respect to micrometer-thick coatings obtained by "conventional" techniques (dip-coating, spin-coating, microvolume evaporation) are critically discussed.

The second part of the talk deals with the development and electroanalytical use of a new kind of nanostructured electrodes named nanoelectrode ensembles (NEEs). They are prepared by template deposition of metal nanofibers within the pores of microporous tracked-etched polycarbonate membranes. NEEs can find application in a variety of fields, from sensors to electronics, from energy storage to magnetic materials.

From an analytical viewpoint, NEEs display improved electroanalytical detection limits relative to conventional electrodes because the Faradaic current (signal) is proportional to the total geometric area of the ensemble (nanodiscs and insulator), while the background current (double-layer charging current) is proportional only the nanodiscs (active) area.

NEEs show also peculiar kinetic properties since they allow the determination of very high heterogeneous charge transfer rate constants. They behave, in fact, like partially blocked electrode surfaces. Therefore, the heterogeneous electron transfer kinetics is ruled by an apparent rate constant which is diminished with respect to the true rate constant by a factor which depends on the ratio between the nanodiscs (active) area and the blocked area (membrane).

Prospects for applying the discussed electrode devices to sensing purposes are critically evaluated. In particular, advantages and limits of the use of LB- and LS-ionomer-coated electrodes and NEEs for shuttling electrons to redox mediators and (possibly) directly to redox proteins are discussed.

Bibliography

P. Ugo, L.M. Moretto, F. Vezza, *ChemPhysChem*, (2002), 3, 917-925 (and references cited therein.)

11:55 - 12:35

Tutorial  
lecture

## Microelectrochemistry. From Materials to Biological Applications

**Wolfgang Schuhmann**<sup>1)</sup>

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

Miniaturization and exact positioning of needle-type electrodes opens new ways for the visualization of chemical and biochemical activity on surfaces. In scanning electrochemical microscopy (SECM) a needle-type ultramicroelectrode is positioned in close proximity to a surface of interest, and the Faraday current caused by the redox conversion of a free-diffusing redox mediator is used to visualize with high lateral resolution the electrochemical activity. The tutorial lecture will present the basic considerations concerning SECM in constant-height and constant-distance scanning together with the different operation modes of SECM such as feedback mode, generator-collector mode.

Using different examples from material sciences and biological applications the successful application of SECM and constant-distance mode SECM will be demonstrated:

-fabrication of different types of needle-type nanoelectrodes and high-resolution SECM imaging

-fabrication of feedback-independent nanoelectrodes for high-resolution imaging in pure generator-collector arrangements

-fabrication of combined dual electrode tips and SECM imaging in microdroplets

-studies on the dissolution of CaCO<sub>3</sub> crystal in aqueous solution using a Ca<sup>2+</sup>-selective capillary-type liquid-membrane potentiometric sensor

-application of constant-distance mode SECM for local detection of signaling molecules released from adherently growing biological cells  
 -alternating-current SECM as a tool for imaging of local corrosion phenomena.

The author is grateful to the present and former coworkers in the research group who contributed to the development of SECM namely Christine Kranz, Andreas Hengstenberg, Bernardo Ballesteros Katemann, Thomas Erichsen, Mathieu Etienne, Albert Schulte, Luciana Pitta, Nizam Diab, Sonnur Isik, Sascha Belger, Florin Turku, Marcus Mosbach.

---

### Ion equilibrium in lichen surrounding

**Małgorzata Rajfur<sup>1)</sup>, Andrzej Kłos<sup>1)</sup>, Maria Wacławek<sup>1)</sup>, Witold Wacławek<sup>1)</sup>**

*1) Institute of Chemistry, Opole University (OU), Oleska 48, Opole 45-052, Poland*

Investigation of the lichen use as bioindicators, determining dependencies between atmosphere composition and changes in anatomical and morphological features were carried out since the 70's, when Hawskworth and Rose worked out the 10 gradual lichenic scale for England and Wales which indicates the level of sulphur dioxide contamination of the atmosphere. This method of investigations, now known as the floristic one, is still used also in Poland.

Our investigations showed, that lichen dipped in electrolytes solutions change its composition exchanging cations between the solution and cation-active lichen layer. This mechanism may stabilize the surrounding pH value.

The aim of our research was studies of the dependence between pH of rain and type and quantity of mobile ions bound in the cation-active layer of lichens. The natural cation-active materials, were investigated in accordance with the methods applied for the synthetic ion exchangers. During our investigations the changes in type and concentration of ions between the solution and lichen were not found, however, one should suppose that in accordance with the Donnan's effect this occurrence should take place.

The research was carried out using Hypogymnia physodes lichens, collected in different places from coniferous and leafy trees. Desorption of mobile cations:  $H^+$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ , naturally connected with lichen, were carried out in copper sulphate or hydrochloric acid solutions of concentrations  $c < 2 \cdot 10^{-3} \text{ mol/dm}^3$ . The changes in conductivity and pH of the solutions were measured and the contents of metals before and after desorption process were determined.

Key words: lichen, ion equilibrium, lichen indication.

12:35 - 12:50

Short communication

---

### Closing remarks - Włodzimierz Kutner

12:50 - 13:00

---

### Lunch

13:00 - 14:00

---

### Departure for Warsaw

14:00 - 19:00

On our way back to Warsaw, we will visit an Orthodox Church main center of Poland in Grabarka.

# Address book

<b>Baranski, Andrzej S.</b>	baranski@duke.usask.ca	CANADA University of Saskatchewan
<b>BIDAN, Gérard M.</b>	gbidan@cea.fr	FRANCE CEA-Grenoble, DRFMC/SI3M, UMR 5819 SPrAM
<b>Bilewicz, Renata O.</b>	bilewicz@chem.uw.edu.pl	POLAND Faculty of Chemistry, University of Warsaw
<b>Blanchard, Gary J.</b>	blanchard@chemistry.msu.edu	UNITED STATES Michigan State University, Department of Chemistry (MSU)
<b>Bobacka, Johan B.</b>	johan.bobacka@abo.fi	FINLAND Abo Akademi University, Process Chemistry Centre, Laboratory of Analytical Chemistry
<b>de la Rica, Roberto</b>	roberto.delarica@cnm.es	SPAIN Centre Nacional de Microelectrónica (CNM) - CSIC
<b>D Souza, Francis</b>	Francis.DSouza@wichita.edu	UNITED STATES Department of Chemistry, Wichita State University
<b>Fabianowski, Wojciech R.</b>	wofab@ch.pw.edu.pl	POLAND Chemistry Department, Warsaw University of Technology (PW)
<b>Ferapontova, Elena E.</b>	elena.ferapontova@analykem.lu.se	SWEDEN Centre for Chemistry and Chemical Engineering, Lund University (KC)
<b>Gorton, Lo</b>	Lo.Gorton@analykem.lu.se	SWEDEN Department of Analytical Chemistry, Lund University
<b>Grabiec, Piotr</b>	grabiec@ite.waw.pl	POLAND Institute of Electron Technology (ITE)
<b>Haupt, Karsten</b>	Karsten.Haupt@tbiokem.lth.se	FRANCE Compiègne University of Technology, UMR CNRS 6022
<b>Horvai, George</b>	horvai@ch.bme.hu	HUNGARY Budapest University of Technology and Economics, Dept. Chem. Inf. Techn.
<b>Iwaniuk, Monika</b>	mriwaniuk@wp.pl	POLAND Faculty of Chemistry, University of Warsaw
<b>Kochman, Agnieszka</b>	agakoch@go2.pl	POLAND Institute of Physical Chemistry Polish Academy of Sciences
<b>Kolasińska, Marta</b>	nkolasi@cyf-kr.edu.pl	POLAND Institute of catalysis and Surface Chemistry of the Polish Academy of Science
<b>Krysiński, Paweł G.</b>	pakrys@chem.uw.edu.pl	POLAND Faculty of Chemistry, University of Warsaw
<b>Kulesza, Paweł J.</b>	pkulesza@chem.uw.edu.pl	POLAND Faculty of Chemistry, University of Warsaw
<b>Kutner, Włodzimierz</b>	wkutner@ichf.edu.pl	POLAND Institute of Physical Chemistry Polish Academy of Sciences

---

<b>Labuda, Jan</b>	labuda@chtf.stuba.sk	SLOVAKIA (SLOVAK REPUBLIC)
	Department of Analytical Chemistry, Slovak University of Technology	
<b>Lesińska, Urszula</b>	ulesinska@wp.pl	POLAND
	Faculty of Chemistry, Gdańsk University of Technology	
<b>Lewandowska, Natalia</b>	rumianka@ch.pw.edu.pl	POLAND
	Faculty of Chemistry, Warsaw University of Technology	
<b>Litescu, Simona Carmen</b>	sim,lc@yahoo.com	ROMANIA
	Faculty of Chemistry, University of Bucharest	
<b>Macyk, Wojciech</b>	macyk@chemia.uj.edu.pl	POLAND
	Faculty of Chemistry, Jagiellonian University	
<b>Maksymiuk, Krzysztof</b>	kmaks@chem.uw.edu.pl	POLAND
	Faculty of Chemistry, University of Warsaw	
<b>Mannelli, Ilaria</b>	ilaria.mannelli@unifi.it	ITALY
	Dipartimento di Chimica, Università di Firenze (UNIFI)	
<b>Marczak, Renata</b>	rmarczak@ichf.edu.pl	POLAND
	Institute of Physical Chemistry Polish Academy of Sciences	
<b>Marken, Frank</b>	f.marken@lboro.ac.uk	UNITED KINGDOM
	Department of Chemistry, Loughborough University	
<b>Mazur, Maciej</b>	mmazur@photon.chem.msu.edu	POLAND
	University of Warsaw, Department of Chemistry	
<b>Michalska, Agata J.</b>	agatam@chem.uw.edu.pl	POLAND
	Faculty of Chemistry, University of Warsaw	
<b>Miecznikowski, Krzysztof</b>	kmiecz@chem.uw.edu.pl	POLAND
	Faculty of Chemistry, University of Warsaw	
<b>Mielniczak, Alina K.</b>	omlet@p.lodz.pl	POLAND
	Department of Molecular Physics, Technical University of Lodz (TUL)	
<b>Mikkelsen, Oyvind</b>	Oyvind.Mikkelsen@chem.ntnu.no	NORWAY
	Department of Chemistry, Norwegian University of Science and Technology (NTNU)	
<b>Milczarek, Grzegorz</b>	gregor33@icpnet.pl	POLAND
	Institute of Chemistry and Applied Electrochemistry, Poznan University of Technology	
<b>Nagels, Luc J.</b>	lnagels@ruca.ua.ac.be	BELGIUM
	Department of Physics, University of Antwerp	
<b>Niedziółka, Joanna</b>	joaniek@ichf.edu.pl	POLAND
	Institute of Physical Chemistry, Polish Academy of Sciences	
<b>Nowak, Lucyna</b>	lucyna@chemul.uni.lodz.pl	POLAND
	Department of General and Inorganic Chemistry, Lodz University	
<b>Nyholm, Leif</b>	Leif.Nyholm@kemi.uu.se	SWEDEN
	Uppsala University, Department of Analytical Chemistry	
<b>Oliveira Brett, Ana Maria C.</b>	brett@ci.uc.pt	PORTUGAL
	Departamento de Química, Universidade de Coimbra (UC)	
<b>Opallo, Marcin</b>	mopallo@ichf.edu.pl	POLAND
	Institute of Physical Chemistry, Polish Academy of Sciences	
<b>Orzeł, Łukasz M.</b>	orzel@chemia.uj.edu.pl	POLAND
	Faculty of Chemistry, Jagiellonian University	

---

<b>Paolucci, Demis</b>	demis@ciam.unibo.it Dipartimento di Chimica "G. Ciamician", University of Bologna (UNIBO)	ITALY
<b>Paolucci, Francesco</b>	francesco.paolucci@unibo.it Dipartimento di Chimica "G. Ciamician", University of Bologna (UNIBO)	ITALY
<b>Polak, Beata</b>	wofab@ch.pw.edu.pl Faculty of Chemistry, Warsaw University of Technology	POLAND
<b>Polak, Beata</b>	bepolak@op.pl (no affiliation specified)	
<b>Pomecko, Radoslaw</b>	rip78@wp.pl Faculty of Chemistry, Gdańsk University of Technology	POLAND
<b>Rajfur, Małgorzata</b>	mrajfur@o2.pl Institute of Chemistry, Opole University (OU)	POLAND
<b>Schuhmann, Wolfgang</b>	wolfgang.schuhmann@rub.de Anal. Chem. - Elektroanalytik & Sensorik; Ruhr-Universität Bochum (ELAN)	GERMANY
<b>Shul, Galyna</b>	shul@ichf.edu.pl Institute of Physical Chemistry Polish Academy of Sciences	POLAND
<b>Skogvold, Silje M.</b>	Silje.Skogvold@chem.ntnu.no Department of Chemistry, Norwegian University of Science and Technology (NTNU)	NORWAY
<b>Starodub, Nickolaj F.</b>	nstarodub@hotmail.com A. V. Palladin Institute of Biochemistry, Ukrainian National Academy of Sciences	UKRAINE
<b>Szacilowski, Konrad</b>	szacilow@chemia.uj.edu.pl Faculty of Chemistry, Jagiellonian University	POLAND
<b>Ugo, Paolo</b>	ugo@unive.it Dipartimento di Chimica Fisica, Università Ca' Foscari di Venezia	ITALY
<b>Vitovic, P.</b>	vitovic@center.fmph.uniba.sk Department of Biophysics and Chemical Physics, Comenius University	SLOVAKIA (SLOVAK REPUBLIC)
<b>Winkler, Krzysztof</b>	winkler@cksr.ac.bialystok.pl Institute of Chemistry, University of Bialystok	POLAND
<b>Wittstock, Gunther</b>	gunther.wittstock@uni-oldenburg.de Carl von Ossietzky University Oldenburg, School of Mathematics and Natural Sciences	GERMANY
<b>Zuchniak, Justyna</b>	bilewicz@chem.uw.edu.pl Faculty of Chemistry, University of Warsaw	POLAND

# Index

- Achmatowicz, Selim, 22  
Amatore, Christian, 23  
Amaud-Neu, F., 31  
Asfari, Z., 31
- Bala, Camelia, 13  
Baranski, Andrzej S., 19, 36  
Bartlett, P. N., 21  
Ben Ali, Samia, 21  
Beton, Peter H., 33  
BIDAN, Gérard M., 36  
Bidan, Gerard M., 14  
Bilewicz, Renata, 15  
Bilewicz, Renata O., 36  
Blanchard, Gary J., 17, 20, 36  
Bobacka, Johan B., 25, 36  
Bochenska, M., 31  
Bochenska, Maria, 26
- Chiorcea, Ana-Maria, 32  
Chojak, Malgorzata, 27  
Ciszewski, Aleksander, 31  
Compton, Richard, 23  
Cook, D. A., 21
- D Souza, Francis, 32, 36  
de la Rica, Roberto, 36  
Desbat, Bernard, 21  
Deschenaux, Robert, 33  
Domański, Krzysztof, 20
- Fabianowski, Wojciech R., 21, 36  
Farace, Giosio, 28  
Ferapontova, Elena, 24  
Ferapontova, Elena E., 13, 36  
Filipiak, Marian, 22
- Gadomski, Adam, 22  
Gajdos, Victor, 28  
Gorton, Lo, 24, 36  
Grabiec, Piotr, 20, 36
- Haupt, Karsten, 12, 28, 36  
Hianik, Tibor, 19, 28  
Hoffmann, Maria, 26  
Horvai, George, 12, 36  
Hubscher, V., 31
- Iwaniuk, Monika, 36
- Janus, Paweł, 20
- Kłos, Andrzej, 35  
Karnicka, Katarzyna, 27  
Karpinska, Aleksandra, 21  
Klett, Oliver, 18  
Kochman, Agnieszka, 28, 36  
Kolasińska, Marta, 14, 36  
Krysiński, Paweł G., 17, 36  
Kuhn, Alexander, 21  
Kulesza, Paweł J., 27, 36  
Kutner, Włodzimierz, 28, 36
- Labuda, Jan, 33, 37  
Lesińska, Urszula, 37  
Lesinska, Urszula, 26  
Lewandowska, Natalia, 37  
Lewis, R.N.A.H., 19  
Liljegren, Gustav, 18  
Litescu, Simona Carmen, 13, 37
- Macyk, Wojciech, 26, 37  
Maksymiuk, Krzysztof, 19, 37  
Mannelli, Ilaria, 30, 37  
Marcaccio, Massimo, 33  
Marczak, Renata, 37  
Marken, Frank, 25, 37  
Marty, Jean-Louis, 13  
Mascini, Marco, 30  
Mazur, Maciej, 20, 37  
McElhaney, R.N., 19  
McKenzie, Katy J., 25  
Michalska, Agata J., 20, 37  
Miecznikowski, Krzysztof, 27, 37  
Mielniczak, Alina K., 29, 37  
Mikkelsen, oyvind, 30  
Mikkelson, Oyvind, 16, 17, 37  
Milczarek, Grzegorz, 31, 37  
Minunni, Maria, 30  
Moriarty, Philip, 33
- Nagels, Luc J., 16, 37  
Niedziółka, Joanna, 28, 37  
Nowak, Lucyna, 37  
Nyholm, Leif, 18, 37

Oczkowski, Tomasz M., 22  
Oleinick, Alexander, 23  
Oleinick, Alexander I., 23  
Oliveira Brett, Ana Maria, 32  
Oliveira Brett, Ana Maria C., 37  
Opałło, Marcin, 28  
Opallo, Marcin, 27, 29, 37  
Orzeł, Łukasz M., 37

Paolucci, Demis, 33, 38  
Paolucci, Francesco, 33, 38  
Pap, Timea, 12  
Polak, Beata, 38  
Pomecko, R., 31  
Pomecko, Radosław, 38  
Prato, Maurizio, 33

Rajfur, Małgorzata, 35, 38  
Ruzgas, Tautgirdas, 24

Schroder, Knut H., 16, 17, 30  
Schuhmann, Wolfgang, 34, 38  
Shul, Galyna, 29, 38  
Skogvold, Silje M., 16, 17, 30, 38  
Starodub, Nickolaj F., 18, 38  
Stoica, Leonard, 24  
Svir, Irina B., 23  
Szacilowski, Konrad, 31, 38

Tombelli, Sara, 30

Ugo, Paolo, 34, 38

Vadgama, Pankaj, 28  
Vicens, J., 31  
Vitovic, P., 19, 38

Wacławek, Maria, 35  
Wacławek, Witold, 35  
Wandelt, Barbara J., 29  
Wang, Ronghui, 30  
Warszyński, Piotr, 14  
Winkler, Krzysztof, 24, 38  
Wittstock, Gunther, 26, 38

Zaborowski, Michał, 20  
Zuchniak, Justyna, 38