The 9th Spring Meeting

of the International Society of Electrochemistry

Electrochemical Sensors: From nanoscale engineering to industrial applications

May 8 to 11, 2011 Turku, Finland

Book of Abstracts

Conference Schedule

Sunday, 8 May	Monday, 9 May	Tuesday, 10 May	Wednesday, 11 May
	09:00-09:40 **Keynote Address**	09:00-09:40 **Keynote Address**	09:00-09:40 **Keynote Address**
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Book of Abstracts of the

9th Spring Meeting of the International Society of Electrochemistry

Electrochemical Sensors: From nanoscale engineering to industrial applications

May 8 to 11, 2011, Turku, Finland

Organized by:
ISE Division 1 Analytical Electrochemistry
ISE Division 5 Electrochemical Process Engineering And Technology
ISE Region Finland

International Society of Electrochemistry
Rue de Sébeillon 9b
1004 Lausanne
Switzerland

Printed in Finland

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Ari Ivaska, *Åbo Akademi University, Finland*
Chee-Seng Toh, *Nanyang Technological University, Singapore*

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IYC 2011

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Christopher Brett *(Departamento de Quimica, Faculdade de Ciencias e Tecnologia, Universidade de Coimbra, Coimbra, Portugal)*

Why Electrochemistry and What Can It Do For Us? The Achievements of Electrochemistry and the Future

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Christian Amatore *(Ecole Normale Superieure et CNRS, Department of Chemistry, UMR 8640, Paris, France)*

Finding Out Egyptian Gods' Secret with MicroElectrochemical Sensors: Biomedical Properties of Egyptian Black Makeup Revealed by Microamperometry at Single Cells

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Reception

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Auditorium

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Gordon Wallace *(ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Wollongong, Australia)*

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Xuemei Wang *(State Key Laboratory of Bioelectronics, Chien-Shiung Wu Laboratory, Southeast University, Nanjing, China)*

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Li Niu *(Engineering Laboratory for Modern Analytical Techniques, c/o State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China),* Ari Ivaska

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15:50 to 16:00

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Lucio Angnes *(Instituto de Quimica, Universidade de São Paulo, São Paulo, Brazil)*

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Rui Campos *(Department of Chemistry, Durham University, Durham, United Kingdom),* Ritu Kataky

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Ricardo Carvalho *(Dept. de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, Coimbra, Portugal),* Aziz Amine, Christopher Brett, Adil Mandil

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IYC 2011

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Finding Out Egyptian Gods' Secret with MicroElectrochemical Sensors:

Biomedical Properties of Egyptian Black Makeup Revealed by Microamperometry at Single Cells

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Ancient Egypt black eye make-up is reputed. However, surprisingly, most social categories used materials similar in textures and composition.

The Louvre scientific laboratory added to this puzzle by demonstrating that the basic material used for such make-up was not natural but resulted from a long and elaborate, thus expensive, chemical transformation involving raw (galena, cerussite) and artificial (laurionite, phosgenite) lead materials. Ancient chemical procedures disclosed in papyri (Dioscorides) could be cast in modern chemical language and reproduced to afford the same micrometric facetted crystals with identical chemical composition and size. This is in fact the first reported example of "industrial-scale" wet chemistry.

A possible clue to the puzzle came upon remarking that ancient Egypt was a wet country copiously irrigated by the Nile and its overflows. A combination of water, heat and rich organic matter is tantamount to bacterial soup. As happens today in tropical countries, ancient Egyptians had to control endemic bacterial diseases which proceed essentially through eye contact with contaminated water.

This prompted us to investigate the possible effects of the make-up composition on single cells. These studies revealed that these crystals have specific anti-bacterial effects absent from its raw materials, by provoking NO°-based oxidative stress into exposed cells. In turn, the released NO° induces chemical signalling and vasodilatation of blood capillaries thus increasing the flux of macrophages to the eye further protecting it from most bacterial intrusion.[1]

Hence, this study established that ancient Egyptians chemically engineered more than 26 centuries ago the first mass production of a bioactive material for its medicinal properties.

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Why Electrochemistry and What Can It Do For Us? The Achievements of Electrochemistry and the Future

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The International Year of Chemistry is an excellent opportunity to celebrate the achievements and future prospects of chemistry, and, today, focusing on electrochemistry. Electrochemistry, through the investigation of oxidation and reduction reactions, played a crucial role in the understanding of natural phenomena and the development of the periodic table. It has become part of our everyday life and in many ways is all-pervasive, being dependent on the essentially clean energy that arises from the transfer of electrons, seen through many applications which range from biological processes, sensors through to industrial processes and energy sources. This lecture will illustrate the successes of electrochemistry in the energy, transport, chemical industry, sensor and biosensor areas as well as contributions made in the area of environment, health and food. Prospects for future progress and applications will also be indicated.

Keynote Lectures

Nanoparticle Architectures for Improving Selectivity and Sensitivity of Electrochemical Affinity Biosensors

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Nanoparticles have attracted enormous interest in biosensing related to a range of unique properties they possess. Here we will present two aspects of using nanoparticles in electrochemical sensing where the nanoparticles provide opportunities to improve the selectivity and sensitivity of electrochemical biosensors

In the first aspect electrode are modified with self-assembled monolayers (SAMs) that passivate the electrode. Gold nanoparticles (NP) are then attached to give electrode-SAM-NP constructs. The electrode-SAM-NP system shows efficient electron transfer to the underlying bulk gold electrode [1]. These electrode-SAM-NP constructs allow detection of specific analytes whilst preventing nonspecific interaction of other species in the sample with the underlying electrode; thus improving selectivity. These biosesing interfaces are then applied to the detection of metal ions [2], antibodies and other proteins.

The second aspect focuses on using gold coated magnetic nanoparticles as dispersible electrodes that can be sent out into the sample, collect the analyte and bring it back to an macroelectrode for detection. This strategy is shown to give highly sensitive sensors that have much faster response times than classical macroscopic sensors. Here how the particles are made [3] is discussed followed by modification strategies to convert these nanoparticles into nanoelectrodes selective again for metal ions [4] and proteins.

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Work Function Potentiometric Sensors

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Electrical properties of organic semiconductors (OS) are controlled by the primary and secondary doping[1]. These highly versatile materials have found sensing application in modern potentiometric sensors for ions[2] as well as for potentiometric sensing of gases[3]. Operation of the equilibrium ion sensors is governed by the modulation of the potential at the interface between the solution and the selective material, according to the Nikolskij-Eisenman equation. Exchange of ions with the OS can be seen as form of secondary doping of the latter. For the operation of such potentiometric sensors a stable and well-defined external reference electrode is needed[4].

When OS are exposed to a gas or vapor that can donate or accept electrons a charge transfer complex is formed between the OS and the gas. Such interaction is called *secondary doping*, which results in modulation of work function (WF) of the OS. Experimentally, the interaction can be measured with a Kelvin Probe or with a chemically sensitive field-effect transistor (CHEMFET). The quantitative relationship between the partial pressure of the dopant gas P_G and the shift of the WF-dependent parameter of the transistor can be expressed as

$$V_G = V_G^* + \frac{kT}{2\delta_G}\ln(P_G + \sum_i K_i P_i)$$

In this equation, which formally resembles the Nikolskij-Eisenman equation, P_i and K_i stand for partial pressure and selectivity coefficients of the interfering gases and δ_G represents the fraction of charge shared between the OS and the primary gas. This relationship allows not only the direct evaluation of the shared charge, but also yields information about preferential donacity of different gases with respect to the OS. From the sensing point of view the biggest difference and advantage of WF-CHEMFET *vis-à-vis* ion sensors is the fact that no external reference electrode is needed because WF of silicon is stable under normal operating conditions. That fact alone makes the WF-CHEMFETs ideally suited for miniaturization, leading to gas-sensing arrays.

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Chiral Sensing and its significance

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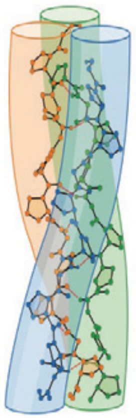
Chirality is ubiquitous in nature. Information on chirality and the ability to determine the enantiomeric excess is crucial to the basic understanding of biochemical processes in industries such as the pharmaceutical and cosmetics industry amongst others. Present methods of chiral detection and separation are based on chromatographic techniques and spectroscopic methods such as circular dichromism spectroscopy and NMR.

Electrochemical methods using enzymatic and non-enzymatic methods can offer an attractive alternative to probe chirality and its effects. In this paper, an overview of chemical and biochemical chiral sensing and electrocatalysis will be debated. Can electrochemical separation and sensing at a liquid-liquid interface (Figure 1) and ion-selective potentiometry for chiral drugs offer alternatives?[1][2]. For redox active molecules, such as the drug precursor 1 phenyl ethanol, can amperometric chiral sensing be elicited using chiral catalysts (Figure 2)[3]. The feasibility of using a chiral biomimetic co-factor for separation and sensing will be presented[4] (Figure 3). Finally the effects of biopolymers on inverting' the chiral selectivity of oxidase enzymes will debated[5].



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Nanoscale Electrochemical Sensors Prepared by Electrodeposition

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New methodologies have been developed for preparation of nanometer-sized electrochemical sensors by electrodeposition at disk-type, polished or recessed nanoelectrodes. The produced probes range from Hg nanoelectrodes to nanosensors for reactive oxygen and nitrogen species [1] prepared by etching polished Pt nanoelectrodes and depositing Pt black into the resulting cavity. The size and geometry of such electrodes were verified independently by voltammetry, chronocoulometry, scanning electrochemical microscopy (SECM), and scanning electron microscopy (SEM). Needle-like, polishable nanoelectrodes are suitable for quantitative SECM experiments. Potential applications include spatially resolved amperometric and potentiometric experiments inside biological cells [2].

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Oral Presentations

Modeling the Time Response of Electrochemically Controlled Membrane Electrodes

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In recent years, the field of membrane based ion-selective electrodes has continuously approached that of electrochemistry at the interface of two immiscible electrolyte solutions (ITIES), giving rise to fruitful synergies and a range of possible new applications. This includes the detection of ions that exhibit irreversible extraction characteristics, the coulometric delivery of ions, the design of absolute electrochemical sensors by means of a controlled current coulometric detection, and the design of novel biosensors concepts.

This talk will discuss a simplified model on how the functioning of types of membrane electrodes can be effectively described. This is achieved by combining phase transfer equilibrium characteristics, on the basis of modern ion-selective electrode theory, with mass transport kinetics, in a finite difference model.

This approach yields important design features of such sensor concepts that will be discussed in view of recent experimental results. Required materials characteristics for future sensor design will also be shown based on the results of the model.

Potentiometric Biosensors Based on Thiolated Polyaniline

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Fast, easy-to-use and stable biosensors are needed for developing efficient and selective analytical devices. Conducting polymers are suitable materials for biosensors because of their ability to transduce molecular recognition into an electrical signal [1]. In order to prepare electrochemical biosensors an essential step is to immobilize the biological probe on the electrode surface. Thiolated probes can be easily attached on e.g. polyaniline surfaces. Thiolation, however, alters the conjugated polymer backbone by causing a steric hindrance and by changing the electrochemical behavior and properties of the conducting polymer [2].

A promising approach for DNA recognition is to attach thiolated single-stranded oligonucleotides (ssODNs) on polyaniline and to monitor the hybridization by using potentiometry [3]. Non-specific binding can be blocked by co-immobilisation of hydroxylated thiols to the electrode surface. The sensitivity of electrodes can be optimized by a careful choice of the electrode material, the electrode surface, pH and buffer solution.

Potentiometric sensor materials based on functionalized polyaniline were studied. Polyaniline was electropolymerized on glassy carbon and ITO electrodes. Alkanethiols and ssODNs were used to form functionalized polyanilines. The modification of polyaniline was studied and the electrode membranes were characterized by cyclic voltammetry, electrochemical impedance spectroscopy, *ex situ* FTIR spectroscopy and *in situ* UV-vis spectroscopy in order to optimize the surface conditions. Also the potentiometric response of the electrodes is presented.

Acknowledgement: Financial support from the Finnish Funding Agency for Technology and Innovation (Tekes, Dnro 2920/31/08) is gratefully acknowledged.

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A Calibration-Free Coulometric Detection System for Remote Sensing Applications

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Advancements in microelectronics and microfabrication enable the possibility of remote analytical systems for environmental, industrial, and security applications that are capable of long-term autonomous operation. These particular design requirements demand a robust and *calibration free* analysis method that can function without on-site maintenance by trained personnel. One electrochemical analysis which performs absolute measurements is exhaustive coulometry, where a precisely defined volume of analyte is oxidized or reduced completely, leaving only the converted product in solution. In principle, if the cell volume is accurately known and the electrolysis is carried out to completion, the corresponding charge is an absolute determinant of the analyte amount and concentration; and no additional experiment is required for quantitation. Therefore, exhaustive coulometry greatly simplifies the over-all system by eliminating the need for in-the-field calibration. The objective of this work is the development of a microfabricated sensing platform suitable for coulometric analysis and the examination of its performance in several potentially important applications.

The sensors consist of a silicon platform containing patterned gold electrodes (Figure 1) occupying an oval area of 4 mm x 8 mm. One electrode is converted via electroplating to a Ag/AgCl pseudo-reference electrode. The designs and sizes of electrodes are varied (ranging from two to six electrodes) in order to test the optimum arrangement, to achieve better detection limits by reducing the working electrode area, and to permit the incorporation of redundant sensing electrodes. The sensors are incorporated onto the bottom part of a custom flow cell (Figure 2) that establishes a fixed cell volume. The cell consists of two compartments that are separated by a semi-porous membrane to isolate the working and counter electrode chambers.

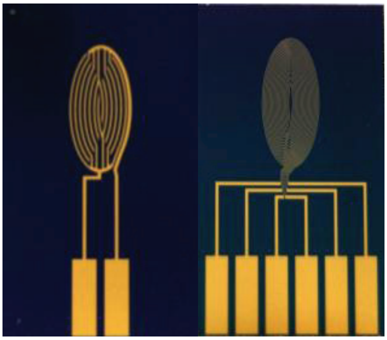

Figure 1: Microfabricated sensor with (a) two and (b) six electrode design

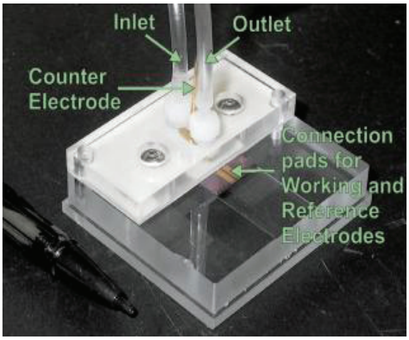

Figure 2: First generation flow cell

A Label-free Impedance Array Biosensor for Detection of Multiple Antibody–Antigen Interactions Based on a Novel Conductive Linker

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Impedance biosensors show great promise for point-of-care applications due to advantages such as low cost and ease of miniaturization. Label-free operation enables the quantification of biomolecule in real time. In this manuscript, we demonstrated a label-free array sensor for detecting multiple antibody-antigen interactions based on impedance methodology. To enhance the redox reaction on the self-assembled monolayer (SAMs) modified gold electrode, we used a novel low-impedance linker to replace conventional long chain alkanethiol. Compare to the conventional long chain alkanethiol, this new linker remarkably increases the redox current which can be easily observed in the cyclic voltammetry results. Further examinations lead to the understanding that as the impedance of gold electrode modified with this conductive linker is 3 orders lower than the conventional 12-Mercaptododecanoic acid, matched corresponding parameters in Randles circuit combined to offer this significant improvement in signal-to-noise ratio. More specifically, the decrease in impedance indicates the increase in measurable current. The higher current response makes the electronic circuit design much easier. We also found the impedance response of antibody-antigen interaction is distinct at 4 Hz (Fig.1). By simplification of Randles model and mathematical deviation with the help of this low-impedance linker, we found the total impedance change is close to the change of electron transfer resistance. This will help us simplify the analysis steps. Moreover, by applying only one frequency to our proposed array, we can substantially reduce the detection time from 24 minutes to 10 seconds. To further increase the signal-to-noise ratio, we used the lock-in principle to extract clearer signal from the noisy environment. Using our proposed array, it is viable to use compact instruments to detect multiple biomolecular interactions with a small volume of sample which is crucial for reaching the point-of care implementation we have in mind.

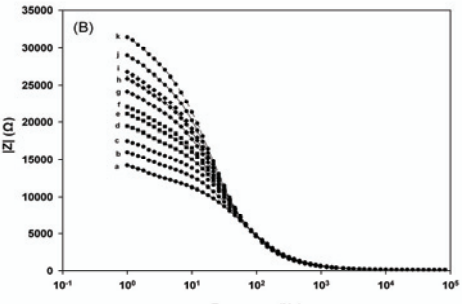

Fig.1 The impedance response of antiS100-S100 interaction at different concentrations.

Why 'Nano'? Is There Changed Electrochemistry at the Nanoscale?

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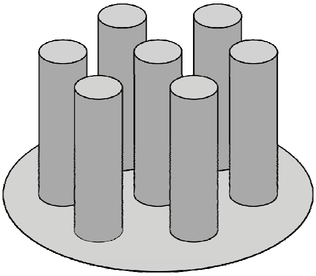
Nanoparticles and nanomaterials are widely employed in electroanalytical sensors, particularly in amperometric devices, with significant improvements in performance often claimed, if not demonstrated. This lecture will present a critical overview seeking to identify where authentic *changed* behaviour exists between the macro- and micro-scale on the one hand and the nano-scale on the other. The following areas may be addressed.

- Adsorption on nanoparticles and nanotubes.
- The use of carbon nanotubes (CNTs) as electrode modifiers and the roles of (i) impurities in the CNTs arising from their manufacture via CVD, and (ii) the role of the CNTs in changing the mass transport regime to the electrode by virtue of altering a flat surface to a nanoporous one.
- The role of nanomaterial porosity in general.
- The investigation of electrode kinetics at nanoparticulate materials where the heterogeneity of the surface *must* be considered for correct mechanisms and kinetics to be inferred.
- The modelling of transport to nano-sized electrodes where the diffusion and diffuse layers are of comparable size.



Modifying a planar macroelectrode surface to make it nanoporous can enhance selectivity, e.g. *for dopamine over common interferences.*[1]

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On the use of ionic liquids to immobilize biomolecules onto different sensing platforms

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The dissolution of biomolecules and the maintenance of their effective reactivity require the preservation of their highly ordered structure, a condition that is difficult to achieve. Ionic liquids are presented as suitable compounds for this purpose because most of them seem to have ability to solubilize proteins without denaturation[1.] Therefore, many methods are attempted to immobilize proteins using carbon nanotubes, hydrogels, nanoparticles, hybrid compounds, ionic liquids and others[2,3]. Recently, the investigation of room temperature ionic liquids in biosensors has been increasing attention because their unique chemical and physical properties, such as high chemical and thermal stabilities, negligible vapor pressure, good ionic conductivity and ability to dissolve a wide range of organic and inorganic compounds.[2,3]

In the present work the different methods of immobilization of glucose oxidase (GOx) and cytochrome c using the ionic liquid tetrafluoroborate of 1-butyl-2,3-dimethyl imidazolium ($BMMIBF_4$) will be studied showing their electrochemical behaviour and amperometric detections.

Table 1. Comparison of different glucose biosensors

Biosensor	GOx (mg)	Sensitivity ($\mu A\ mmol^{-1}\ L\ cm^{-2}$)
GC/CuHCNFe/Ppy/Gox/$BMMIBF_4$/Glut	0.05	17.1
nanoCuHCNFe/Ppy/Gox/BSA/Glut (2)	0.07	12.0
Au/Chit/$BMMIBF_4$/Gox (3)	-	5.2

GC: glassy carbon; CuHCNFe/PPy: hybrid of Copper hexacyanoferrate/polypyrrole ; Glut: glutaraldehyde ; Chit: chitosan; Au: gold; BSA: bovine serum albumin

In the case of glucose oxidase (table 1) the method of immobilization enhances the performance of the biosensors more than the amount of immobilized protein. Besides, our results has shown that the use of ionic liquids improve the detection of glucose due the biomolecule stabilization avoiding denaturation; consequently, increasing the sensitivity. Moreover, cytochrome c with chitosan hydrogel studies presented a good electrochemical estabilization in presence of ionic liquid without conformational structural changes.

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Enzyme stabilization by vegetable polysaccharides in layer by layer electrodes

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A major difficulty in constructing enzyme biosensors is related to the stability of the biological molecule. One technique that has received great attention for better immobilization of bio-component in the construction of biosensors is layer-by-layer reducing the denaturation of the enzyme by incorporation of friendly molecules, easy construction and low cost. Electroactive nanostructured membranes have been produced by the layer-by-layer (LbL) technique, and studied the electrochemical enzyme stability. Fluor tin oxide (FTO) glass electrodes were modified with up to four bilayers of laccase (Novozym ® 51003) and electrolyte PDDA (poly (diallyldimethylammonium chloride). On the other hand, some electrodes was build up using a four trilayers incorporating also different vegetable polysaccharides. We used starches from corn and cassava as alternatives enzyme friendly molecules. The adsorption of laccase was studied by monitoring the mass uptake with a quartz crystal microbalance and the enzyme electrochemical activity was determined by 2,2′-azinobis-3-ethylbenzothiazoline-6-sulfonate (ABTS) in solution.

Parameters such as pH and scan rate were assessed at this stage and demonstrated that for the electrode constructed with cassava starch shows the best response for ABTS measured by cyclic voltammetry (Figure 01). Also the electrodes were tested to detect phenol. When the electrodes were immersed in air-saturated 0.1 M KCl in 0.1 M acetate buffer, pH 5.5 solution containing phenol, the cathodic peak current of laccase increased. The biosensor had a good operational and storage stability.

The sensitivity found for this electrode was 0.56 mA cm^2 mol^{-1} L. Thus the interaction between laccase and polysaccharide played an important role in the direct electron-transfer behavior as well as a high-electrocatalytic activity.

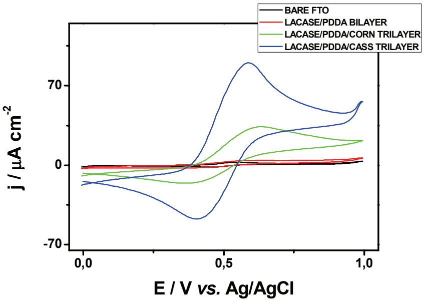

Figure 1 - Cyclic voltammetry for modified electrodes with laccase in a solution containing 0.02 mmol L^{-1} ABTS electrolyte. Electrolyte of all experiments was 0.1 M KCl in 0.1 M acetate buffer pH 5.5, scan rate 25 mV s^{-1}.

The use of modified starch from cassava emerged as an effective and inexpensive compared to the modified corn starch. It is believed that the cassava starch provides a better film forming and more rigid layer applied, yet it is known that the cassava starch has a molecular chain greater than that of corn starch.

Mesoporous platinum microelectrodes as sensors for the detection of small organic molecules (SOMs) in direct SOMs fuel cells

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Fuel cells powered by small organic molecules (SOMs) such as methanol, ethanol and formic acid have rapidly progressed due to rising energy demands, depletion of fuel reserves and environmental pollution issues. Polymer electrolyte membrane fuel cells based on SOMs are promising, in particular, for application in portable electronic devices. A problem related to the efficiency of direct SOMSs fuel cells is the crossover of the fuel through the polymer. The latter phenomenon affects the overall fuel cell efficiency, because it reduces fuel utilization, while SOMs can act as poison for the cathode material. Therefore, SOMs sensors are required to detect their level both in the fuel fed in the anodic compartment of the cell and in the cathodic zone where SOMs can permeate through the membrane.

Electrochemical methods are suitable to this purpose, as they allow an easy and rapid detection of compounds even on line with simple and relatively inexpensive apparatuses. Electrochemical SOMs sensors can be developed by exploiting miniature electrodes, based on the same catalyst materials typically employed as anode for the efficient electrooxidation of SOMs. Platinum-based catalysts are some of the most efficient materials for SOMs oxidation. However, platinum is susceptible to poisons, which strongly adsorbs onto the electrode surface active sites resulting in a dramatic decrease in catalytic efficiency. However, under given conditions, the activity of platinum towards the electrooxidation of SOMs can be promoted by using either nanostructured platinum electrodes or platinum electrodes modified by foreign metal ad-atoms.

This paper focuses on the use of platinum microelectrodes modified by a film of mesoporous platinum, which can prepared by templating techniques from lyotropic liquid crystalline phases of non-ionic surfactants. In particular, the normal topology hexagonal (H_I) liquid crystalline phase has been used as a template for the synthesis of mesoporous platinum thin films via the electrochemical reduction of platinum salts dissolved in the aqueous domain of the liquid crystalline phases. The effects of SOMs concentration, temperature, anions and irreversibly adsorbed bismuth atoms on current responses are investigated in detail.

Ultra thin overoxidized polypyrrole membrane for the design of amperometric biosensor.

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Biosensors are important to various fields such as food safety, medical diagnostics, environmental regulation, and many others. For enzymatic sensors, the enzymes are linked to polymeric substrates or entrapped in it. The activity, stability, and quantity of the immobilized enzyme impact the sensitivity of such devices. Moreover for enzymatic amperometric biosensor the redox interferents have to be rejected. Recently, numerous oxidase-based biosensors have been developed for a wide range of analyte. Hydrogen peroxide is a side-product of the reactions catalyzed by the oxidase enzymes which means that the concentration of H_2O_2 should be directly related to the concentration of the substrate *i.e.* the analyte.

$$\text{analyte} + O_2 \xrightarrow{\text{oxidase}} \text{product} + H_2O_2$$

$$\text{Transduction :} \qquad H_2O_2 \rightarrow O_2 + 2\,e^- + 2\,H^+$$

In order to develop glucose amperometric biosensor, it has been shown that an ultra thin (10 nm) overoxidized polypyrrole membrane (OPPy) obtained directly in one step by pyrrole electropolymerization[1] allows ascorbic acid and dopamine rejection[2]. Moreover this membrane leads to rapid and excellent H_2O_2 determination[2] (Fig.1). Finally, glucose oxidase (GOD) was entrapped into the OPPy membrane leading to a glucose biosensor. Its response in the presence of various glucose concentrations is shown in Fig. 2. Its sensitivity is very good.

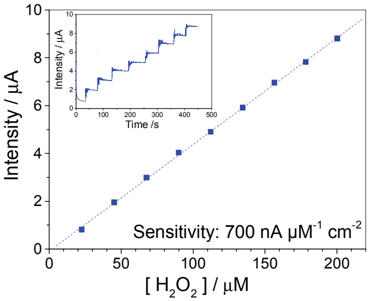

Fig. 1. **H_2O_2 determination**. Intensity vs. H_2O_2 concentration recorded at an **OPPy/Pt** electrode polarized at 0.65V/SCE. Ω = 600 rpm

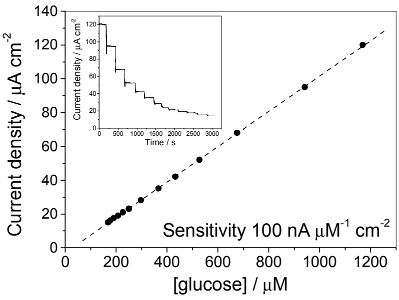

Fig. 2. **Glucose determination**. Current density vs. glucose concentration at an **OPPy-GOD/Pt** electrode polarized at 0.65V/SCE. Ω = 600 rpm

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Novel Glutathione Biosensor based on Electrochemiluminescence of Quantum Dots Composites

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Since pioneering works from Bard's group that reported for the first time the electrochemiluminescence (ECL) properties of CdSe[1], and CdTe nanocrystals[2], analytical applications of the ECL from QDs have increased dramatically over the last years. This is primarily due to the significant advantages of the ECL over conventional spectroscopic techniques, in particular, low background signals and the ability to control both time and position of the light emitting reactions accurately[3].

Positively charged 4-(dimethylaminoethanethiol) (DAET)-protected core-shell CdSe/ZnS quantum dots (QDs) were incorporated within negatively charged Nafion films. The ECL behaviour of such films was characterized using hydrogen peroxide and peroxidisulfate as the coreactants. The results showed an enhancement of the ECL signal for the Nafion/QDs composite film in comparison with the bare QDs deposited on the electrode surface when hydrogen peroxide was used as a coreactant. Interestingly, Nafion/QDs composite films were completely insensitive when peroxidisulphate was used as the coreactant, as an indication of the permselectivity of Nafion towards negatively charged species. To show the suitability of Nafion/QDs composite films for ECL detection, we have investigated the ECL quenching of Nafion/QDs composite film at different concentrations of glutathione. The results showed a linear relation of the quenching of the ECL signal with the increase of the concentration of glutathione using hydrogen peroxide as the coreactant. These results pointed out the suitability of Nafion/QDs composite films for electroanalytical applications.

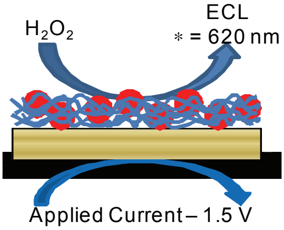

Fig. 1: Schematic of ECL production from Nafion/QD films.

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How can Scaled-Up Deployments of Ion-Selective Electrodes in Remote Autonomous Instruments be Achieved?

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The primary market for Ion-Selective Electrodes is for profiling blood electrolytes in clinical samples, a situation has remained unchanged for the past 30 years. This is despite the pioneering breakthroughs of the past 15 years or so that have driven down the limit-of-detection by several orders of magnitude, in principle opening up new applications in areas like environmental monitoring.

However, in spite of some early indications that ISEs with these enhanced characteristics could meet the analytical requirements of, for example, detecting heavy metals in drinking water, the literature has remained disappointingly silent in terms of convincing practical methods for using these sensors in new applications. History tells us that adoption of new technologies does not happen easily, typically taking many years if successful. Often established, less effective technologies can survive, remaining in place despite the existence of a superior technology. The reasons for this are complex, but it is clear that established technologies can only be dislodged by a new approach that offers such a clear advantage that there can be no debate about the relative merits of the case, and adoption depends on changing work practices and/or retraining of operators.

Therefore the dramatically improved performance of ISEs that has been clearly demonstrated in recent years is not enough in itself to ensure adoption by end-users. The entire analytical approach must be sound, and offer obvious advantages in terms of the quality of the data, ease of use, acceptable cost, and reliability. Often the enhanced performance is obtained through relatively complex conditioning steps, and maintenance of this performance over time is challenging, as membrane characteristics can shift dramatically, particularly when the sensors are moved from the lab to the field, and exposed to real samples. Coping with these circumstances typically involves introduction of a complex washing and calibration process, which in turn requires fluidic handling components such as pumps and valves, that drastically drive up the price of the equipment, making scaled deployments impossible.

In this paper, I will present practical solutions to these issues, based on the use of arrays of low-cost ISEs and a simple fluid handling system that in principle could allow multiple measurements to be made reliably at low cost at remote locations. The example of Pb^{2+} determinations in water samples will be used to exemplify the approach.

Electrochemical sensors for *Aeromonas hydrophila*

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Aeromonas hydrophila are ubiquitous waterborne bacteria associated with some human infections. The microorganism is distributed in aquatic environment, sewage, drinking water, it was isolated from wide range of foods [1]. The bacteria can grow at low temperatures (4^0 C) and wide range of pH (4 – 10). Because of their broad metabolic capabilities identification of *Aeromonas spp*. by conventional methods is difficult.

The aim of this work is to develop a simple method of detecting *Aeromonas hydrophila* with the use of electrochemical biosensors. A recognition element of biosensing devices was a DNA probe covalently immobilized on carbon paste (CPE) or gold (AuE) electrodes. Surfaces of the both electrodes were specifically prepared in order to bind DNA probes in a way facilitating an efficient detection. The carbon paste electrode was modified with stearic acid and ethylenediamine, as previously described [2]. The recognition layer of Au electrode was prepared by mixed self-assembled monolayer consisting of thiolated DNA probe and diluent molecules of mercaptohexanol [3]. A probe was a DNA fragment at the sequence 5'CAGCCCACCACCGTCTTGAC complementary to target DNA specific for aerolysin gene (*aerA*). Aerolysin is a cytotoxic enterotoxin responsible for the pathogenicity of *A. hydrophila*. A recognition event in the biosensors was a hybridization between an immobilized probe and target DNA detected by an electrochemical response of hybridization redox indicators. In the CPE biosensor two compounds, tris(2,2'- bipyridyl)cobalt(III) complex and daunomycin were used as hybridization indicators whereas methylene blue and Hoechst 33258 were applied for Au biosensor. Performance of recognition interfaces was carefully evaluated by some electrochemical parameters and optimized. Both biosensors were used for the detection of synthetic oligonucleotides (10 µM) serving as target DNA in the presence of non complementary DNA fragment. Also the detection of specific fragment of aerolysin gene from *Aeromonas hydrophila* (0.15 µg cm^{-3}) amplified with Polymerase Chain Reaction (PCR) was carried out by the biosensors. All evaluated procedures gave rise to successful detection of *Aeromonas hydrophila* bacteria. Some typical features of both biosensing devices are compared and discussed.

This work is supported by the Polish Ministry of Science and Higher Education (Grant No. N N312 2067 36.

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Molecularly imprinted polymer-based electrochemical sensors: a new strategy combining aryl diazonium surface chemistry and surface-initiated photopolymerization.

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Molecularly imprinted polymer grafts (MIPs) were prepared by surface-initiated photopolymerization using covalently attached 4-benzoyl phenyl groups acting as photoinitiators and dimethyl aniline as co-initiator (hydrogen donor). Dopamine was chosen as the template molecule (T), methacrylic acid as the functional monomer (F), and ethylene glycol dimethacrylate (EGDMA) as the crosslinking monomer (C). The electrodes were gold-coated silicon wafers or Indium Tin Oxide electrodes (ITO). The photoinitiating 4-benzoyl phenyl groups were grafted through the electrochemical reduction of the corresponding 4-benzoyl benzenediazonium tetrafluoroborate. Electrografting took less than 5 minutes and was found to be efficient to graft a dense aryl layer of ~2-3 nm. The ultrathin MIP grafts were prepared in chloroform/methanol over a short period of 15 min. Dopamine was electrochemically or solvent-extracted and the resulting MIPs served for its electrochemical detection by stripping voltammetry.

The Gold-MIP and ITO-MIP hybrids were then incubated in PBS solutions of dopamine to rebind the latter and further served as electrodes for the electrooxidation of the immobilized dopamine. The electrochemical detection by stripping voltammetry was found to be specific and selective towards dopamine. Indeed, the electrodes modified by non-imprinted polymers (NIPs) gave a flat response due only to a capacitive current. Selectivity was tested with L-3,4-dihydroxyphenylalanine (L-dopa) as interferent. The dopamine-imprinted MIP graft gave again a flat response compared to the detection of dopamine. The detection limit was better than 1 nanomole for a starting T/F/C ratio of 1/4/15 in the presence of photoinitiator-modified ITO.

The strategy devised so far is new, very fast and efficient for the specific and selective detection of dopamine. The same strategy can be extended to a broad range of templates. The originality of the process of fabrication of the electrochemical sensors described above lies in the combination of the surface chemistry of diazonium compounds and photopolymerization for the production of ultrathin MIPs. The whole process is versatile and easy to implement by a non-specialist. All these scientific and technical characteristics enabled us to recently patent this process [1] hence the high potential for industrial applications.

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Template Synthesis of Macroporous Copper Hexacyanoferrate/Polypyrrole Transducers. Influence of Pore Size on H_2O_2 Detection.

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The chemical approach to nanoscience has generated nanostructured transducers direct to increase sensitivity, selectivity and durability of electrochemical sensors.[1] Among the strategies presented in literature, the utilization of three dimensional close packed arrays of monodisperse polystyrene particles have attracted attention because their potential to produce high density deposited materials, since the compounds are electrodeposited inside the template voids and around the surface of the colloidal particles. When the template is removed, there is no shrinkage of the material and the resulting film is a true cast of the template structure.[2] Here, this technique is used to synthesize macroporous copper ferricyanide/polypyrrole (CuHCNFe/Ppy) transducers.[3] Spherical particles with different diameters (300, 460, 600 and 800 nm) were applied with this purpose and all the transducers were evaluated by their performance on H_2O_2 detection. The analytical results are depicted on table 1, where it is also possible to find data referent to a bulk CuHCNFe/Ppy transducer. Systems had their charge controlled to produce sensors with the same amount of CuHCNFe/Ppy.

Table 1. Analytical performances of CuHCNFe/Ppy transducers.

	300nm	**460nm**	**600nm**	**800nm**	**Bulk**
Sensitivity ($\mu A\ cm^{-2}\ mM^{-1}$)	202	218	188	195	206
Detection Limit (M) S/N=3	10^{-5}	10^{-5}	10^{-5}	10^{-5}	10^{-5}
Linear Range (mM)	up to 3.25	up to 3.50	up to 2.50	up to 2.00	up to 4.25

The analytical measurements were performed at electrodes able to be observed at FESEM microscope, where homogeneous nanoporous films were visualized at all proposed sizes. One of the possibilities to explain the similarity among all sensors can be related with the macroporous transducers wettabilities. Contact angle measurements have shown that the interaction at material/solution interface is not so favorable in half height macroporous systems ($\theta > 100^o$ for all situations) as in bulk CuHCNFe/Ppy ($\theta = 66^o$). This fact can be related to the air remaining inside the pores, which makes the accessibility to all active sites difficult. Efforts have been driven now to develop a vacuum cell, in order to remove the air localized into the macroporous transducer before adding the electrolyte solution utilizing in the H_2O_2 detections.

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11Ionophore-Modified Nanopores as Solid-State Ion-Channels for Potentiometric Sensing

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The superb selectivity of ion-selective electrodes (ISEs) made possible the separation-free monitoring of ionic activities in complex matrices, such as blood. Although clinical applications of ISEs account for more than a billion of blood electrolyte measurements per year, comprising a large share in the in vitro diagnostic sensor market, chemists still consider ISEs primarily as simple, routine tools for direct potentiometry and potentiometric titrations. However, not only application wise, but also theoretically ion-selective potentiometry experienced recently a dramatic progress that enabled ultimately their use for ultra-trace analysis.

Still ISEs have important limitations originating from the formulation of commonly used polymeric ion-selective membranes (ISMs), e.g., limited life-time due to leaching out of active components and extraction of lipophilic sample components with selectivity-altering effect into ISMs. This communication introduces novel ionophore modified nanostructures and their use for ion sensing in an attempt to relieve the above mentioned major limitations of ISEs.[1] Most importantly, shows that by using the selectivity filters of biological ICs as inspiration, fully synthetic ion channels based on ionophore-modified gold nanopores can be constructed for selective potentiometric detection of ions.[2] Using dithiolane functionalized silver ionophores excellent selectivities and detection limits in the lower nanomolar ranges were obtained for $Ag+$. This required adjusting the hydrophobic, ion exchange, and selective ion complexation properties within Au nanopores of less than 5 nm effective diameter by modifying their surface with a mixed self–assembled monolayer consisting of three different thiol derivatives having distinct functionalities. The new ISE construction preserves the exquisite selectivity of ionophores in a robust, solvent-free, solid-state membrane format with all active components covalently immobilized. This new concept of inducing ion selectivity is likely to be extended to other type of complexing agents and nanoporous materials, which beyond sensing might find application in ion separation and characterization of relevant host-guest interactions.

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Miniaturized cylindrical porous electrodes for sensing applications

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A large active surface area and good mass transport are essential for electrochemical devices used in analysis, catalysis and energy conversion systems.[1] A promising way to elaborate materials combining those properties was demonstrated in previous works with the elaboration of planar macroporous electrodes.[2] Here we propose a miniaturized cylindrical device exhibiting small overall geometries and a controlled degree of porosity.[3]

The Langmuir-Blodgett (LB) technique is used to transfer a desired number of layers of monodisperse silica beads onto cylindrical gold wires of various diameters ranging from 250 to 25µm. The voids present in these silica opals can be filled in a subsequent electrodeposition step with metals (see Fig.1a) or conducting polymers (see Fig.1c). Potentiostatic electrodeposition leads to current oscillations that arise from a periodic change of available surface area in the colloidal template. They present a very precise way of controlling the filling degree of the template. Dissolution of the inorganic template reveals the macropores on the gold wire.

The associated gain in electroactive area is beneficial for electrocatalytic processes (see Fig.1b) leading to a higher efficiency of the device or to an increased sensitivity or lower detection limits for sensor applications.

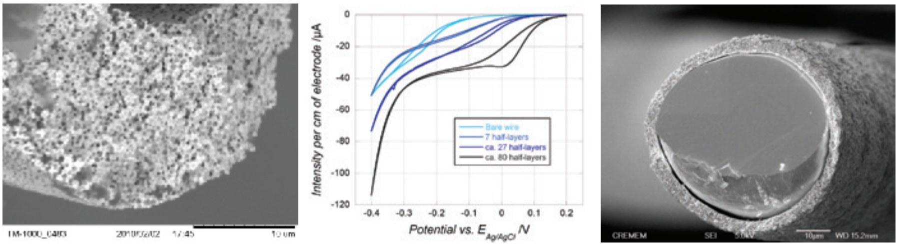

Fig.1 a) b) c)

SEM images of macroporous a) gold (pore size 690nm) and c) polypyrrole (pore size 420nm) on a 50µm gold wire. b) Electrocatalytic activity of gold wires (d = 50µm) with increasing thickness of macroporous overlayers (0.05MH_2SO_4, O_2 sat., 5mV/s)

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Electrodeposition of Gold Nanoparticles on Glassy Carbon for Hg(II) Trace Determination in Aqueous Media

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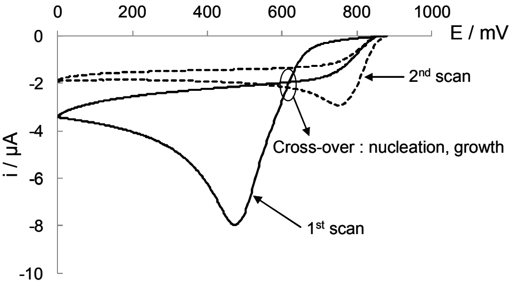
Mercury is considered to be amongst the highest toxic heavy metals. It is toxic in almost all its species, mainly as organic forms such as methylmercury, whatever the level of its occurrence in the environment. Hence, it is of dramatic importance and a challenging purpose (since very low levels down to picomolar are commonly encountered in naturals waters) to develop fast response time, sensitive and selective sensors for monitoring its concentration.

Recently, metallic nanoparticles (NPs) appeared as a new promising research field for the analysis of ultra-trace elements. They offer many advantages for low-level determination thanks to very high active surface area, enhancement of mass transport and catalysis. Gold NPs (AuNPs) have been reported for Hg(II) determination by means of stripping voltammetry. Indeed, Au has a great affinity for Hg which increases the preconcentration effect during the first step of stripping techniques. To the best of our knowledge, no study dealing with the optimizing of the electrodeposition conditions of AuNPs on glassy carbon (GC) electrode for the detection of very low Hg(II) concentrations has been reported till now.

We report here a comparison between three techniques of AuNPs electrodeposition on GC, namely cyclic voltammetry, chronoamperometry and potentiostatic double-pulse, aiming at low Hg(II) concentration measurements. The characterization of the modified surfaces using FEG-SEM and AFM techniques as well as XPS and XRD analyses will be reported. These different techniques were used to characterize several physico-chemical parameters of the deposited AuNPs, such as surface composition, morphology, average diameter and density. The data for the three electrodeposition strategies will be compared and discussed on the basis of electrochemical measurements of Hg(II) in 0.01 M HCl by square wave anodic stripping voltammetry.



Typical cyclic voltammograms of 0.25 mM $HAuCl_4$ in 0.1 $NaNO_3$ at a GC (ϕ_{GC} = 3 mm) electrode, v = 50 mV s^{-1}.

Fabrication of Nanoporous Metal Materials for Biosensing Applications

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Nanoporous metal materials such as nanoporous gold (NPG) and nanoporous copper (NPC) are fabricated by two methods. One is the dealloying of alloys. During the dealloying, the active metal is leached out and the left noble one will self-diffuse and aggregate, forming pores and ligaments. For example, NPG can be obtained by dealloying Au/Ag alloy. The other is the electrochemical treatment of bulk pure metals, i.e., square-wave potential perturbation. During the treatment, a repeated electrochemical oxidation/reduction made the metal atoms removable. At the same time, the produced H_2 bubbles would act as a template for the formation of pores. For the former one, the microstructure (pore and/or ligament size) of NPG was tuned by changing the ratio of alloy components, dealloying time, or post-treatment. For the later one, the microstructure of the nanoporous film was adjusted by changing the treatment time, the applied potential step, frequency, and the size of the H_2 bubbles, etc.

The NPG exhibited an excellent electrocatalytic activity towards the oxidation of glucose, ascorbic acid and dopamine; while the NPC had an excellent catalytic effect on the electroreduction of nitrate and H_2O_2. Based on these properties, several electrochemical sensors with high selectivity and sensitivity have been developed.

The obtained nanoporous metals were also used as carrier for the immobilization of enzymes. In addition to the microstructures of NPG and NPC, the effects of the immobilization strategies including physical adsorption, electrostatic attraction and covalent coupling, on the enzymatic properties were investigated. Both NPG and NPC were demonstrated to be good substrates for enzymes. For laccase, an efficient direct electron transfer phenomenon was observed on NPG. Based on the electrocatalytic activity of NPC towards the reduction of the oxidized aniline and the biocatalytic activity of horseradish peroxidase on NPC by adsorption, an electrochemical sensor for aniline has been developed. Similarly, an electrochemical biosensor for ethanol or glucose was also developed on the basis of an enzyme-modified NPG; its high performance was due to the good biocatalytic activity of alcohol dehydrogenase or glucose oxidase on NPG and the electrocatalytic activity of NPG towards the oxidation of NADH or H_2O_2.

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Poly-Adenylic Acid and DNA Films Based on Layer-by-Layer Deposition with Positively Charged Carbon Nanoparticles

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The deposition of nano-composite films is described based on combining negatively charged poly-adenylic acid (or ssDNA or dsDNA) and positively charged carbon nanoparticles (ca. 10 nm diameter with amine functionalities [1]). A layer-by-layer process is developed to vary the film thickness from ca. 10 nm to 40 nm (based on AFM images). Voltammetric responses are investigated in phosphate buffer solution. A capacitive current component is observed due to the carbon nanoparticles.

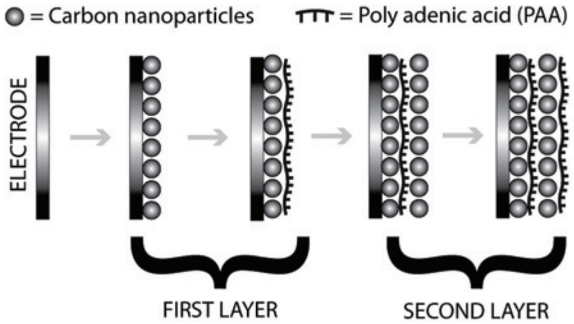

Figure 1. *Schematic drawing of the layer-by-layer deposition of negatively charged DNA and positively charged carbon nanoparticles.*

Experiments with $Co(phen)_3^{3+}$ [2] show binding of the cobalt metal complex depending on the thin film composition and structure. Hybridisation processes are investigated by voltammetry.

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Potentiometric/Amperometric Rod-type YSZ-based Gas Sensor Attached with Mn-based Solid Reference-electrode

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Recently, we discovered that Mn-based spinel-type oxides sensing-electrode (SE) used in YSZ-based gas sensors were insensitive to most of hazardous gases as well as independent of the change in oxygen concentration at temperature below 600°C[1]. In this present study, we examined the preliminary gas sensing characteristics of miniaturized planar-like rod-type YSZ-based sensors using different SEs and Mn_2O_3 as reference-electrode (RE) operated under potentiometric/amperometric mode.

Initially, the sensing characteristics of the miniaturized planar-like rod-type YSZ-based sensor attached with Mn_2O_3-RE were examined at 550°C by using the potentiometric technique. The developed sensor using a pair of Pt-SE and Mn_2O_3-RE exhibited negligible responses to all examined gases, whereas the sensor using Au-SE vs. Mn_2O_3-RE was found to respond well to C_3H_4, providing also the high responses to CO, unsaturated HCs and hydrogen. However, it is well-known that Au-SE is not stable enough over the sensor's wide operational temperature. Thus, the substitution of Au-SE to other more stable materials seems to be necessary.

At the second step, the sensing performance of the miniaturized planar-like rod-type YSZ-based sensor was evaluated at 550°C in amperometric mode. As a result (Fig. 1), the sensor using three-electrode system, namely In_2O_3-SE, Pt counter-electrode (CE) and Mn_2O_3-RE exhibited a comparatively large response and high selectivity to NO_2. Moreover, the sensor showed rather quick response and recovery rates attaining a steady-state response in a short period of time.

It can be concluded that Mn_2O_3 appears to be a highly promising material for its implementation as an all-solid-state RE and also could be successfully utilized in YSZ-based gas sensors for the monitoring of concentrations of various hazardous gases under both potentiometric and amperometric modes.

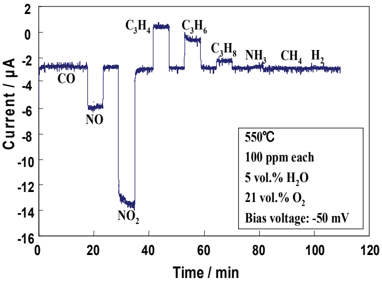

Fig. 1: Cross sensitivities to various gases at 550°C for the rod-type YSZ-based sensor using In_2O_3-SE, Pt-CE and Mn_2O_3-RE in ampreromeric mode.

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Scanning Electrochemical Microscopy with Nanoprobe arrays – Towards Stamp Electrochemical Lithography ?

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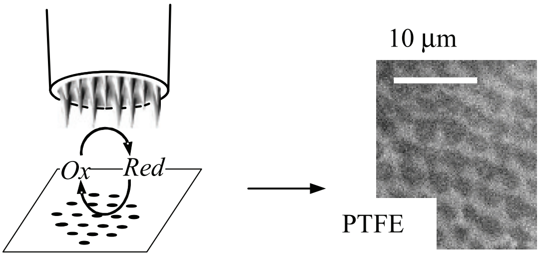
Scanning Electrochemical Microscopy (SECM) has been widely used to investigate surface reactivity. To a lesser extent, it was used promisingly as a surface modification technique able to decorate surfaces with various organic functionalities at the micrometer or nanometer scale. For example, it was successfully devoted to the local deposition or etching of polymers and to the local etching of self-assembled monolayers. The surface patterning by SECM requires to move the tip over the substrate, slowing down the writing process as each structure has to be written individually. It corresponds to an inherent limitation of such a scanning technique. The ability to pattern surfaces with micro/nanostructures in a parallelized and high-throughput manner with stamp electrodes, as in microcontact printing (µCP) with masks, is important for applications in biosensing, plasmonics, nanoelectronics, *etc*.
Here, we present a new type of multiscaled electrochemical probe for SECM, which consists of a high density electrode array of 6000 nanotips fabricated by chemical etching of an optical fiber bundle. The electrochemical and SECM behavior of these probes have been characterized experimentally and confronted to simulations. The SECM behavior is mainly governed by the fiber bundle macrostructuration (its convexity) rather than its microstructuration (the nanotips). [1] Such new SECM probes are then used to pattern a non-conductive polytetrafluoroethylene (PTFE) surface. The positioning of the probe arrays is achieved by SECM approach curves combined with shear-force measurement. The imprint of the probe nanostructures on the substrate is obtained by confining the diffusion layer generated at each single nanotip. This allows to pattern sub-micrometer arrays on PTFE surfaces which could be applied for parallel biosensing.



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Corrosion of Zinc in Chloride Media Analyzed by Zn^{2+} and pH Potentiometric Microsensors

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Zinc is an important metal in materials science used in galvanizing of steel, as anode in cathodic protection of iron and steel, in batteries, brass metallurgy, in protective coatings and as catalyst. The drawback of zinc application is localized corrosion occurrence. Metallic corrosion takes place in different forms, depending on the surrounding medium. Some important parameters are pH, oxygen content, medium resistivity, temperature and presence of aggressive or inhibitive species. To fully describe the corrosion mechanism in confined places, it is necessary to know the local distribution in solution of the chemical species that are important for the process. In this case miniaturized ion-selective electrodes can be of great value.

In this work the corrosion of pure zinc immersed in NaCl was characterized experimentally using Zn^{2+} and pH potentiometric microelectrodes. The microelectrodes were prepared from single-barrelled glass capillaries with tip diameter of 2 μm and contain neutral carrier based cocktail as sensitive membrane. Values of corrosion potential (E), pH and pZn (-log a_{Zn2+}) were obtained in selected places of the corroding sample. An interpretation of the local chemical environment can be done by Geochemical Modeling Software. The stability and Pourbaix diagrams presented were generated by the Medusa and Hydra [1] software for different Zn concentrations. Experimental data (E, pH and pZn) were added to the diagrams enabling the comparison between theory and experiment. Valid models will allow predicting corrosion and its mitigation without the need of experimental work.

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Electrochemical Sensing of Metal Ions Based on Molecular Switching

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Electrochemical studies with host compounds that are capable of selective association with guest ions or molecules are getting recent interests for selective analytical sensing of guests. One group of such hosts is macrocyclic calix[4]arene compounds which are known as selective ionophoric hosts for a wide range of metal ions depending on the ring size and on the modification with functional groups [1]. In this presentation, selective associations such as antigen-antobody interaction and nucleotide base with mercury ion are discussed.

The ability to detect trace amounts of mercury ion is important because of it's toxic effect on many living organisms. Most detection methods based on spectroscopic and spectrometric methods require expensive instrumentation and complicated sample preparation processes. In this study, we demonstrate a simple, easy and reusable method for Hg^{2+}.

Hg^{2+} detection is based on electrochemical signal by conformational change based on the formation of T–Hg^{2+}–T complex formation [2,3]. The "signal-on" upon Hg^{2+} binding is attributed to the conformation change from open structure to hairpin structure. Among the various metal ions studied, Hg^{2+} shows the highest signal gain compare to the other metal ions. The sensor is reusable simply by unfolding the ferrocene-labeled DNA in 10 uM cysteine at 80 °C to denature hairpin structure [4] and then immersed in 1 M $NaClO_4$ electrolyte at room temperature. The regenerated electrode is ready for reuse for Hg^{2+} solution. A little decrease in response is due to the loss of probe DNA from the electrode surface because of heating and rinsing in addition to detaching of thiolate linkage. This sensor responds closely to the original performance after three regeneration cycles. This sensor has good selectivity, with a detection limit of 0.1 uM. It also offers simple, operational convenience and cost-effective for mercury detection.

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In Situ Monitoring of the Electrochemical Degradation of Polymer Films on Metals Using the Bending Beam Method and Impedance Spectroscopy

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Charge and mass transports in conductive polymer films can be investigated by electrochemical methods. In many cases, if the positive potential limit is extended into the region in which the (over)oxidation of the polymer takes place, an oxidation peak (without a corresponding reduction peak) appears, but only little changes can be observed in the properties of the cyclic voltammograms taken in the “stability region” before and after “overoxidation”. In contrast to this, the impedance spectra recorded after “overoxidation” differ completely from the spectra measured for electrodes kept below the potential at which “overoxidation” of the polymer occurs. The “voltstressograms” recorded by using the electrochemical bending beam technique before and after overoxidation of the polymer film also show significant differences.

The most probable explanation for the observed electrochemical behavior relates directly to the structure of the film. The changes of the stress in a thin film, which is deposited onto a metal layer on one side of an insulator strip, and is immersed into an electrolyte solution, can be estimated from the changes of the radius of curvature of the strip. If the potential of this electrode changes, electrochemical processes resulting in the change of the stress can take place only on the metal side of the sample. The change in the stress induces a bending moment and the strip bends (Fig.1.).

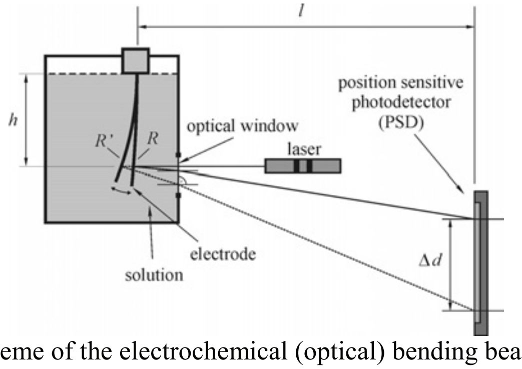

Fig.1. Scheme of the electrochemical (optical) bending beam setup

While the degradation proceeds, it can be monitored in situ by observing the change of the radius of curvature of the strip. Some selected results obtained using this method are presented and discussed in the present work.

Acknowledgement: This work was supported by the grant OTKA-67994/OMFB-01078/2007 from the Hungarian Scientific Research Fund.

Conducting Polymers as sensitive layers for the electrochemical and gravimetric detection of small organic molecules: influence of the chemical and structural properties of the layers on the recognition process

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Sensitive layers based on conducting homopolymers (polyEDOT, noted PEDOT) and copolymers (molecularly imprinted and non-imprinted poly(EDOT-co-AAT), noted MICP and NICP respectively) are electrosynthesized on gold substrates and used for the electrochemical [1,2] and gravimetric detection of atrazine [3]. These sensitive layers are characterized by cyclic voltammetry and square wave voltammetry techniques coupled to another method of signal transducing: surface acoustic wave "SAW" as gravimetric transducing method. ATR-FTIR spectroscopy, and AFM microscopy were used to study the effect of the chemical functionalities and of the structural properties of these conducting polymers on the physical chemistry of the interaction with atrazine targets and with the aim to improve the sensitivity of the recognition process. In particular, due to the presence in their backbones of pre-shaped functionalized cavities which keep the molecular memory of the targets, MICP layers present a remarkable sensitivity, a low detection threshold (10^{-8} mol L^{-1}) and a large range of detection (10^{-8} to 10^{-2} mol L^{-1}).

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Progress towards Understanding Electroadsorption of Ions in Nanoporous Carbons: EQCM Studies

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Supercapacitors based on a variety of activated carbons containing nanoscale pores present an important class of energy storage devices suitable for many applications. They store electric energy in electric double layer (EDL) formed by excess (or deficiency) of the electronic charge carriers on the porous carbon surface, counter-balanced by the oppositely charged electrolytic ions transported from the bath solution.

Conventional view of ions adsorption in nanoporous carbon electrode can be summarized as follows: At the potential of zero charge (pzc), the carbon electrode surface does not bear any excess electric charge. When the potential is swept positively with respect to the pzc, and hence the carbon pores walls become positively charged, the anions from bath solution move to the nanopores interior in order to counter-balance the positive charge of the carbon surface. In contrast, as the potential is shifted negatively with respect to the pzc, its surface becomes negatively charged, and as a result the cations from the bath solution are transported into carbon nanopores in order to compensate the negative charge of electrode the surface.

We have recently discovered [1-4] that electrochemical quartz crystal microbalance (EQCM) technique can be used to trace compositional and concentration changes in the ionic part of the EDL of the activated carbon electrodes during their charging. Determining experimentally the mass per charge ratio allows separation of the total mass change into the individual population changes of ions ($\Delta\Gamma$) and solvent molecules, providing unique information on both equilibrium EDL structure, and dynamics of ions and solvent insertion into nanoporous carbon electrodes. Comparison between the experimental and theoretical $\Delta\Gamma/Q$ ratios, provides insight into the composition of the ionic part of the EDL of carbon electrode as a function of its charge density, solution composition, presence of functional groups on carbon surface and doping impurities in its bulk, cycling conditions, etc. This composition appears to be much more complicated compared with the conventional view of ions adsorption outlined above.

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Nernst-Planck-Poisson model (NPP) as a comprehensive and powerful tool for modeling non equilibrium potentiometry

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The majority of current theoretical interpretations of potentiometric ion-sensor response focus on phase boundary potentials. They assume electroneutrality in the membrane and equilibrium or steady-state, thus ignoring electrochemical migration and time-dependent effects, respectively. These theoretical approaches, owing to their idealizations, make theorizing on ion distributions and electrical potentials in space and time domains impossible. Moreover, they may be in conflict with numerous experimental reports on ion-sensors in which both kinetic (time-dependent) discrimination of ions to improve selectivity, and non-equilibrium transmembrane ion-transport for lowering detection limits, are deliberately used [1].

For the above reasons, the Nernst-Planck-Poisson (NPP) equations are employed to model the non-equilibrium response in a mathematically congruent manner [2]. In the NPP model, electroneutrality and steady-state/equilibrium assumptions are abandoned. Consequently, direct prediction of selectivity, low detection limit variability over time, and the influence of other parameters, i.e. ion charges, mobility, membrane thickness and dielectric permittivity, on the ion-sensor responses are possible [3,4].

Unlike the other models the NPP can be used for the interpretation of Electrochemical Impedance spectra (EIS) of ion-sensors without using the analogy-type concept of the "equivalent electric circuit" but directly addressing the physicochemical properties of the sensors modeled. Additionally, the NPP allows for physically relevant and adequate solving *the inverse problem* i.e. searching for optimal sensor properties and measurement conditions via target functions and effective algorithms. It is demonstrated the interpretation of EIS spectra of ISEs.

The above theoretical approach is an important new tool in enhancing effectiveness of practical use of ion-selective electrodes during fabrication and operation, e.g. by avoiding or reducing the need for calibration.

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Water Uptake of Ion-selective Membranes and Its Correlation with the Potential Stability of Solid-contact and Coated-wire Ion-selective Electrodes

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In solid-contact ion-selective electrodes (SCISEs) an ion-to-electron transducer layer is placed between the electrode substrate and the outer ion-selective membrane (ISM), whereas the ISM is deposited directly on the electrode substrate in coated-wire electrodes (CWEs). Due to the water uptake of the ISM thin aqueous layers or islands of water can be formed at the different membrane interfaces involved in both of these electrode configurations. The accumulation of water at these interfaces (substrate/SC and SC/ISM (SCISE); substrate/ISM (CWE)) will convert both of these all-solid-state electrode types partially into a conventional ISE with a very small inner solution volume.

The diffusion of interfering ions through the ISM into the aqueous layers or the water pools may lead to instability and drift in the electrode potentials and it is therefore essential to use hydrophobic ISM membranes to decrease the water uptake of the SCISEs and CWEs.[1] Outflux of accumulated primary ion in the ISM may also bias the electrode potential at low sample concentrations and thus affect the limit of detection. The water uptake of plasticized poly(vinyl chloride) (PVC), silicone rubber (SR) and acrylate based ISMs was recently studied by the FTIR-ATR technique.[2,3] It was shown that the water uptake of plasticized poly(vinyl chloride) (PVC) membranes were much higher than for silicone rubber (SR; RTV 3140).

In this work, the water uptake of ISMs and its correlation with the potential stability of Ca^{2+}-selective SR and plasticized PVC based SCISEs and CWEs will be discussed. The presentation focuses also on other aspects of the water uptake of ISMs.

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Lowering of the Detection Limit of Solid-State Lead(II) Selective Electrodes

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Lead(II) is a major pollutant in the environment. The monitoring of Pb^{2+} distribution is undeniably crucial in preventing uncontrolled release of this component to ecosystems. The requirements for the reliable determination of lead(II) in industrial wastes and environmental samples has resulted in a number of publications [1,2]. A lowering of the detection limit of ion-selective electrodes (ISEs) became a significant part of electroanalysis and created the possibility of measurements at extremely low concentrations of analyte. The detection limit has been an issue of interest since early stages of the history of ISEs and initially solid-state membranes were in focus [3,4]. The possibility of lowering the detection limit for ISEs with plastic membranes was reported later[5].

Solid-state lead (II) ion-selective electrodes were used and their performance at low concentrations of Pb^{2+} ions was inspected by different methods. The electrodes were applied in direct measurements of ultra-low concentrations of Pb^{2+}. The lowering of the detection limit of Pb^{2+}-ISE was achieved by a procedure based on concentration-time dependent adsorption of the analyte to the surface of the membrane as well as tuned galvanostatic polarization of the solid-state membrane. By this research we revitalize the area of solid-state membranes used for lowering of the detection limit.

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Applications of Chronopotentiometry to Study and Modify Composition of Ion-Selective Electrodes Membranes

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Galvanostatic polarization of ion-selective electrodes (ISE) is a simple and effective method of improving some analytical parameters (e.g. detection limit lowering) [1] or obtaining data concerning concentration and mobility of ionophore and ions in the membrane [2]. This method is also useful in diagnostics and response optimization of all-solid state ISEs with conducting polymer solid contact as a medium undergoing charge transfer reactions [3,4].

In this presentation versatility of chronopotentiometric method was shown on three examples of applications to ISE membranes, concerning (i) studies on ion distribution in the membranes, (ii) determination of amount of primary ions, and (iii) controllable modification of membrane composition.

(i) Using mass spectrometry with laser ablation of the membrane material (LA ICP MS), contents and spatial distribution of ions in the membrane under influence of galvanostatic polarization as well as accumulation / release reversibility were studied and compared with theoretical predictions.

(ii) Accumulation of primary ions in ISE-membrane under open circuit conditions, the role of composition of conditioning solution for this process was studied on example of silver-selective poly(vinyl chloride) based membrane. The obtained results were consistent with data collected by LA ICP MS method.

(iii) Optimal potentiometric characteristics is dependent on membrane composition and particularly on molar ratio of primary / interferent ions amount. A simple galvanostatic method of controllable primary ions incorporation into the membrane was proposed. A relation between membrane composition and potentiometric calibration plots and their stability is presented.

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Electrochemical Devices Sensing Surrounding Conditions

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Electrochemical reactions of conducting polymers are considered as consecutive n events of one electron charge transfer reaction each involving polymer chains and balancing counterions. For those materials with a prevailing interchange of anions with the ambient the reaction can be summarized as:

$$[(pPy^{c+})(A^{-})_{c}(S)_{d}]_{gel} + A^{-} + uS \rightarrow [(pPy^{(c+1)+})(A^{-})_{c+1}(S)_{d+u}]_{gel} + e \qquad (2)$$

Where pPy^{c+} is a polymeric chain inside a dense gel. By statistical reasons over 99.9 of the charge transfer occurs from chains located inside the film. This elemental reaction transfer is not usual in electrochemical texts because there only electron transfers through bidimensional solid or liquid interfaces are considered. The second reactant is the anion, A^- required to keep the charge balance during the electron transfer is located outside the film, in solution.

If the oxidation reaction of a polymer film occurs under flow of an anodic constant curren (i_a) the reaction rate will be defined by:

$$i_a = F\ V\ k_a\ [A^-]^a\ [Pol^*]^b = F\ V\ k_{a0}\ [A^-]^a\ [Pol^*]^b \exp\{[(1-\alpha)\ F\ (E-E_0)]/RT\}$$

And the potential should evolve during the reaction time, t, as:

$$E_a = E_0 + \{RT/(1-\alpha)nF\}\ \{\ln(i_a t/FV) - a \ln[A^-] - b \ln[Pol^*] - \ln k_{a0}\}$$

This is a sensing equation indicating that the potential evolution of the reactive material with the time of current flow is a function of: the electrolyte concentration $[A^-]$ in solution, volume changes (V, or mechanical conditions) and temperature (also included in k_{a0}).

By changing one of the variables every time (keeping a constant value for the other variables) the potential evolution of the reactive material is a sensor of the studied variable. Consequently the consumed electrical energy ($i\int E dt$) also senses the variable.

Polypyrrole materials having prevalent interchange of anion or prevalent interchange of cations during the reaction and able to sense temperature, electrolyte concentration or mechanical conditions should be presented.

New reactive and sensing devices, as tactile artificial muscles constructed with those materials and sensing surrounding working conditions under flow of constant currents are emerging. A new technological paradigm of biomimicking reactive sensing actuators is rising.

Systematic selection and design of metalloporphyrin based oxygen sensors by tuning the donor-acceptor intermolecular hardness

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Metalloporphyrins and related N_4-macrocyclic complexes are well known catalysts for oxygen reduction. The activity of these complexes for the oxygen reduction reaction depends on the nature of the central metal atom, and the nature of substitution groups on the porphyrin ring. We invoked the concepts of activity dependency on the number of electrons in the d-orbital of the central metal, and the concept of molecular hardness proposed by [1], to plot the dependency of the activity of manganese bearing porphyrins on the nature of substitution groups in the form of 3-D activity plots (**Fig 1**). The 3-D plots reveal an activity trend which is dependent on the nature of substituents at the meso positions of the ring. It is evident from the trend that higher activity is promoted by electron donating groups notably pyridine and methoxy groups. Guided by this systematic criterion, we present nano- and microfabrication of a very active oxygen sensor using Manganese 5,10,15,20-tetra(4-pyridyl)porphyrin. Additionally, we show that the problem of instability which is often associated with porphyrin complexes can be overcome by intelligent attachment of the porphyrin complexes by coupling individual metalloporphyrin units by means of suitable linkers using electropolymerization. The preparation, optimization and specific properties of the proposed micro sensor will be discussed.

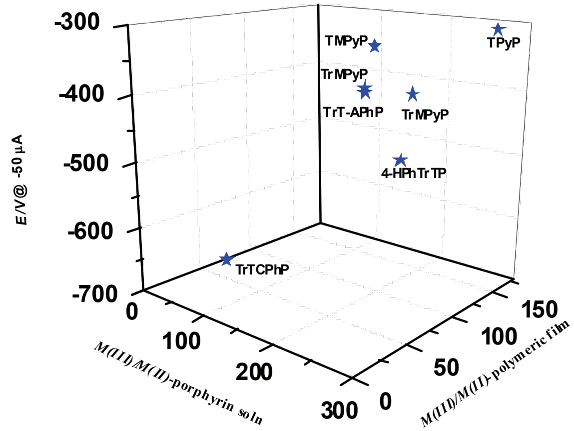

Figure 1: 3-D activity plots (potentials against Ag/AgCl/3M KCl electrode)

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Use of Electrospun Polyaniline for Sensor Applications

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Use of conducting polymers, like polyaniline (PANI), in electrochemical sensors has gained much interest and focus of researchers. This is due to the well-known attractive characteristics of conducting polymers that enable simultaneous passage of current, ion-to-electron transduction and functionalization of the polymer by e.g. covalent binding of biological recognition sites to the polymer backbone. Electropolymerization is often used to obtain a film of conducting polymer directly on electrically conducting substrate [1].

Electrospinning of different polymer material results in thin fibers with diameters even down to few nanometers, having very high surface area to volume ratio [2]. Electrospun conducting polymer fibers are promising materials in sensor applications in addition to the film-type sensors [3]

Here suitability of elecrtospun PANI/PLA (polylactic acid) fibers as sensor material is investigated and their electrochemical characteristics are compared to electropolymerized PANI films. In the beginning of the work, fibers are spun on aluminum foil changing the parameters (voltage, distance, concentration), and analyzed with scanning electron microscopy. This is followed by spinning fibers directly on a glassy carbon electrode surface, and so-formed GC/(PANI/PLA) electrodes are characterized by impedance spectroscopy, cyclic voltammetry and potentiometry. Results are compared to similar measurements on electropolymerized PANI films.

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Micro- and Nanostructrures for Ion-Selective Electrodes

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Micro- and nanostructures are reaching significant attention across electrochemical community with special emphasis for catalysis purposes. Sensor applications, especially ion-selective electrodes (ISEs) to our knowledge, have not benefit much from these structures[1,2]. This presentation gives examples of recent research done in our group focused on different micro- and nanostructures applications in ion-selective electrodes to improve their operational parameters.

Polyacrylates are well established membrane materials yielding selective and stable sensors despite relatively high impedance. An effective method of lowering electrical resistance of poly(n-butyl acrylate) is introduction of Pt nanoparticles to the sensing membrane[3]. As shown on example of K-selective sensor the analytical parameters of Pt enriched membranes were well comparable with those of classical ones. In contrast to Pt substrate coated wire electrodes, known for unstable potentials, introduction of Pt nanoparticles to the membrane resulted in significantly increased stability of potential readings even compared to conducting polymer based solid-contact arrangement.

Synthesis of microstructured materials, especially preparation of micro- and nano-capsules is also extremely promising for sensor application. Microvessels can be used to deliver reagents to the sensor structure. For example, polypyrrole based capsules filled with electrolytes watery solutions can be used as tailored solid-contact materials[4]. Choosing electrolyte and its concentration, different levels of saturation of the Ca-selective membrane are achieved, enabling tuning of sensor analytical performance (linear response range, selectivity) irrespectively of conditioning solution. Similarly electrochemical parameters, resistance and capacitance of the electrode can be altered in a significantly wider range compared to conducting polymer based solid-contact ISEs.

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Unique contact-type measurement of ions using planar multielectrode platform

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A method for measurement of ions in small (20-30 μL) sample volumes is developed. The measurement is performed with planar galvanic cell containing several solid-state ion selective electrodes and a reference electrode [1].

The key novelty is in applying routine microscope slide glasses. A drop of the sample is placed by micropipette on glass and a flat multielectrode platform placed to allow touch-contact with this drop. By virtue of a physical adhesion the sample evenly spreads to cover all electrode spots. In this way the potentiometric measurement is possible. The advantage of this unique measurement mode is in limiting evaporation of the sample which results in long-term stability of readouts. The parameters of responses are comparable to these known from a conventional measurements with ion-selective electrodes. To prove the usability of the method the measurements were performed with watery calibration solutions used in clinical analyzers, serum samples and in selected pharmaceutical preparations.

Acknowledgment

The Finnish Funding Agency for Technology and Innovation (TEKES SHOK IMO **Intelligent Monitoring for Health and Well-being (IMO) program**) is acknowledged

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Lowering the Detection Limits of Ion-selective Electrodes by Galvanostatic Polarization: Practical Achievements vs. Fundamental Uncertainties

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Efforts aimed at lowering the detection limits of Ion-selective Electrodes (ISEs) with ionophore-based membranes comprise the mainstream of the experimental and theoretical research in the field of this kind of sensors [1]. Among various approaches to improve the detection limit, those based on galvanostatic polarization of the electrodes are of special interest. The easiness of the tuning the polarizing current density makes this approach flexible and in this sense superior to other approaches based on the optimization of the composition of the internal electrolyte, or the composition and/or the geometry of the ISE membrane [2]. On the other hand, measurements with ISEs under current suggest major change of the very concept of the ISEs, traditionally considered as purely potentiometric sensors.

We recently succeeded with extending linear Nernstian response of Ca^{2+} and Cd^{2+} ISEs down to 10^{-10} M by tuned galvanostatic polarization [3-5]. Simple linear relations between the polarization and the current density, and between the optimal current density and log of the analyte ion concentration, have been revealed experimentally. From the practical point of view, these simple relations are very useful for tuning the current density and obtaining linear Nernstian response. More of this, Ca^{2+} and Cd^{2+} concentrations in artificial samples were measured with sufficient accuracy by the ISEs in chronopotentiometric mode.

On the other hand, the fundamentals behind these practical achievements are under question. The discussion will focus on the following issues: (i) how the polarization is distributed between the aqueous phase and the membrane phase; (ii) what is the impact of the background electrolytes in the sample phase and in the membrane phase to the overall effect; and (iii) whether the polarization is of only concentration type while the interface between the membrane and the sample is at electrochemical equilibrium.

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Sensorial Properties of Carbon-Polymer Composite

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Ionic electroactive polymer (EAP) composites are materials that exhibit changes in mechanical properties when stimulated by (relatively low) voltage. Ionic EAPs typically consist of two layers of conductive material, separated by an ion-permeable membrane. The system contains some mobile ionic groups. An electric potential applied between the opposite conductive layers induces electro-osmosis. The resulting transverse dislocation or re-orientation of ions causes bending of the whole sandwich. Therefore, these types of composites can be used as actuators.

The opposite process occurs when EAP material undergoes deformation caused by an external force. In case of many types of EAPs, the external deformation causes transversal dislocation of ions in the composite, which can eventually be registered as an open-circuit voltage [1], short-circuit current, or changes in impedance of different parts of the composite [2]. Therefore, many EAPs can also be used as position or motion sensors [3].

This work concentrates on the properties of Carbon-Polymer Composite (CPC). This material consists of two layers containing carbon with high specific surface area and sufficient electric conductivity, supported by polymer matrix. The carbon layers are separated by a thin polymer membrane. The whole system contains ionic liquid as an electrolyte. The electromechanical properties of CPC transducers are described e.g. in [4], [5]. So far, the sensorial behavior of CPC material is still not studied in detail.

The current work is dedicated for investigation of charge formation processes caused by external mechanical deformation of nanoporous system containing ionic liquid. In the experimental section, the CPC material is bent with external force. Charge formation is registered both as a change in voltage and short-circuit current between the opposite electrodes. The mechanoelectrical transduction is investigated in wide frequency range. A possible mechanism for describing this process is proposed.

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Photosensing System Composed of Photosystem I and Molecular Wire on Electrode

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Photosynthesis demonstrates the most efficient and optimized photoconversion performance seen in nature, with a quantum yield of nearly 100%. This performance is realized via a carefully tuned electron transfer pathway, through which photoelectrons are transferred via a redox cascade in a stepwise fashion after photoinduced charge separation occurs in the chlorophyll reaction center. The properties of photosystem I (PSI), which constitutes a major component of the photosynthetic apparatus in nature, were artificially reproduced by replacing vitamin K1 (VK1) with a synthetic mimic in the PSI structure, to employ PSI as a photoelectric conversion component. We have achieved that bio-conjugation between PSI, Au nanoparticles (AuNPs), and field-effect transistor (FET) produced a bio-photosensor [1], and further developed related photoelectronic conversion systems [2, 3]. The merit to include small AuNP between PSI and electrode in the first system is to use the minute capacitance, which enables the observation of the single electron transfer (SET) events in electrolyte solution even at room temperature. The SET is not easily observed in aqueous solution because of the high dielectric constant of water, but we have recently found that redox peaks of AuNPs were observed in the presence of the two surfactants [4]. In the present study, we sought to develop an enhanced photodetection method by combining AuNPs and surfactants. Photosensing performance of a system composed of PSI, VK1-like molecular wire, and AuNPs in an aqueous solution was increased considerably by the addition of double surfactants, hexylamine and dodecylbenzenesulfonate [5].

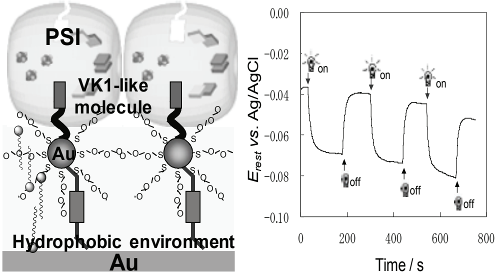

Fig.1. PSI-molecular wire-AuNP photosensing system.

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Ionic Liquid-Functionalized Nanocomposites toward Electroanalytical Applications

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Ionic liquids (ILs) have attracted an increasing amount of interest, owing to their low volatility, non-flammability, high chemical and thermal stabilities, high ionic conductivity, and broad electrochemical windows. In our group, ILs have been widely used as dispersant, supporting electrolyte, stabilizer/protector, and/or modifier for the functionalization of carbon nanomaterials and metallic nanocomposites, which exhibited a promising application to electrochemistry and electroanalytical chemistry due to their unique properties of ILs. In addition, to facilely immobilize ILs onto solid substrates for its further electrochemical applications, we also designed polyelectrolyte-functionalized ionic liquid (PFIL). The PFIL-modified electrode is wettability-controllable and exhibits electrocatalytical activity toward the oxidation of various target species. In view of the high conductivity, exchangeability of counter anions, enhanced diffusion of target species across the film matrix, and large electrochemical potential window of ILs, the PFIL was also used for the electrochemical detection in supporting electrolyte-free solution, and enhanced electrochemical polymerization of conducting polymer, etc. In conclusion, whether as “green solvents” or as functionalized materials, imidazolium-based IL materials exhibited a significant potential toward the application in electrochemistry and electroanalytical chemistry.

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On-chip Electrochemical and Mass Spectrometric Detection Techniques

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Electrochemical sensors and detectors are well-suited for use in conjunction with chip-based analytical systems[1]. The main reason for this is that electrochemical devices can be miniaturised without loss of performance employing standard microfabrication techniques.

This presentation will focus on our research[2-5] aiming at the development of on-chip electrochemical detection techniques suitable for use in chip-based separation devices. It will be demonstrated that an external electric field can be used to drive amperometric detection anywhere within a microfabricated flow channel containing an array of microband electrodes[4,5]. This approach facilitates electrochemical detection in lab-on-a-chip devices involving capillary electrophoretic separations, which otherwise is difficult due to the interference of the separation voltage on the detection. The influence of the electrode material on the stability of on-chip microfabricated electrodes[5] will also be discussed.

In addition, a PDMS based device[6] allowing an on-chip coupling of an electrochemical cell to electrospray mass spectrometry (ESI-MS) with sub second transfer times will be described. This on-chip coupling of an electrochemical cell to ESI-MS provides very good possibilities to identify and quantitate electrochemically produced oxidation and reduction products present in very small sample volumes.

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Fast Batch Injection Analysis of H_2O_2 Using an Array of Modified Gold Microelectrodes Obtained from Split Electronic Chips

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Hydrogen peroxide plays an important role in industrial, clinical and environmental fields. It occurs naturally at low concentration levels in the air, in natural water, in body fluids and in plant tissues and can be also present in foods and drinks. Considering the H_2O_2 high reactivity, which makes its precise quantification difficult, the development of a rapid and precise method is highly desirable. In order to speed-up the routine work, flow injection analysis (FIA) methods associated with different types of detectors have been proposed for H_2O_2 determination. A simpler but less versatile alternative to FIA, the batch injection analysis (BIA) introduced by Wang and Taha [1], assures fast response with comparable sensitivity. Electrochemical detectors have been widely used for BIA applications, being the most popular, the voltammetric and amperometric based on the use of conventional or chemically modified electrodes [2]. Despite the attractive characteristics offered by microelectrodes such as high current density, independence of sensitivity to hydrodynamic conditions and the ability of use in highly resistive media, their use in BIA applications is still scarce. In the present study, a rapid and highly selective method to determine low H_2O_2 concentrations with amperometric detection is proposed and evaluated. The BIA procedure is based on H_2O_2 detection at +0.6 V vs. Ag/AgCl on an array of gold microelectrodes modified with platinum. The hydrogen peroxide determination was made by a differential measurement, quantifying H_2O_2 directly and after its enzymatic destruction with catalase in 10 mmol L^{-1} phosphate buffer solution, pH 7.0. The gold microelectrodes array (n=14) was obtained from electronic chips developed for surface mounted device technology (SMD), whose size offers advantages to assemble microelectrode arrays to be adapted in batch cells. The effect of the dispensing rate, volume injected, distance between the platinum microelectrodes and the pipettor tip, as well as the cell volume on the analytical response were evaluated. By injecting 50 μL sample volume at 76.9 $\mu L.s^{-1}$ flow-rate, the method allows the H_2O_2 amperometric determination in the concentration range from 0.8 μmol L^{-1} to 100 μmol L^{-1}. The analytical frequency can attain 300 determinations per hour and the detection limit was estimated in 0.25 μmol L^{-1} (3σ). The anodic current peaks obtained after a series of 23 successive injections of 50 μL of 25 μmol L^{-1} H_2O_2 showed an RSD < 0.9%. A practical application of the analytical procedure involved H_2O_2 determination in rainwater of São Paulo City. A comparison of the results between the method here proposed and a well-established FIA-spectrophotometric method showed good agreement ($R^2 = 0.998$).

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Heavily Nitrogen-Doped Nanocrystalline Diamond Electrodes: Transition to Metal-Like Electrochemical Behavior

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Different diamond-like or diamond-based materials can be an inexpensive alternative to the “traditional” polycrystalline diamond films. In this report, the electrochemistry of the nitrogenated nanocrystalline diamond thin-films will be discussed, with relation to their use as electrodes.

Ultrananocrystalline nitrogenated diamond films, a few microns thick, were grown on polished Si substrates from Ar-CH_4-H_2-N_2 gas mixtures, using microwave plasma CVD-reactors. The N_2 content in the feeding gas varied from 0 to 90%. The films are characterized by spectroscopic and electrical measurements. The electrodes were studied using cyclic voltammetry and electrochemical impedance spectroscopy in solutions of indifferent electrolyte (1 M KCl) and “model” $[Fe(CN)_6]^{3-/4-}$ redox couple.

The ultrananocrystalline nitrogenated diamond electrodes showed good electrochemical properties. They demonstrated rather wide potential window ($\geq$1.5 V) and low background current (~10 μA/cm^2). With the increase of the N_2 content in the feeding gas, the electrodes’ differential capacitance increased, the electrode reaction in the $[Fe(CN)_6]^{3-/4-}$ redox system became more reversible. By and large, with the increasing of the nitrogenation the electrochemical behavior of “poor conductor” gives way to that of metal-like conductor: in particular, the current peak separation in cyclic voltammograms approaches 60 mV, a “theoretical” value for reversible reactions. Some peculiar “saturation” of the electrochemical activity appears: at ~30% N_2 in the feeding gas it does not change further. This “electrochemical” conclusion agrees with the Raman spectra of the films, which show some stabilization of the diamond-graphite structure in the material at ~30% N_2.

Comparing the ultrananocrystalline nitrogenated diamond electrodes with nitrogenated amorphous carbon (a-C:N:H) electrodes, we concluded that the electrochemical behavior of the nitrogenated nanocrystalline diamond is mainly determined by the N-containing amorphous carbon matrix, rather than the diamond nanocrystallites proper.

The ultrananocrystalline nitrogenated diamond is a promising electrode material for electrochemical applications.

This work was supported by the Russian Foundation for Basic Research, project 10-03-00011.

pH-Dependent Properties of Thin Film Obtained from the Electrografting of Diazonium Salt in Ionic Liquid

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Electografting of diazonium salts on solid substrates is an interesting way for the preparation of functionalized materials with new promising properties for sensing applications. However, when using electrochemical grafting, formation of multilayer films was frequently observed. Recently, we have reported the electrochemical reduction of diazonium cation in ionic liquid media [1]. By combining, electrochemical investigation, FT-IR, AFM and XPS, we showed that formation of thin and less dense layer in ionic liquid media [2].

Here, we investigated in buffered aqueous solution the electrochemical responses of an organic film that was previously obtained from the electrochemical reduction of 4-nitrophenyl (NP) diazonium salt in ionic liquid. To gain additional insights into the structural uniformity of the tethered aryl overlayer, redox systems such as $Fe(CN)_6^{-3/-4}$, $Ru(NH_3)_6^{+3/+2}$, and ferrocene methanol (FcMeOH) were used to probe the electrochemical barrier properties of the phenyl groups by means of cyclic voltammetry, and electrochemical impedance spectroscopy (EIS). We showed drastic increase of the charge transfer resistance R_{ct} for $Ru(NH_3)_6^{+3/+2}$ redox system at pH = 2.3. On the other hand, a drastic increase of R_{ct} for $Fe(CN)_6^{-3/-4}$ was observed at pH = 11.3. The difference in the behaviors of the redox probes might be due to the electrostatic interaction (repulsion) with the grafted groups. However, the hydrophobic/hydrophilic interaction with the modified surface should be considered. In this context, the electrochemical responses of FcMeOH were very instructive. We showed that R_{ct} of FcMeOH varied with pH; R_{ct} for FcMeOH in acidic medium (pH = 2.3) was higher than that was observed in basic medium (pH = 11.3). Since R_{ct} was defined from the exchange current density then it included both the standard rate constant and local concentrations. These results indicated that the blocking effect of the grafted layer depended on the charge and the hydrophobicity (hydrophilicity) of the redox probe as well as the nature of the solvent of the electrolyte.

The electrografted NP groups can then be subsequently reduced to 4-aminophenyl groups. This approach should serve to both lower the surface hydrophobicity and allow for the subsequent attachment of a wide variety of biomolecules. The approach developed here introduces new opportunities for chemical functionalization of carbon-based interfaces toward applications in the field of bio- and nanotechnology, and to develop a new class of sensors as "ion-channel sensors".

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Electrochemical Determination of Pentachlorophenol from Water on Multiwalled Carbon Nanotube–Epoxy Composite Electrode

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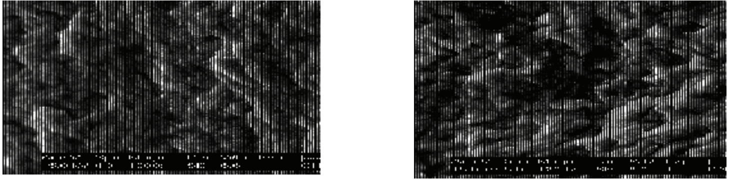
Two types of MWCNTs- epoxy composite electrodes containing 20 % and 25 %, wt. respectively MWCNTs (MWCNT20 and MWCNT25) were obtained and tested for the electrochemical sensing of pentachlorophenol (PCP). SEM images of surfaces of the composites were taken to qualify the bulk distribution and the structure of the conductive fillers (Figure 1). The electrical conductivities of both composites were determined using the standard four point probe technique, and MWCNT25 electrode exhibited the better conductivity. The electroactive surface areas of the composite electrodes were determined using potassium ferricyanide. The assessment of both composite electrodes for the electrochemical determination of PCP is described. Cyclic voltammetry technique was used to characterize the electrochemical behaviour of PCP in 0.1 M Na_2SO_4 supporting electrolyte in order to establish the parameters for amperometric/voltammetric determination of PCP. The linear dependence of the current versus PCP concentration was reached in the concentration range from 0.75 to 15 μM PCP using cyclic voltammetry (CV), differential-pulsed voltammetry (DPV), chronoamperometry (CA), and multiple-pulsed amperometry (MPA). Under the conditions of CA application, the fouling of the electrode occurred, which was avoided by MPA application that assures in-situ electrochemical cleaning of the electrode. The best electroanalytical parameters of the sensitivity, the relative standard deviation, the lowest limit of detection and the limit of quantification were obtained by MPA application, revealing that both MWCNTs electrodes exhibited useful characteristics for electrochemical determination of PCP from aqueous solution. In addition, some mechanistic aspects regarding PCP oxidation on composite electrodes were discussed by performing CV at different scan rates.



a b

Fig.1-SEM images of electrode surfaces: a- MWCNT20; b- MWCNT25

Potentiometric sensors based on carbon nanotubes. From invention to innovation

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The nanosensors group at Tarragona has recently shown that carbon nanotubes (CNTs) can act as very efficient ion-to-electron signal transducers in potentiometric sensors, including ion-selective electrodes (ISEs) and aptasensors [1,3]. The characteristics of carbon nanotubes such as their large capacitance, hydrophobicity, insensitivity to light or easy handling make them very appropriate as transducers, overcoming some drawbacks of previous materials used in solid-contact potentiometric electrodes. In this way, single-walled and multi-walled CNTs have been used to develop ISEs for different cations and anions, and aptasensors for different biological compounds, with improved analytical performance.

In this presentation we will show the process from invention to innovation, that is, the different steps necessary to introduce the new electrodes in the market. We will first review the main aspects of the scientific development. We will look at the steps performed to protect the intellectual property in form of a patent. After failing to sell the patent to any of the companies currently making ion-selective electrodes, we will describe the process of creating the own spin-off "NT Sensors, S.L". However, the big challenge is not to establish a new company but to introduce a new product in a market and to be able to grow up in this business world so different from the scientific environment.

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An Electrochemical Method to Monitor the Content of Dissolved Alumina in Electrolytes of Aluminium Electrolysis Cells

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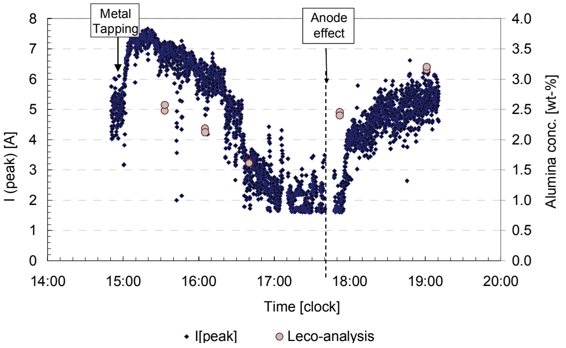
In the established process for electrowinning of aluminium the feed material is alumina which must be dissolved in a molten fluoride electrolyte. In modern electrolysis cells the feed is added semi-continuously in small batches. Ideally the feed rate should equal production rate of aluminium, less the unwanted losses. This is difficult to predict precisely, and semi-empirical techniques are used to control the feed based on knowledge of the main operating parameters. This has been incorporated into mathematical models, and modern cells can now be run for weeks without an exact knowledge of the alumina concentration during this time. In practice sampling and analysis are carried out routinely to verify that the electrolyte composition is within a target range. If too much alumina is added it may accumulate as sludge at the bottom of the cells. If too little alumina is added a so-called anode effect may occur, manifested as an abrupt rise in cell voltage because the transfer rate of oxide ions to the anode becomes too low.

The anode effect phenomenon on a sensor electrode can be used to monitor the alumina content of electrolyte. The principle is a controlled rapid increase in the current on a small graphite anode immersed in the electrolyte. The limiting current for the anode reaction is dependent upon the alumina concentration in the electrolyte, and a relationship between the peak current and alumina concentration can be found and a calibration curve established. At SINTEF a prototype of oxide analyser based on this principle has been developed. A specially designed probe has been developed and the system tested in an industrial cell. The critical current (Ipeak) plotted as a function of time shows good agreement with analyzed alumina content (Fig. 1). The high experimental scatter is compensated by the high frequency of measurement. The measurements are continuously displayed on-line on the screen of the controlling laptop computer where they also are stored for later analysis. Control experiments have been run for 10 – 12 hours.

Figure 1. Alumina concentration measurements in an industrial aluminium electrolysis cell. ♦ Critical current (Ipeak) - left scale; ○ Analyzed alumina content of bath samples - right scale.



Pt Nanoparticle/Carbon Nanofiber-Modified Screen-Printed Electrodes for Amperometric Detection of H_2O_2

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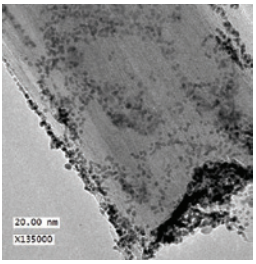
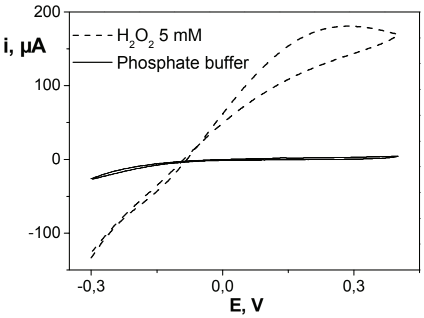
Nanostructuring electrode surface represents an effective way to increase sensitivity and selectivity in electrochemical sensors. In particular, carbon nanotubes (CNT) and nanofibers (CNF) promote electron transfer reactions at low overpotentials, which has motivated extensive coupling of these nanomaterials with enzymes in biosensors. Modification of CNT with Pt nanoparticles enables further lowering of the overpotential for amperometric detection of H_2O_2, the enzymatic by-product of oxidase-based biosensors and hence of great relevance. Pt nanoparticle deposition on CNT/CNF-modified electrodes is normally conducted by electrochemical methods, which leads to large particles and broad size distributions and cannot be regarded as a fast and large-scale preparation method.

Here we will show the excellent sensing properties of nanostructured home-made screen-printed electrodes (SPE) prepared by drop casting solutions of graphitized carbon nanofibers (GCNF) decorated with well-dispersed ultra-small Pt nanoparticles featuring very narrow size distribution (2-3 nm). The Pt/GCNF composites (left figure) are prepared by chemical reduction of the Pt precursor. The analytical features for H_2O_2 detection of GCNF-modified SPEs with Pt nanoparticles deposited by electrochemical and chemical routes (with same Pt loading per sensor) have been compared. Results obtained show that Pt utilization in the composites prepared by the chemical route is much higher, leading to considerably higher sensitivity and lower detection limits at a low detection potential (+0.2 V vs Ag/AgCl pseudoreference electrode, right figure) than the electrochemically prepared ones. The good electroanalytical properties of these Pt/GCNF composites combined with the intrinsic advantages of SPE technology represent a promising alternative towards the development of a straightforward, reproducible and large-scale production method of oxidase-based biosensors.





YSZ-based Sensors Using Oxide Sensing Electrodes for Detection of Hydrocarbons in ppb Level

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Hydrocarbons (HCs) are one of the most serious air pollutants which emanate from heavy industry and automobiles. Therefore, the development of highly sensitive HCs sensors for monitoring applications remains a challenging issue. Recently, we reported that the yttria-stabilized zirconia (YSZ)-based sensors using In_2O_3-based sensing electrode (SE) and NiO-SE could detect ppb concentration levels of propene (C_3H_6) [1] and toluene (C_7H_8) [2]. In this study, the detailed sensing characteristics of each sensor was investigated for low concentration HCs sensing in atmospheric air.

The oxide-SEs and Pt-reference electrode (RE) were fabricated by applying the respective paste on the surface of YSZ followed by sintering at 1000°C for 2 h in air. The sensing characteristics of the fabricated sensors were evaluated at 450°C under the wet condition (+1.35 vol.% H_2O).

Among the various oxide-SEs tested for the sensing of HCs at the ppb level, sensors utilizing In_2O_3-based SE and NiO-SE demonstrated high sensitivity and selectivity to 50 ppb C_3H_6 and C_7H_8, respectively. Figure 1 shows the electromotive force (*emf*) response transients to C_3H_6 and C_7H_8 in the concentration range of 10 to 300 ppb (or 150 ppb) for each of sensors operated at 450°C under the wet condition. It is clearly seen that both sensors exhibited relatively high *emf* responses to concentrations as low as several tens ppb of C_3H_6 or C_7H_8, with acceptable 90% response and recovery time in the range of several minutes.

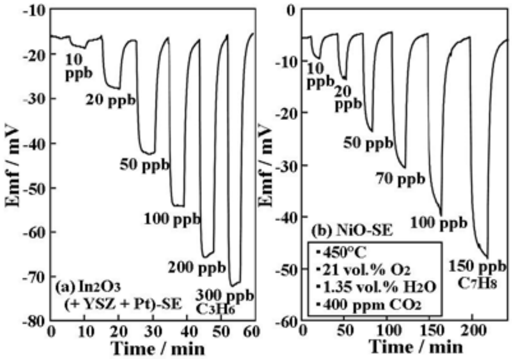

Fig. 1 Response transients to C_3H_6 and C_7H_8 for the sensor using each of (a) In_2O_3-based SE and (b) NiO-SE operating at 450°C under the wet condition.

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Screen-printing Dissolved Oxygen Sensor with Ag/C/CeO_2 Particle and Polydimethylsiloxane Film

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Dissolved oxygen sensor is useful for many applications of environment and bioanalytical chemistry. In the present study, we fabricated a disposable-type thin dissolved oxygen sensor by screen-printing technique. We used a Ag/C/CeO_2 ink and a polydimethylsiloxiane ink. We previously reported that silver-carbon-cerium oxide (Ag/C/CeO_2) particle exhibits a good catalytic activity of oxygen reduction [1]. The use of noble metal for preparation of the oxygen sensor can be reduced by using the Ag/C/CeO_2 particle. In addition, a polydimethylsiloxiane film is known to have good selective permeability of oxygen [2].

Figure 1 shows the schematic illustration of the screen-printing dissolved oxygen sensor. A silver lead was formed on a polyimide substrate. Then, home-made Ag/C/CeO_2 ink, resist ink (Taiyo ink Co. Ltd.) and polydimethylsiloxiane emulsion (Dow Corning Toray Co. Ltd. BY 22-826 EX) were printed successively. The electrochemical measurements were performed by two-electrode method in a phosphate buffer solution in which oxygen concentration was controlled by flowing oxygen and nitrogen gas before the measurement.

Figure 2 shows the linear sweep voltammogram of the oxygen sensor with different concentration of oxygen. The oxygen reduction current increased with increase of the dissolved oxygen concentration. It was found that the plot of the current increment at 1.5 V vs. oxygen concentration gave a straight line with good reproducibility. In the present paper, we discuss the characteristics of the sensor with oxygen reaction mechanisms on the Ag/C/CeO_2 particle.

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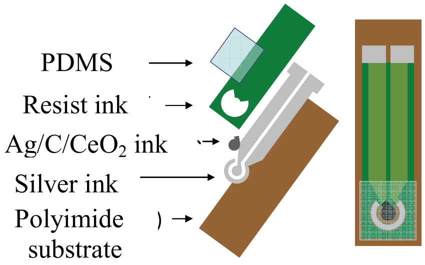

Fig. 1 Schematic illustration of the dissolved oxygen sensor.

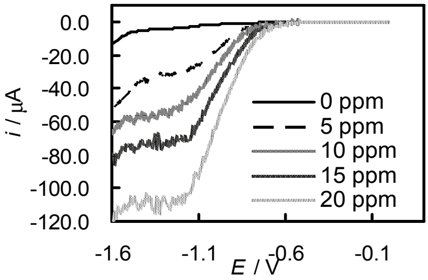

Fig. 2 Linear sweep voltammogram of dissolved oxygen sensor with different concentration of oxygen.

Changes in Performance of DNA Biosensor Caused by Hydroxyl Radicals

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Free radicals are generated in living cells by normal metabolism and by exogenous sources, including carcinogenic compounds and ionizing radiations. Free radicals can oxidize all kinds of biological macromolecules such as proteins, lipids and DNA.

The sensor used for the examination of the damage done by the radicals was based on the self-assembly bonding of the capture probe (a 20-mer single stranded DNA), diluted with MCH molecules, to the surface of a gold disc electrode. The sensor was exposed to OH radicals at various stages of its preparation/activity. The visualization of the changes in the performance of the sensor was done in two different ways. One was related to the monitoring of the change in charge transfer resistance of the ferrocyanide/ferricyanide couple and the other one to the voltammetric peak of methylene blue bound to dsDNA and ssDNA at the sensor surface. Both: the EIS and voltammetric data let us conclude that the reaction between OH radicals and ssDNA, compared to dsDNA, stronger influences the performance of the sensor. The experiments presented in this work clearly indicate that the difference in the affinity of the MB indicator to single and double stranded DNA can be successfully used for the detection of nucleic acid damage. A significant change in the activity of the biosensor appears when the percentage of damaged nucleotides is higher than circa 15%. A disadvantage of our approach is the lack of a possibility of identification of the type of the damage.

Electrochemical Properties of Aryl-Modified Glassy Carbon and Gold Electrodes

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Surface modification of carbon and metal electrodes by electrochemical reduction of aryldiazonium salts has been the subject of intense research activity [1-3]. The aryl modified electrodes have been used for various applications, including electrocatalysis and electroanalysis [3]. The barrier properties of aryl groups grafted to an electrode surface by the reduction of diazonium compounds have been extensively studied [1].

The electrochemical modification of glassy carbon (GC) and gold electrode surfaces was carried out using the diazonium reduction method. The electrodes were grafted with biphenyl, naphthyl, 4-bromophenyl, 4-decylphenyl and 4-nitrophenyl groups. The surface modification was performed in acetonitrile containing 1 mM of the corresponding diazonium salt. In order to alter the surface coverage of aryl groups, the number of potential scans applied was varied.

The blocking behaviour of aryl films towards O_2 reduction in 0.1 M KOH was studied using a rotating disk electrode. A clear blocking effect by the aryl layers on the kinetics of O_2 reduction was observed [4,5]. The modifier films block those active sites of GC responsible for the high reduction current at pre-wave potentials. The 4-bromophenyl-modified GC electrode showed the highest blocking efficiency towards O_2 reduction. However, none of the modifiers completely suppressed the O_2 reduction current. Defects in the modifier film allow O_2 molecules to reach the underlying electrode.

Comparative measurements for evaluating the barrier properties of the aryl-modified electrodes were also carried out using the $Fe(CN)_6^{3-}$ redox probe [4,5]. Electrochemical measurements were performed in 0.1 M K_2SO_4 containing 1 mM $K_3Fe(CN)_6$ using cyclic voltammetry. A much larger extent of blocking was evident for the $Fe(CN)_6^{3-/4-}$ couple than for oxygen reduction. This effect was explained by hydrophobic properties of the aryl films and by differences in size between the $Fe(CN)_6^{3-}$ ion and O_2 molecule.

The electrochemical response of dopamine on the aryl-modified electrodes was also investigated and the blocking action varied depending on the surface modifier used.

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Nickel modified boron doped diamond electrodes as electrocatalytic sensors

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The electrocatalytic properties of nickel and nickel modified electrodes have been explored extensively since the early work of Fleischmann et al [1] in the 1970s. The redox couple of $Ni(OH)_2/NiOOH$, formed in an alkaline medium, is highly catalytic towards the oxidation of small organic molecules, specifically the Ni(III) species. Nickel electrodes have therefore been used in the determination of alcohols, amines, sugars and numerous other organic materials.

Over the past decade metal nanoparticle modified boron doped diamond (BDD) electrodes have been used in the electroanalysis of a number of inorganic and organic analytes [2-5]. BDD electrodes are versatile and sensitive analytical tools in their own right, yet simple surface modification with a specific metal can greatly enhance these properties. The heterogeneous nature of the semi-metallic BDD electrode is also found to promote nanoparticle growth rather than film like modification. Thus nanoparticle modified surfaces with favourable diffusional properties and high surface area to weight ratios may be readily obtained.

Nickel nanoparticle modified BDD electrodes have been recently applied to the electrocatalytic oxidation of glucose and small primary alcohols [3-5]. The success of these systems are discussed, focusing on the consistent and simple modification of the BDD electrode, and the high sensitivity, linearity and low detection limits obtained in conventional electrochemical analysis without chromatographic stages.

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Fabrication of Pt Nano-dot Patterned Electrode using AFM-based Indentation Method

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Electrochemical characterization of Pt-loading carbon (Pt/C) is one of the central issues to develop electrocatalytic performances from viewpoints of Pt size and Pt inter-particular distance. However, it is difficult to evaluate the Pt/C architecture electrochemically because of its nanometer-order structure. A modeled electrocatalyst seems to be an effective way to understand the Pt/C. In order to fabricate a modeled Pt/C, a nano-indentation technique was applied to an insulating polymer/glassy carbon layered structure to deposit Pt nano particles on the scratched parts.

A glassy carbon plate (Tokai Carbon, GC-20SS) was cut into 1 cm^2 pieces, and its one side was polished to a mirror finish. The arithmetic average roughness (R_a) of the polished surface was around 2.2 nm. The glassy carbon was immersed in a perfluorinated resin solution (Asahi glass, Cytop, CTX-109), and it was pulled up using a motorized micromanipulator. After this dip coating procedure, the glassy carbon was dried at 150°C in an oven chamber for 1 hour to form a 10 ± 1 nm thick polymer overcoat layer. Subsequently, pinholes were formed to the insulating layer by an indentation of AFM cantilever with a loading force of 0.9–4.5 μN and an interdistance of 500 nm.

AFM image of the sample reveals that the shape of the pinholes resembles that of the Si cantilever. The indentation depth is proportional to the loading force. And, the depth is larger than the polymer thickness when the loading force is larger than 3.6 μN.

Next, the indentation sample with the loading force of 3.6 μN was used as a working electrode for a Pt deposition. By using a potentiostat, Pt plating was conducted in a 5 $mmol\cdot dm^{-3}$ H_2PtCl_6 + 40 $mmol\cdot dm^{-3}$ HCl for 5 s at an electrode potential of 0.12 V vs. RHE. Figure 1 shows an SEM image of the Pt deposited sample. The bright nine dots are identified to be Pt by an SEM-EDX analysis. It is realized from the figure that the Pt deposition of 30–60 nm in diameter successfully occurred at the indented sites with the 500 nm interdistance. It is also known from the result that the small Pt particles can be deposited in arbitrary interdistance based on the indentation method.

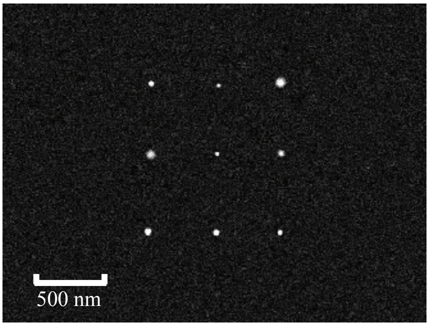

Figure 1 SEM image of nine AFM-based indents after the Pt electrodeposition.

Use of multisine EIS in the development of advanced screening techniques for cell cultures

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Electrochemical Impedance Spectroscopy (EIS) is considered one of the most powerful techniques to investigate complex systems. Cell cultures brought into contact with active species represent one of these very challenging systems. At present even a number of EIS-based machines for the study of cell cultures are commercially available. These applications however do not exploit the full potential of this technique as they only focus on a very limited number of frequencies.

The present paper presents the initial results of a project aimed at more elaborately exploiting the technique's possibilities in this field of research. Starting point is a commercially available array of test wells. Their inherent EIS behavior is thoroughly investigated using a redox system with a well-known behavior: Ferri-Ferro cyanide. Comparing the impedance response of this system in a classical 3-electrode setup with the response in the test wells allows isolating out the key impedance characteristics of the wells themselves. These are related to test well geometry as well as the materials used in such a well.

In a second phase the response of cell cultures present in the test wells are investigated. Deconvoluting this response with the aid of the known response of the well itself will lead to the identification of the characteristic response of the cell culture present. This operation will act as the first step in formulating a usable EIS model for the study of cell cultures.

Once such a model is available, identification and quantification of specific processes taking place in the studied cells is possible. This in turn will reduce the need to perform additional complex or time-consuming experiments.

Two-dimensional Condensation of Nucleic Acids Components and Oligodeoxynucletides at the Mercury Electrodes

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In 1965 one of us (VV) has discovered, that purine and pyrimidine derivatives currently occuring in nucleic acids posses an extraordinary high ability of self-association at the electrode surface and can form there by a two-dimensional condensation a monomolecular self assembled monolayer, a compact film[1,2]. By this high condensation ability nucleic acid bases differ from most of the other purine and pyrimidine derivatives which currently do not occur in nucleic acids. This property was probably significant for the origin of life at the earth[3]. For the time being it is not known why just only a restricted number of purine and/or pyrimidine derivatives show the tendency to self-association. We have studied the effect of halogen substituents and halogen ions in the supporting electrolyte on 2D condensation of cytosine. With polymeric DNA and/or polynucleotides the 2D condensation was not observed up to know. However, recently we have found that 2D condensation can be observed with certain homopyrimidine oligodeoxynucleotides (ODN)[6] at negatively charged mercury electrode surface. DNA adsorption at the electrode surfaces is of fundamental interest for the development of DNA-based biosensors[7].

Acknowledgements.
This work was supported by the Academy of Sciences of the Czech Republic (KAN200040651 to S.H.), the Czech Science Foundation (202/08/1688 to V.V. and 205/10/2378 to S:H.), and institutional research plan (AV0Z50040507).

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Solid-state single-rod measuring cells for electrochemical analytics in the liquid phase

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Potentiometry is an electrochemical method of analysis and the basis for a number of chemosensors. Ion selective electrodes (ISE) and solid electrolyte gas sensors shall be listed here. The former basically consist of the ion selective membrane and the internal reference system that in most cases contains liquid components. This fact often limits the applicability of the sensors substantially. So, e.g. temperature and pressure range are limited and there is a position dependence on storage and usage of the electrodes [1]. Most of the reference electrodes (RE) which have to be used in combination with aforementioned indicator electrodes also show the same disadvantages. Here, electrodes of the 2nd kind dominate, whereby silver chloride and calomel electrodes are preferably applied in practical use. Both include aqueous chloride containing solutions [2].

For a long time, a lot of work has being done to create solid state indicator as well as reference electrodes. Embodiments that combine both kinds of half cells in solid design which than form so-called single-rod measuring cells are considered quite effective.

In this contribution on the one hand solid-state potentiometric indicator electrodes based on glass and metal oxid membranes for ion analysis as well as also for redox potential determination are introduced. On the other hand experiments are presented concerning the fabrication of all-solid-state REs based on filled polymers.

As result of extensive screenings of a number of epoxy and polyester resins which were filled with varying amounts of KCl as reference electrolyte for electrochemical REs, it was found that castings of special epoxy resins with >50 wt% salt and an internal Ag/AgCl electrode represent a very suitable operational element. An important point is that the polymeric covering of the reference element should be advantageously designed in that way that the electrode impedance becomes lower than 200 MΩ. Potential changes when switching from one analyte solution to another is smaller than 4 mV. For REs based on extrinsic conducting polymers this is an excellent value. The developed electrodes can resist temperatures up to 100°C!

Finally, using the examples of a pH and a redox combination sensor the coaction of both all-solid-state half cells is demonstrated.

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Electroanalysis at Carbonized Layer-by-Layer Cellulose-PDDA-TiO_2 Composite Thin Films

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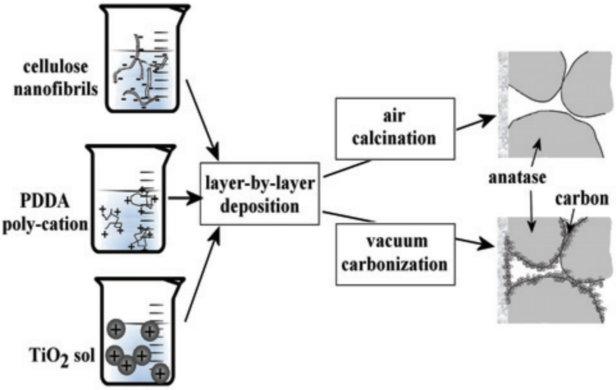
Mesoporous TiO_2 (anatase) materials immersed in aqueous electrolyte are known to behave as bulk electrical conductors at applied potential negative of the apparent flat band potential, whilst exhibiting insulator properties at more positive potentials. In this report we demonstrate a versatile cellulose nano-whisker-based surface carbonisation method [1] that induces surface conductivity and thereby makes TiO_2 surface states and surface reactions accessible to direct electrochemical control also in the positive potential range.



A layer-by-layer electrostatic deposition process based on TiO_2 nanoparticles, cellulose nano-whiskers, and poly(diallyldimethylammonium) or PDDA are employed to control the ratio of surface carbon to TiO_2. Dopamine binding at the anatase surface and redox cycling aided by the thin carbon film in mesoporous TiO_2 are demonstrated and dopamine is detected at micromolar concentration.

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Recent Trends in Development and Applications of Silver Amalgam Electrodes in Environmental Analysis of Biologically Active Organic Compounds

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Ten years elapsed from introduction of silver solid amalgam electrodes in voltammetric analysis of electrochemically reducible organic compounds [1]. During these ten years, working electrodes based on silver amalgam have gone through extensive development [2]. Polished silver solid amalgam electrodes (p-AgSAE) and mercury meniscus modified silver solid amalgam electrodes (m-AgSAE) were the first variants applicable not only for sensitive voltammetric determinations, but for amperometric detection in flowing systems (HPLC and FIA) [2,3] as well. Recently developed polished silver solid amalgam composite electrodes (p-AgSA-CE) [2], which under certain circumstances behave as an array of microelectrodes, can be very useful as well as silver solid amalgam paste electrodes with an organic pasting liquid (AgSA-PE) [4] or silver amalgam paste electrodes without pasting liquid (AgA-PE) [2] with an extremely easy renewability of their surface. At present, very promising results were obtained with solid amalgam microelectrodes based on single silver amalgam crystals (SCAgAE) [5]. Possibilities, advantages and limitations of these useful electrode materials will be demonstrated at a number of methods for the determination of biologically active organic compounds developed in our UNESCO Laboratory of Environmental Electrochemistry in the last five years. The determined analytes were hazardous organic chemical carcinogens and genotoxic environmental pollutants, pesticides, antitumor, antibiotic and antivirotic drugs, and explosives containing electrochemically reducible nitro, nitroso, azido, and oxo groups.

Financial support of this work, provided by The Ministry of Education, Youth and Sports of the Czech Republic (Projects MSM 0021620857, LC 06035, and RP 14/63), by the Grant Agency of the Czech Republic (Project P206/10/P087), and by the Grant Agency of Charles University in Prague (Projects SVV 261204, 89710/2010/B-Ch/PrF, and 267711/2011/B-Ch/PrF), is gratefully acknowledged.

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Electrochemical Stripping Analysis with Antimony-Based Carbon Paste Eletrodes

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As notoriously known, electrochemical stripping analysis developed from classical direct current polarography employing dropping mercury electrode, which was replaced by either stationary mercury drop or mercury film electrodes However, the toxicity of mercury or more precisely, well-known toxicity of its salts, initiated researchers and electrochemists to search for new electrode materials. In 2000, the bismuth film electrode was first introduced in anodic stripping voltammetry, exhibiting an impressive electroanalytical performance which compared favorably to its mercury analogue [1]. Since that time, bismuth-based electrodes have been presented in numerous interesting configurations and dimensions, and by now, they have been generally accepted in many electroanalytical laboratories (see an extensive review [2] and references therein published in a special issue of *Electroanalysis* dedicated to a decade of bismuth electrodes in contemporary analytical electrochemistry).

The first attempt to prepare an analogous antimony-based film electrode (SbFE) was not very successful because the same medium appeared less suitable [3]. Nevertheless, such electrodes were subsequently investigated in more acidic solutions using a glassy carbon and carbon fiber substrate electrodes [4]. In this contribution, we are focused on preparation of antimony films onto surface of carbon paste electrodes (SbF-CPEs) and their applications in electrochemical stripping analysis in both voltammetric and chronopotentiometric modes. As shown, SbF-CPEs exhibit some unexpected behaviour and offer measuring of trace concentration levels of numerous metal ions. In case of stripping chronopotentiometry, SbF-CPEs are prepared in situ and the excess Sb(III) salt serves as a chemical oxidant. Compared with similar total substitution of traditionally used Hg(II) by Bi(III) salts, the use of Sb(III) offers higher sensitivity. Corresponding examples are given [5-8].

Acknowledgments: This work was supported by the Ministry of Education, Youth, and Sports of the Czech Republic (projects MSM0021627502 and LC06035).

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Nanostructured Carbon Electrodes

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Carbon electrodes have found widespread application in a wide range of electrochemical applications including energy storage, energy conversion, medical bionics and electroanalysis.

The world of carbon electrodes has been revolutionized more recently with the development of **nanostructured** carbon electrodes - this includes electrodes based on carbon nanotubes and graphene. These nanodimensional building blocks can be used to enhance electron transfer kinetics improving sensitivity and the carbon chemistries developed over the years (1) can be used to anchor electro catalytic and/or molecular recognition sites to enhance selectivity.

Here we will describe advances in the preparation and utilization of

- Aligned carbon nanotube electrodes and their modification with conducting polymers (2) or electrocatalytic nanoparticles (3).
- Carbon nanoweb electrodes that have demonstrated very high electrochemical surface area (4).
- Nanostructured mats: we have found that additional functionality can be introduced into carbon nanotube mats by impregnating with a range of polymer materials (5).
- Carbon nanotube fibers: wet spinning approaches have been developed to produce long lengths of carbon nanotube fibers with excellent mechanical and electrical properties (6).
- Graphene electrodes: we have developed simple chemistries to isolate graphene sheets (7). These can be assembled into novel electrode structures by filtration (8).

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Highly Sensitive Detection of Cancers based on New Electrochemical Probes and Multifunctional Nano-Interface

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The efficient diagnosis and therapy of cancers is still a hot topic in the relative biomedical areas involving in the disease diagnostics and treatments as well as patient care. The multidrug resistance (MDR) is often one of the major obstacles in cancer therapies due to disease-causing organisms to withstand a wide variety of structurally and functionally distinct drugs or chemicals. Diagnosis and therapy in combination with nanotechnology may offer an alternative promising and overcome the difficulty. And the early diagnosis based on nanobiotechnology could be crucial for a successful treatment of cancer.

In this study, we have explored the possibility of the application of new electrochemically active supramolecular probes (such as tetrathiafulvalene derivatives) combining nanomaterials in relevant biomolecular recognition and high-sensitive detection of cancers. Especially, we have developed a new strategy for the fast and high sensitive recognition of the drug sensitive genes and relative cancer cells by combining the molecular probe and functionalized nanocomposites interface, such as nano-TiO_2 interface, the interface of TiO_2/CNT, β-CD/CNT, CNT/ TiO_2/Au, Au/PLA or graphene nanocomposites, with the electrochemical detection. Our observations demonstrate that the modified electrode based on specific nanocomposites with the new molecular probes could provide a multifunctional interface for the rapid and high selective identification of cancer cells, with a broad detection range and low detection limit. It is evident that different types of cancer cells could be readily distinguished on the relevant nanocomposites modified indium tin oxide (ITO) electrode or glassy carbon electrode, which have the promising application to be adopted as a significant way to detect and identify various cancer cells and advance the clinic diagnosis and monitoring of tumors with the aim of successful chemotherapy of human cancers.

Acknowledgements
This work has been supported by National Natural Science Foundation of China (90713023), National Basic Research Program of China (2010CB732404) and National High Technology Research and Development Program of China (2007AA022007).

A mediatorless lactose/glucose biosensor using cellobiose dehydrogenase and Au nanoparticles

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Cellobiose dehydrogenase (CDH) is an extracellular enzyme produced by a variety of different fungi. CDH consists of two domains, which are connected by a linker region, containing one flavin adenine dinucleotide (FAD) and one heme *b* as cofactors. CDH is an emerging enzyme in the field of biocatalysis, applied in biosensors and biofuel cells [1].

A lactose/glucose biosensor was fabricated by immobilizing *Corynascus thermophilus* cellobiose dehydrogenase (*Ct*CDH) on Au nanoparticles (AuNPs) (around 20 nm) modified Au electrode. *Ct*CDH was covalently bound by the amine group in the protein to the amine group-terminated thiol absorbed on AuNPs. The immobilized *Ct*CDH on the AuNPs surface is capable to catalyze the oxidation of a series of sugars, such as cellobiose, lactose and also glucose, in the absence of any redox mediator. Direct electrochemistry of the heme domain in *Ct*CDH was observed on AuNPs, which has a redox potential of $E_{1/2}$ = -122 mV vs Ag|AgCl(s). The heme in the cytochrome *b* domain of *Ct*CDH functions as a build-in mediator to communicate the electron transfer from the catalytic FAD domain to AuNP surface.

The performance parameters for this AuNP/*Ct*CDH amperometric biosensor at physiological pH=7.4 are displayed in Table 1.

Table 1. Analytical parameters of the AuNP/*ct*CDH biosensor for lactose and glucose

Sugar	Linear range (mM)	Sensitivity (nA/mM)	Detection limit (mM)	R^2
Lactose	0.01-0.5	1.02×10^3	0.01	0.999
Glucose	1-20	6.62	1	0.963

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Microfabrication and characterisation of cone-shaped boron-doped diamond and gold nanoelectrodes for simultaneous AFM and SECM imaging

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Combined AFM-SECM (atomic force microscopy-scanning electrochemical microscopy) has recently emerged as a promising technique for high resolution simultaneous topographical and electrochemical imaging [1-4]. Compared to traditional SECM using ultramicroelectrodes, the lateral resolution of AFM-SECM with bifunctional AFM probes can be significantly improved to the sub-micron or nanometer level. Moreover, the tip-substrate distance can be precisely controlled using the AFM feedback loop.

We have demonstrated a reliable microfabrication process for bifunctional AFM-SECM cantilevers [5]. Integrated cone-shaped nanoelectrodes of boron-doped diamond (BDD) or gold were fabricated from commercially available AFM probes. The electrode fabrication process is based on mature semiconductor processing techniques, including focused ion beam machining and highly selective reactive ion etching. Nanometer sized BDD electrodes for AFM-SECM applications have been fabricated for the first time. Compared to traditional electrode materials such as gold or platinum, BDD electrodes have a larger potential window in water, lack surface electrochemistry like oxide formation and dissolution and are remarkably resistant to electrode deactivation and fouling. These properties make them ideally suited for imaging in complex electrolytes containing e.g. corrosion inhibitors or biomolecules. The geometry of the tips has been determined by scanning electron microscopy. Their electrochemical behavior was studied by cyclic voltammetry. The amperometric tip response will be compared to a general expression for the steady state limiting current derived from numerical simulations of conical electrodes as function of their insulation sheath thickness and cone aspect ratio [6].

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A highly selective potassium ion sensor based on amphotericin B artificial ion channel

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Potassium ion plays a leading role in the regulation of intracellular enzymatic function, membrane transport and electrical functioning of excitable tissues. All of these functions are remarkedly affected by changes in extracellular potassium levels, since most of the potassium ions are intracellular[1]. As a result, the detection of potassium levels provides valuable information on a variety of diseases and disorders, such as nephropathy, endocrinopathy and cardiopathy. Several methods are extensively employed to detect K^+ ion, including flame photometry, potentiometry,capacitance measurement, SPR spectroscopic analysis[2] and liquid chromatography. Because some of these methods are limited by complex instrumentation, potentially expensive and troublesome operation, ion-selective electrode (ISE) is the most commonly used method currently. However, interference from foreign ions in the sample hinder the specificity of ISE.

It is well known that the antimycotic activity of amphotericin B (AmB) depends on its ability to form ion channels that cause membrane leakage[3]. In this paper, artificial ion channels were formed from AmB and Ca^{2+} in hybrid bilayer membranes (HBMs), and were characterized by atomic force microscope (AFM) and UV spectroscopy. The biomimetic membrane and transmembrane ion transport of channels were studied by means of electrochemical measurement, including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and amperometric i-t curve, for designing ion sensor with highly specificity. Results showed that the AmB induced voltage-dependent K ion channels across HBMs, and the conductance of channels can be enlarged by decreasing AmB concentration to a certain extent. The channel currents were inhibited in the presence of tetraethylammonium (TEA), a potassium channel blocker. The ion channels-containing biomimetic membrane showed highly selectivity and sensitivity toward potassium ion over other cations and anions. From a simple amperometric i-t curve analysis, we were able to determine potassium ion concentration in a wide range of 3.5×10^{-6} mol/L to 1.5×10^{-2} mol/L in a 50 mmol/L Tris-HCl buffer solution with a pH 7.2 at the detection potential of -0.2V. The detection limit was 4.8×10^{-7} mol/L, and the RSD was 2.4%. This K ion channel sensor was applied to the detection of potassium level in serum and drinking water. Experimental results showed an useful methods feasible for the simple and selective detection of potassium ion in clinical, environmental and industrial samples.

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Graphene-DNA hybrids: novel electrochemical sensor

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Graphene, which was available for experimental studies in 2004, is bringing new epoch for the development of many fields such as electronics, optics and composites. Due to its unique electrical property, high surface area and high-activity surface, graphene is also considered as candidate for sensors. Several reports have shown that graphene and graphene-based materials can exhibit extremely low detection limits for a variety of gases and vapors, meanwhile graphene has been used as a biosensor for the detection of DNA and other biomolecules[1]. Our group has made great efforts on large-scale production of graphene[2], assembly of graphene-based macro- and micro-structure materials [3, 4] and their applications on electrochemical energy storage[2, 5] and electrochemical detection[6]. Since monolayer graphene is hard to manipulate at the macro-state and graphene-based membrane is a potential material for biosensor, we propose a convenient method to prepare ordered graphene oxide membrane at the liquid-air interface, and have extended this method for graphene-composite membrane and the assembly of conductive graphene membrane using graphene oxide as sticking component and template. Preliminary results show that all these graphene-based membranes are candidate materials for sensors and have good electrochemical detection performance. In this talk, we will report the latest advances in our group on electrochemical sensing based on graphene and lay the emphasis on the graphene-DNA hybrid. As we reported previously [6], graphene can combine with single-stranded DNA by a self-assembly process under strong ultrasonication. Graphene-DNA membrane modified electrode reveals enhanced electron transfer on the electrode surface compared to the unmodified electrode, and demonstrates good sensing performance towards hydrogen peroxide and other species, which is characterized by large detection range, rapid response and high sensitivity.

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Nanosheet-Based Titania Microspheres with Hollow Core-Shell Structure Encapsulating Horseradish Peroxidase for the Fabrication of a Mediator-Free Biosensor

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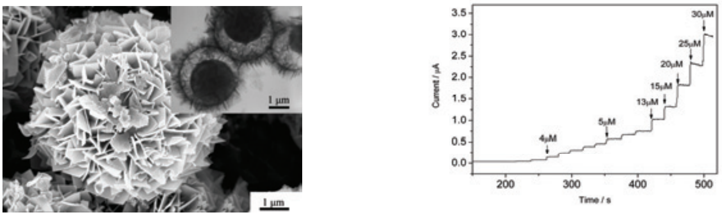
Hollow spheres with complex core-shell structure have attracted increasing interest as a result of their superior properties, such as lower density, high specific surface area, delivering ability and surface permeability [1-3]. The present study was designed to synthesize the nanosheet-based titania (TiO_2) microspheres with hollow core-shell structure and investigate immobilization of horseradish peroxidase (HRP) on the spheres. The morphology and structure of TiO_2 microsphere are characterized by X-ray diffraction, scanning electron microscopy and transmission electronic microscopy. Spectroscopic and electrochemical researches reveal the TiO_2 microsphere is a biocompatible immobilization matrix for enzymes with good enzymatic stability and bioactivity. Due to the nanosheet-based hollow core-shell structure of TiO_2 microsphere, the direct electron transfer of HRP is facilitated and the prepared biosensor displays good performance for the detection of H_2O_2, with lower detection limit of 0.05 μM in the wider linear range of 0.4 to 140 μM, fast response and excellent long-term stability. The nanosheet-based TiO_2 microsphere with hollow core-shell structure could be used efficiently for the entrapment of other redox-active proteins and may find wide potential applications in biosensors, bioelectronics, biocatalysis and biomedical devices.



(a) (b)

Fig. 1 (a) SEM and TEM (insert) images of the nanosheet-based TiO_2 microsphere with hollow core-shell structure. (b) Current–time curves of the HRP–TiO_2–Nafion/GC electrode for successive addition of H_2O_2 in a stirred pH 7.5 phosphate buffer solution.

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Modification of Solid-state Cu_2O-doped RuO_2–based Sensors Aiming Improvement of Their Antifouling Resistance

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Doping of nanostructured sensing electrode (SE) by another nano-oxide has been shown to be an effective method of achieving improvement in both physical properties and electrochemical response of the SE. Specifically, solid-state sensors using 5, 10, 15 and 20 mol % Cu_2O-doped RuO_2-SEs were fabricated and tested in the real sewerage (South-Eastern Water Treatment Plant, Carrum, Australia) for 3 months in order to explore their antifouling capabilities. It was found that 10 mol % Cu_2O-doped RuO_2-SE provides the highest DO sensitivity at various temperatures with the sensitivity slope of -46 mV/decade. Moreover, selectivity measurements revealed that the presence of such dissolved ions as PO_4^{3-}, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Li^+, NO^{3-}, F^-, Na^+, K^+ and Cl^- in the test solution had no significant effect on the sensor's *emf.* Improvement in the sensing characteristics and selectivity was attributed to the enhancement of the SE structure and to the optimization of electrochemical catalytic activity of the oxide-SE/measuring solution interface. Cu_2O-doping of the RuO_2-SE not only extended sensing characteristics of the device, but also improved its antifouling resistance. Although both 10 and 20 mol % Cu_2O–doped RuO_2-SEs have similar morphology and micro-structure, further analysis of the areas affected by bio-fouling during the field trial confirmed that the SE containing 20 mol % Cu_2O was less affected by bio-fouling development compare to the SE with 10 mol % Cu_2O-doped RuO_2 (Fig. 1).

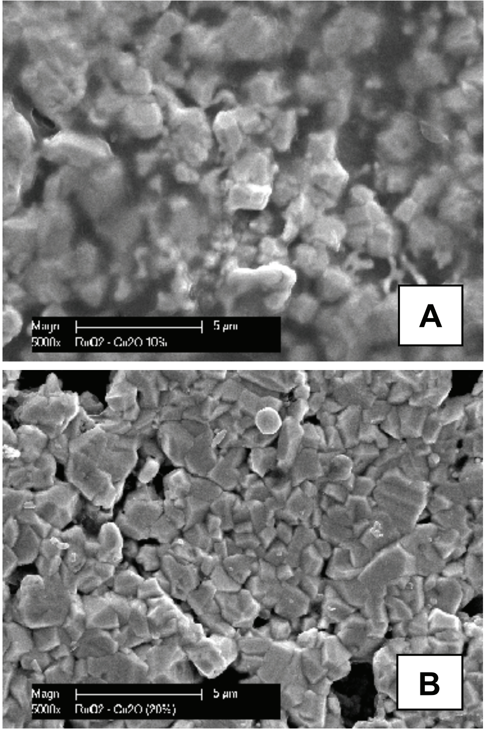

Fig. 1 SEM image of 10 mol % Cu_2O-doped RuO_2-SE with heavy deposits of bio-fouling (A); SEM image at the same scale of 20 mol % Cu_2O-doped RuO_2-SE with no apparent bio-fouling on the SE grain boundaries (B).

Poster Presentations

P-001

Enzymatic activity of glucose oxidase covalently wired potassium ferricianyde to electrically conductive polypyrrole films

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The surface functionalization of an electrically conductive polypyrrole film (PPY) with potassium ferricyanide for the covalent immobilization of glucose oxidase (GOD) has been carried out. The ferricyanide was introduced directly in the pyrrole polymerization solution. It then served as an anchor via its cyanide groups for the covalent immobilization of GOD. The results were compared with those obtained in similar conditions without ferricyanide. The surface composition was characterized by X-ray photoelectron spectroscopy (XPS). The activity of the immobilized GOD was compared with that of free GOD and the kinetic effects were also obtained.
The cyclic voltammetric (CV) response of the GOD-functionalized PPY substrates was studied in a phosphate buffer solution under an argon atmosphere. The CV results support the mechanism in which ferricyanide acts as mediator to transfer electron between the electrode and enzyme, and hence regenerating the enzyme in the enzymatic reaction with glucose. High sensitivity and linear response of the enzyme electrode was observed.

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Acknowledgements: The financial support of this research, received from POSDRU/88/1.5/S/60203 COMPETE and CNMP 71-067 REMORESE projects, is gratefully acknowledged.

P-002

Determination of nimesulide in pharmaceutical products using square wave voltametry and flow injection analysis

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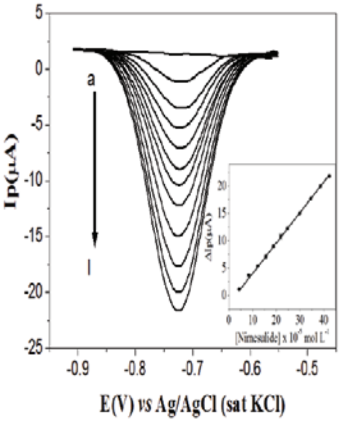
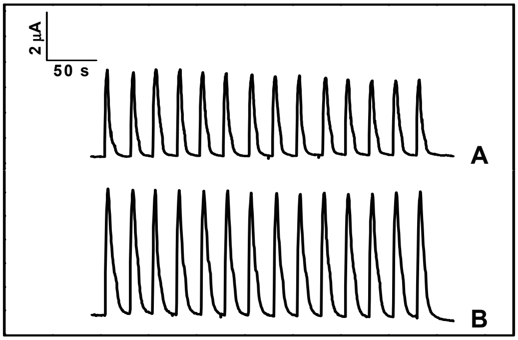
Nimesulide (N-(4-nitro-2-phenoxyphenyl)-methane-sulphonamide) - a methanesulphonic acid anilide derivative - is a relatively new non-steroidal anti-inflammatory drug with analgesic and antipyretic properties that does not induce gastrointestinal ulceration. This compound is administrated in the treatment of chronic rheumatoid arthritis or osteoarthritis, inflammation of genitourinary system, otorhinolaryngological diseases, odontostomatological practice and in postoperative pain. It is almost completely transformed to 4-hydroxynimesulide in both forms, free and conjugated and this metabolite appears to contribute to the anti-inflammatory activity of the compound. The determination of nimesulide in pharmaceutical formulations and other samples has been carried out mainly by high-performance liquid chromatography and determinations utilizing voltammetric methods are relatively scarce. In this communication, we describe the development and validation of a procedure for the direct determination of nimesulide in pharmaceutical products by reductive square wave voltammetry (SWV) without pre-treatment of sample. Alternatively the oxidation of nimesulide was investigated on pyrolitic graphite electrode, a substrate on which intense fouling occurs. During this study, it was verified that the use of pulses to clean the electrode was an effective strategy to solve this problem. Main results are shown bellow.

SWV of nimesulide



FIA measurements



Left side: SWV of (a) supporting electrolyte (NaOH = 1.0 mol L^{-1}); (b) 4.35 x 10^{-5}; (c) 8.37 x 10^{-5}; (d) 1.21 x 10^{-4}; (e) 1.56 x10^{-4}; (f) 1.88 x10^{-4}; (g) 2.19 x10^{-4}; (h) 2.47 x10^{-4}; (i) 2.99 x10^{-4}; (j) 3.45 x 10^{-4}; (k) 3.86 x 10^{-4}; (l) 4.24 x 10^{-4} mol L^{-1}. Right: Amperometric signals for oxidation of 5 x 10^{-5} mol L^{-1} nimesulide on a pyrolitic graphite electrode: (A) using a constant potential, fixed at 1.3 V. (B) Amperometry with multiple pulse (E_1 = 1.3 V for 100 ms; E_2 = 1.6 V for 150 ms; E_3 = 0.2 V for 150 ms). Carrier solution: H_2SO_4 = 0.1 mol L^{-1}. Flow rate: 2.0 mL min^{-1}; volume injected: 75 μL.

P-003

Characterization of Glucose Oxidase and Glycerol-containing Microcapsule Immobilized Electrode

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An enzyme-immobilized electrode is normally stored with buffer solution in a refrigerator prior to use. Long storage stability is expected to improve if the enzyme-immobilized electrode can be stored in a freezer with an antifreeze agent. Recently, we investigated electrochemical responses of a glucose oxidase (GOx)-containing microcapsule immobilized electrode [1].
In the present work, we newly prepared a GOx and glycerol-containing microcapsule and investigated electrochemical response of the microcapsule-immobilized electrode. Microcapsules containing GOx, glycerol and phosphate buffer solution were prepared by interfacial polymerization method. The microcapsules were subsequently immobilized on the surface of a screen-printed carbon electrode with the mediator (tetrathiafulvalene) by nitrocellulose film. The microcapsule-immobilized electrodes were stored in a freezer and thawed in a refrigerator for 2 hours before the measurement.
Fig. 1 shows the cyclic voltammograms of the microcapsule-immobilized electrode perfomed in the 67 mmol dm^{-3} phosphate buffer solution with and without glucose. The glucose concentrations are 0 mmol dm^{-3} (dashed line) and 35 mmol dm^{-3}(solid line), respectively. In 35 mmol dm^{-3} glucose solution, the oxidation current increased between 0.1 V and 0.4V, and the redox peak was not observed, which was observed in the absence of glucose. Fig. 2 shows amperometric response of the microcapsule-immobilized electrode to glucose. As can be seen in the figure, the oxidation current increased in response to the injection of glucose. These results proved that the GOx in the microcapsule retained the enzymatic activity and showed the catalytic oxidation reaction with mediator and electrode.

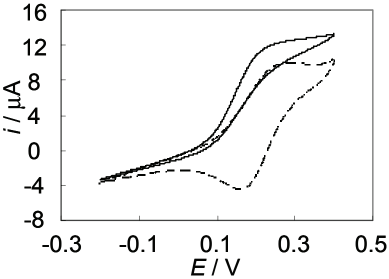

Fig.1 Cyclic voltammograms of the microcapsule-immobilized electrode in the absence of glucose (solid line) and in 35 mM glucose (dashed line)

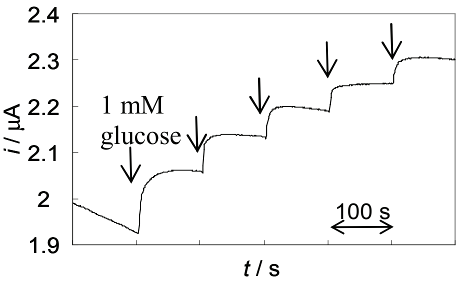

Fig.2 Amperometric response of the microcapsule-immobilized electrode to glucose

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P-004

Voltammetric determination of hair dye in wastewater by multiwalled carbon nanotubes modified electrode

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The usage of hair colors has increased dramatically worldwide and it is a very important segment in the industrial hair dyes. A great concern has been addressed to the use of hair dyes, since the principal ingredients of synthetic hair dye are aromatic amines or they can generate it after oxidation/reduction processes, which consequent mutagenic and carcinogenic properties. Consequently, development of reliable analytical methods for checking the prescribed level of marker compounds in commercial hair dyes or in surface water containing residues due inadequate treatment of effluents have become utmost important. The present work describes the development of a voltammetric sensor for determination of hair dyes in wastewater using a glassy carbon electrode modified with multiwalled carbon nanotubes (MWCNT). Voltammetric measurements were performed with an AUTOLAB PGSTAT 30 potentiostat connected to a microcomputer controlled by software GPES 4.9 for data acquisition. A three electrode system (EG&G PARC) consisting of an SCE as reference electrode, a platinum wire as auxiliary electrode and a modified glassy carbon electrode as working electrode were used. The electrode was coated by dispersion of 5 μL of solution containing 1 mg mL^{-1} MWCNT in dimethylformamide (DMF), added to the surface glassy carbon electrode pre-cleaned with dry alumina. The electrode was dried at 55°C for 20 min and kept at room temperature for 24 h.. Cyclic voltammograms obtained for oxidation of $1x10^{-4}$ mol L^{-1} of Basic Brown 16 dye in BR buffer 0.04 mol L^{-1} pH 7.0 on modified electrode presents a well defined peak at +0.38V higher 10 times in relation to the conventional electrode. A well-defined anodic peak is observed in the anodic scan, with ratio of i_{pa}/i_{pc} equal to 1 and values $\Delta Ep = Epa - Epc = 60$ mV, indicating that the hydroxyl group of the dye is oxidized in a reversible one-electron process. Several experimental parameters were investigated such as different procedures in the modification of the film, influence of pH, scan rate, accumulation time and different forms of loading the dye into the film. After optimization of the best experimental conditions it was possible to construct calibration curves of the Basic Brown 16 dye determination using square wave voltammetry from 500 to 0.01 μmol L^{-1}, following the equation: I_{pa} (μA) = $1.63x10^{-7} + 0.682$ C (C = μmol L^{-1}) correlation coefficient of 0.997 for n = 9. The limit of detection [3 x (standard deviation of blank) / sensitivity] was 2.94 x 10^{-7} mol $L^{-1.}$ The method was successful applied to the determination of Basic Brown 16 dye in wastewater samples.

P-005

Bioelectrocatalysis on optimized electrodes

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Biosensors commonly use enzymes such as dehydrogenase or oxidoreductase as key elements for substrate detection [1]. The immobilization of these biomolecules, the efficiency of electron transport and the substrate diffusion to the sensor working electrode are major challenges that can be addressed by an appropriate design of the electrode surface.

To solve partially these problems we propose in the present work macroporous gold working electrodes [2] which have their inside coated with an ultra-thin layer of mesoporous silica that serves as a matrix for encapsulating biomolecules. The bio-silica layer is obtained using a sol-gel technique [3] where the polycondensation step is triggered by electrogeneration of local pH changes. The thickness, the roughness and permeability of the film have been investigated as well as the homogeneity of the coating and the interconnection between the pores in the presence of the silica layer [3]. In order to further increase the charge transfer from the gold electrode via a mediator, the co-factor and the redox-active enzyme to the substrate or analyte, the conductivity of the hybrid layer has been improved by incorporating gold nanoparticles (AuNP) in the silica layer. The mediator is chemically adsorbed at their surface via a self-assembled monolayer.

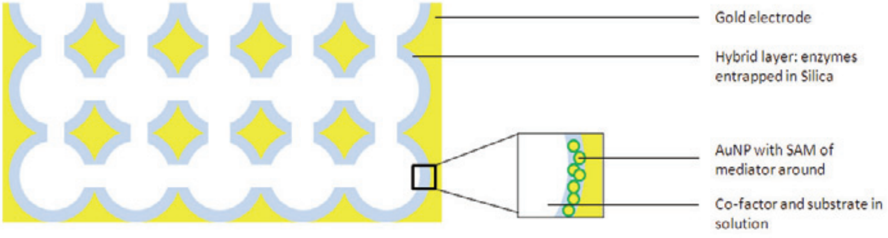

Figure: Scheme of a section of the macroporous gold electrode, the inside of the pores is coated with a silica/enzyme hybrid layer containing Au NP with mediator adsorbed at their surface.

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P-006

Multi-Walled Carbon Nanotube / Poly(Nile Blue) Modified Glassy Carbon Electrode as Ascorbic Acid Sensor

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Carbon nanotubes (CNT), single-walled (SWCNT) and multi-walled (MWCNT), have been recently used extensively due to important properties such as high electrical conductivity and high surface area. They also show good chemical stability to biomolecules, and thus have been used in electrochemical sensors and biosensors [1,2].

Nile blue (NB) is one of the well-known electroactive phenoxazine dyes. Poly(Nile blue) (PNB) has been used as a redox mediator to prepare sensors and biosensors for the oxidation of some important biomolecules such as NADH and NADPH [3].

Multiwalled carbon nanotubes and poly(Nile blue) modified GC electrodes have been prepared. After MWCNT was dispersed with N,N-dimethyl formamide (DMF), coating of GC electrodes was done by using three different loadings of MWCNT in DMF: 20 μL of 0.2%, 10 μL of 1.0%, and 20 μL of 1.0%.

Polymerisation of Nile blue A was performed either directly on the surface of GC electrodes beneath a MWCNT layer (PNB/MWCNT) or on the top of a MWCNT coating (MWCNT/PNB). Polymerisation was carried out in 0.1 M phosphate buffer solution (PBS) at pH 6.0 containing 0.5 mM NB, using potential cycling in the potential region from -0.6 V to +1.2 V. The number of cycles for electropolymerisation was 17 for PNB/MWCNT and 5 for the MWCNT/PNB modified electrode - thicker PNB films led to unstable modification for the MWCNT/PNB electrode.

Characterization of the modified electrodes was carried out by cyclic voltammetry (CV) mainly in 0.1 M PBS at pH 5.3, since best results were obtained in this buffer [4].

The MWCNT, PNB/MWCNT, and MWCNT/PNB modified electrodes were used for the electrochemical determination of ascorbic acid by using CV and fixed-potential amperometry in 0.1 M PBS at pH 5.3. The results were compared for all MWCNT/DMF loadings. The best results were obtained for PNB/MWCNT electrodes prepared using 17 polymerisation cycles of PNB and 20 μL of 0.2% MWCNT/DMF dispersion. The linear range was up to 50 μM and up to 10 μM for CV and amperometry, with limits of detection (LOD) of 9.2 μM and 1.6 μM, respectively.

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P-007

Electron transfer rate constant for Bilayer Lipid Membranes modified with Ubiquinone-10 and α-tocopherol

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Ubiquinone-10 is an integral component of the respiratory chain that mediates electron transfer in the inner mitochondrial membrane. α-tocopherol protects cell membranes from oxidation by reacting with lipid radicals produced in the lipid peroxidation chain reaction. The reduced form of ubiquinone can react with the oxidized α-tocopherol reactivating its capabilities.

A study of the charge transfer across tethered bilayer lipid membranes and across bilayer lipid membranes between two aqueous solutions was carried out using cyclic voltammetry and electrochemical impedance spectroscopy, using $K_3Fe(CN)_6$ and $Ru(NH_3)_6Cl_3$ are probe molecules.

The bilayers were then modified with ubiquinone-10, α-tocopherol and a mixture of both. The electron transfer rates constant were determined and a comparison was made for the modified and unmodified bilayers. The interaction between ubiquinone and α-tocopherol was analyzed.

P-008

Metal and Nanoparticle Modification of Screen Printed Electrode Sensors for Amino Acid Determination

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Amino acids are often added to food samples during their preparation in order to correct for possible dietary deficiencies [1]. So, nowadays the determination of amino acids is important, because of the burgeoning interest and concern with the food that is consumed. Over the past decade, numerous procedures involving high-performance liquid chromatography HPLC have been successfully developed and implemented for the determination of amino acids, but in recent years a detection methodology that does not require derivatization is preferred, when available, for convenience and simplicity.

One of the possibilities for the rapid determination of amino acids is using electrochemical methods. Since amino acids have at least two active functional groups (depending on pH): $-NH_2$ and $-COOH$, they have the ability to complex some transition metals (e.g. nicke1 [2] and copper [3]). One of the easiest metal ions to complex is the Cu(II) ion, which can form different complexes depending on the pH, besides complexing with ligand (amino acid), as well as with H^+, in acidic solution, or OH^-, in alkaline solution, at the same time [4].

The aim of this work was to study and optimize different metal and nanoparticle modified electrodes in a variety of media as potential sensors for the electrochemical detection of the amino acids tryptophan and tyrosine, in the presence and in the absence of copper.

Screen-printed electrodes (SPE), being one of the most interesting alternatives in the design of electrochemical sensors, reported as sensors for biomedical, environmental and industrial analysis, were used in this work as the substrate for different modifications (copper, carbon nanotubes, carbon black and gold) in order to improve amino acid determination. The results of these studies will be reported.

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P-009

The Carbon-Ceramic Nanoparticulate Electrode for Dopamine Sensing

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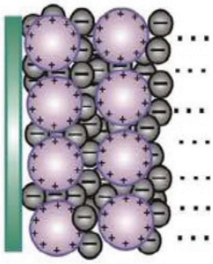
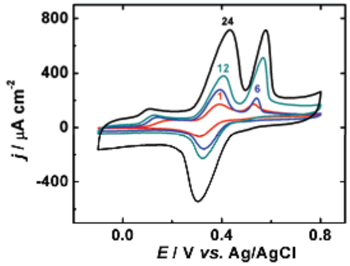
Many people of the world have a various neurological afflictions arising by abnormal dopamine concentration or transmission into the intercellular fluids, for example schizophrenia or Parkinson's disease [1]. The fast and simple determination of dopamine deviation is most important for treatment these sick people. Electrochemical detection is simple, cheap and increasingly popular [2].

The layer-by-layer technique has been frequently used for electrode modification [3]. Usually film is formed by sequential deposition of polyanions and polycations or these polymers and nanoparticles [4]. Such electrodes were earlier applied to neurotransmitters detection [5]. Multilayers formed by electrostatic interaction between different particles only are almost ignored as electrode materials. Following earlier proposition [6] we designed nanoparticulate film electrode from phenyl sulfonate functionalized carbon nanoparticles and tetraalkylammonium functionalized porous silicate submicroparticles. The latters were obtained using modified Stober method [7].



The electrodes were prepared by 1 to 24 immersion and withdrawal steps and examined by SEM, AFM cyclic voltammetry and different pulse voltammetry. The electrodes exhibits well defined voltammetry of dopamine separated from signal corresponding to oxidation of ascorbic and uric acid (see voltammogram).The peak current is proportional to the number of immersion and withdrawal steps. This signal is also not disturbed by presence of NADH, citric acid and tryptophan. The detection limit was calculated as 0.1 µM. The electrodes operate in pH 4.5 - 8.



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P-010

Dopamine imprinted polymers: a comparative study between polymethacrylate and polypyrrole sensing layers

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Molecularly imprinted polymers (MIPs) have attracted a great deal of interest over the recent 5 years given their ability to recognize specifically and selectively molecules, proteins and even microorganisms. These sensing materials can be prepared as powders, colloids and thin films. The latter option is particularly interesting because it limits diffusion of the analytes to the artificial recptor sites within the sensing layers.

When grafted as thin films on substrates, MIPs are amenable to the detection of the analytes by e;g. surface plasmon resonance (SPR) or by electrochemistry. The second option is simple, versatile, easy to implement and has the advantage to detect analytes concentrations in the picomole range.

In this context, this paper aims at comparing two completely different approaches for the preparation of MIP grafts: (i) by radical polymerization using diazonium-derived initiators grafted on the electrode surface; (ii) by electropolymerization of pyrrole. Both methods are conducted in the presence of the template dopamine molecule.

In method (i), one can take advantage of the vast choice of functional and crosslinking monomers and their initial ratios to trap the template and form the MIPs. The performances of the sensor can be optimized by the solvent nature, working temperature and the polymerization initiating system. Although polymethacrylates are insulating, it is possible to reduce the thickness of the MIPs in order to be able to electrochemically detect the template. Method (ii) is simpler because it neither requests an initiator, nor a crosslinker due to the rigidity of polypyrrole and its well known partial crosslinked structure. However, in the case of dopamine imprinting, it is necessary to coat first a pristine polypyrrole thin layer prior to electropolymerization of pyrrole in the presence of dopamine; this will prevent oxidation of dopamine before the onset of pyrrole electrooxidation.

Nevertheless, either electropolymerization or radical polymerization permit to detect dopamine at concentrations lower than 1 nanomole provided that square wave voltammetry is used for the detection of dopamine after rebinding by the MIP grafts.

The two approaches for the MIP-based sensors will be described and compared.

P-011

Direct electrochemical detection of NADH for quantification of oestrogen

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Candida albicans and some other yeast species are known to have an oestrogen binding protein (EBP), which oxidises NAD(P)H to NAD(P)$^+$ (Feldman et al., 1982, Restrepo et al., 1984, Skowronski and Feldman,1989). When oestrogen is present, it binds to an NAD(P)H oxidation site and leads to an increase in the concentration of NAD(P)H (Madani et al., 1994). Our previous research has shown that oestrogen can be quantified by measuring NAD(P)H using double mediator electrochemical system using whole cells as the detection element (Baronian and Gurazada 2007). A single hydrophilic mediator was used to quantify 17*β*-oestradiol using cell lysate in a modification to the whole cell method which reduced the incubation time, expanded the response curve and avoided catabolic responses to sample molecules. We have used modified electrodes to directly detect NAD(P)H in cell lysate to further simplify the assay. The modified electrodes oxidised NAD(P)H at lower potentials to avoid interference by oxidants such as ascorbic acid. We also purified EBP using 17*β*-oestradiol affinity chromatography and provided it with NADH. In these experiments we can differentiate 'with' and 'without oestrogen' samples.

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P-012

Carbon Nanotube-Graphene Nanosheet Hybrid Films for Highly Sensitive Electrochemical Sensing of Biomolecules

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Sensitive measurement of biomolecules is a critical need both for modern biochemical and biomedical research and in the practical applications of clinical diagnostics and treatment. Electrochemical sensors and biosensors have been widely used for this purpose. Carbon-based nanomaterials, such as carbon nanotubes (CNTs) and graphene have been shown to be ideal for electrochemical sensing applications since they are conductive, biocompatible, easily functionalized, and possess very large surface areas [1-3]. However, to our knowledge, combing the CNTs and graphene and applying their hybrid or composite in the electrochemical sensing has been not yet reported.

In the present work, the single-walled carbon nanotube (SWCNT)-graphene nanosheet (GNS) hybrid film was prepared and characterized by scanning electron microscopy (SEM). Electrochemical behaviors of $K_3[Fe(CN)_6]$ and six kinds of important electroactive biomolecules were studied at the SWCNT-GNS modified glassy carbon electrode (SWCNT-GNS/GC electrode). Remarkably enhancing electrochemical responses toward seven probe molecules were observed at the SWCNT-GNS/GC electrode relative to that at only SWCNT/GC or GNS/GC electrode, which was attributed to the synergetic effects between SWCNTs and GNSs. The sensing performance of the SWCNT-GNS/GC electrode towards dopamine (DA) and acetaminophen (APAP) was investigated. The current response of the oxidation (i_{pa}) process was directly proportional to the analyte concentration within 0.1-65.5 μM and 0.05-64.5 μM for DA and APAP, respectively, and the detection limits were 16 nM and 38 nM for DA and APAP, respectively, which are more sensitive than those of previously reported those based on only CNTs or graphene modified electrodes. The results clearly demonstrated that highly sensitive detection was obtained at the SWCNT-GNS/GC electrode. These indicate that the SWCNT-GNS hybrid film may be a better choice for constructing electrochemical sensing of some biomolecules.

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P-013

Producing a biocomposite film using laccase and botryosphaeran layer-by-layer for dopamine bio-sensing

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Currently, there is much interest in designing functional membranes for bio-sensing applications because of their possible use in clinical analysis . The use of enzyme electrodes is an inherently sensitive method for the detection of their substrates. Films incorporating a polyphenol oxidase laccase and the exopolysaccharide botryosphaeran were developed through a layer-by-layer assembly by alternate adsorption with oppositely charged polycations. Laccase and botryosphaeran were isolated from extracelular culture fluids (ECF) where the ascomyceteous fungus *Botryosphaeria rhodina* MAMB-05 was grown under specific and optimal fermentation conditions previously determined. The deposition of five tetralayers onto FTO (fluorine-doped tin oxide)-coated glass plates was followed by cyclic voltammetry profile showing that the current density peak increased gradually with the concomitant addition of each layer, and demonstrated a uniform deposition. These biocomposites retained enzymatic catalytic activity which was proportional to the number of coated enzyme layers. The system was in favor of the substrate accessibility to laccase active site, thus the affinity to substrate was improved greatly to 2,2′-azino-bis-(3-ethylbenzthiazoline-6-sulfonic acid) diammonium salt (ABTS). The major advantages of this biosensor can be for detecting different substrates (ABTS, catechol, and O_2), possessing high affinity and sensitivity, durable long-term stability, and facile preparation procedure. The electrodes were tested for dopamine detection. When they were immersed in an air-saturated 0.1 M KCl (pH 5.5) solution containing ABTS and dopamine, the current peak for laccase oxidation increased. Varying the dopamine concentration the current peaks augment linearly for electrodes with laccase and the polyssacaride. The sensitivity found for this electrode was 0.67 mA cm^2 mol^{-1} L. Based on this work, protein films can be used to electrochemically stabilized the enzyme, that catalyze the reduction of various substrates of biological or environmental significance, suggesting that the films have a promising potential in fabricating biosensors or bioreactors.

P-014

New Biosensors: The Use of Gelatin as a Matrix for the Immobilization of Horse Heart Cytochrome *c*

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Protein film formation by cross-linking and the incorporation of enzymes in hydrogels, adsorbed to electrode surfaces, are new and innovating aspects in the field of bioelectrochemistry. Both offer new perspectives in the development of stable biosensors. In this work we will address the second route. Different types of gelatin, modified or thiolated, have been selected as a possible hydrogel for the encapsulation of proteins or enzymes. Gelatin is a water soluble protein, composed of a variety of amino acids [1]. Through amide bonds it forms a linear polymer with a molecular weight between 15000 and 250000 Da [2]. This hydrophilic polymer network is able to swell in water by absorbing a large amount of water (one tenth to one thousand times their dry weight). Due to the hydrophilic groups or domains, the hydration and native configuration of the encapsulated biomolecules is ensured. Because of the high degree of swelling in water, hydrogels possess other desired characteristics: rapid diffusion of the substrate of the enzyme and the formed reaction product, often an increased enzyme stability and an increased mobility of the counter ions, which is important for fast charge transfer reactions. Horse heart cytochrome *c* has been chosen as a redox protein as it has often been considered as a model system for biological electron transfer [3] and for bioelectrocatalysis [4]. The redox protein was incorporated in different types of gelatin and then immobilized on a gold surface. A full electrochemical characterization of the modified electrode has been performed. Promising prospectives for the development of a new type of biosensor are revealed.

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P-015

Mesoporous Conducting Polymers for Enzymatic Electron Transfer-based Applications

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In the course of the last years the interest of the researchers were addressed towards the development and characterization of enzymatic devices based on electron transfer, mainly biosensors and biofuel cells.

The main problems affecting the development of such electrochemical devices is (i) for biosensors the interference of electroactive species eventually present in the sample under investigation and (ii) for biofuel cells the poor current density generally achievable. To solve this problems several approaches have been followed: in this respect a paramount issue is represented by the efficiency of communication between the electrodic materials and the redox proteins employed in the biodevices to assure an optimal electron transfer. Usually, the choice of proteins is made taking into account their peculiar characteristics, particularly their capacity to exchange the charge with redox mediators (mediated electron transfer (MET)) as well as with the electrode surface (direct electron transfer (DET).

Although the employment of direct electron transfer (DET) displays the most interesting features to this end, it is limited to only those few enzymes whose redox centre is readily accessible. Moreover, since DET can be exploited only after a proper immobilization procedure, a lot of research efforts are focused on the modification of electrodic surfaces with nanostructured polymers able to supply a suitable environment for entrapment of enzymes maintaining its catalytic properties and, at the same time, allowing a good accessibility to the target analyte, redox mediators and an efficient communication with the electrode surface.

In this research we studied the performances of innovative nanostructured mesoporous layers of some conducting polymers such as polypyrrole (PPy) and polyaniline (PANI) obtained by electropolymerization of the corresponding monomers around polystyrene nanoparticles taken as template.

The obtained modified electrodes display not only an enhanced electrochemically active surface thus ensuring higher enzyme loading but also interesting electron transfer properties towards some typical redox enzymes for biosensors and biofuels cells construction.

P-016

Development of the 4-Channel Biosensor for Determination of Carboxylic Acids in Wine

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Wine is a comlex fluid in which the carboxylic acids play important role. Mainly, tartaric, malic and lactic acids influence acidity and tartness of wine. The carboxylic acids level depends on the area of grape´s growth, climatic conditions and effectivity of the fermentation process.

The four-channel flow-through amperometric biosensor developed in our laboratory was used for determination of carboxylic acids. This biosensor was designed as a two electrode configuration consisting of four platinum working electrodes and Ag/AgCl as a common reference electrode. The Pt electrodes were first coated with the copolymer formed from the mixture of *o*-phenylenediamine and resorcinol. Thus formed protecting layer eliminated electroactive interferences as ascorbic acid and phenolic compounds. The four different upper biocatalytic layers contained: 1) sarcosine oxidase, 2) the mixture of sarcosine oxidase and fumarase, 3) lactate oxidase, and 4) bovine serum albumin; the layers were prepared by cross-linking with glutaraldehyde. In all cases, hydrogen peroxide generated by oxidases was monitored at 600 mV vs. Ag/AgCl. The principle of the detection was based on the inhibition of sarcosine oxidase by carboxylic acids except lactic and tartaric acids. Lactic acid was followed by lactate oxidase. For the determination of tartaric acid, a novel system was proposed: transformation of tartaric acid using fumarase resulting in a metabolite inhibiting sarcosine oxidase. The level of tartaric acid was calculated as a difference between signals from channels 1 and 2. The developed system was used for analysis of real wine samples and the obtained data were compared with capillary electrophoresis analysis.

This project was supported by the Ministry of Education, Youth and Sports of Czech Republic, Programme NPV II no. 2B08035.

P-017

Carbon Film-Carbon Nanotube Modified Electrode Sensors for Epinephrine

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Epinephrine is an important neurotransmitter of catecholamines, which is synthesised in the adrenal medulla and sympathetic nerve terminals and influences metabolic processes, especially carbohydrate metabolism [1]. Among the various methods used for the detection of catecholamines, electrochemical sensors offer the advantages of rapidity, low cost, high sensitivity, and low detection limit.

Carbon nanotubes (CNTs) represent promising modifier structures with the ability to promote electron transfer reaction of many compounds by increasing their reaction rates and/or decrease the overpotential [2]. CNTs immobilised into a chitosan matrix using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide together with N-hydroxysuccinimide (EDC-NHS) were recently used for the determination of hydrogen peroxide [3], glucose [4] and dipyrone [5].

Novel electrodes have been prepared and explored as potential sensing systems for epinephrine's electrochemical determination. This was achieved by modifying carbon film electrodes (CFE) with functionalised multi-walled carbon nanotubes using the chitosan immobilization method described above. The resulting electrode was successfully used for the detection of epinephrine by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and fixed potential amperometry (Amp), after identification of the potential for oxidation by cyclic voltammetry in different pH electrolytes. From the techniques investigated, the highest response was obtained by DPV using preconcentration, permitting a rapid determination with the lowest detection limit and the least positive potential for epinephrine oxidation, without any influence from ascorbic acid. The sensor was applied to the analysis of epinephrine injection solutions.

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P-018

PEDOT-modified voltammetric microsensor for the simultaneous assay of ascorbic and uric acids in blood serum

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The assay of ascorbic (AA) and uric (UA) acids has been the subject of tremendous interest for many years. Despite their electrochemical properties, the detection of both species on unmodified electrode surface is hazardous because of the overpotential required. In order to increase the sensitivity and selectivity, many protocols for surface modification have been tested [1]. Our attention has been focused on electrogenerated poly(3,4-ethylenedioxythiophene) (PEDOT) film since this polymer exhibits good electrical conductivity and biocompatibility [2], thus making possible experiments in biological samples.

The voltammetric microsensor was first tested in AA and UA model mixtures [3]. PEDOT electropolymerization parameters (film thickness, monomer concentration, potential range…) were optimized in order to improve the analytical performances and the metrological data (Table 1). Experiments were then carried out in human blood serum and urine by square wave voltammetry (SWV). Measurements were performed directly into the biological samples without preliminary treatment nor dilution. The results compared favorably with those obtained by standardized methods (HPLC and enzymatic methods). It was also verified that the mean biochemical species (dopamine, cysteine, *N*-Acetyl-L-cysteine and xanthine) did not interfere with AA and UA detection. Contrary to bibliographic data [4], the sensitivity for UA increased around 30% when AA was present in the sample. An EC' mechanism of UA regeneration has been highlighted based on both thermodynamic and electrochemical kinetics considerations. This phenomenon has to be taken into account particularly when AA and UA are present in similar concentrations.

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Table 1. Analytical performances of the microsensor in SWV for the assay of AA and UA.

	Detection potential (mV)	Sensitivity (µA.µM^{-1}.cm^{-2})	Detection limit (µM)	Linear range (µM)	repeatability (n =5) (%)
AA	-96	5.75	2.5	5-500	2.8
UA	257	84.90	0.65	0.8-250	3.0

P-019

Characterization of the complex c_1-c_{552} from *Thermus thermophilus*: the protein-protein interaction

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The interaction between proteins is a crucial phenomenon in the biological function of the cell. Signals from the external cell wall are mediated to the inside by protein–protein interactions of signaling molecules.[1] Electron transfer is often accompanied by protein-protein interactions.[2] In this study, we focus on the interaction between two proteins from the respiratory chain of *Thermus thermophilus* : the cytchrome c_{552}, which transfers electrons to the ba_3 oxidase and the cytochrome c_1 one of the constituents of the ubiquinol-cytochrome *c* oxidoreductase [cytochrome bc_1 complex, complex III].

The complex formed between these two proteins has been studied with a combined electrochemical, UV/VIS and FTIR spectroscopic approach with the help of the OTTLE (Optically Transparent Thin-Layer Electrochemical) cell.[3] FTIR difference spectroscopy is a sensitive method to detect the structural changes upon electron transfer and coupled proton transfer and changes occurring in the protein upon complex formation can be described. The midpoint potentials of the proteins have been determined by following the redox dependent changes in the UV/Vis and compared with the values obtained after immobilization of the proteins on gold nanoparticles (AuNPs). The study of individual proteins and the protein complex reveals a modification of the midpoint potentials. These shifts are tentatively attributed to variations on the heme propionate modes, as interpreted on the basis of the FTIR data. Other changes in signals reflecting the reorganization of the hemes, of the polypeptide backbone and amino acid side chains are discussed.

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P-020

A Novel Sensor For Antibiotic Drug Ertapenem Based On Electrochemical Oxidation Using Boron Doped Diamond Electrode

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Ertapenem (ERT) is a member of carbapenem group antibiotics that is structurally related to beta-lactam antibiotics. To the best of our knowledge, no scientific literature regarding the electrochemical behavior and voltammetric determination of ERT has been published. The electrochemical behavior of ertapenem at the surface of a boron-doped diamond electrode (BDDE) is described. ERT exhibits two irreversible anodic responses that are diffusion-controlled at a BDDE. Its responses were obtained in aqueous media over a broad pH range (pH 2–12), as determined by cyclic, linear sweep, differential pulse (DPV) and square wave (SWV) voltammetric techniques BDDE. 0.1 M H_2SO_4, acetate, phosphate and Britton-Robinson buffers were tested as the supporting electrolyte to find the optimal pH value. These responses are irreversible in nature, and diffusion-controlled.

Different parameters were tested to optimize the conditions for the determination of ertapenem. The optimal pH value was 2.0 for Britton-Robinson buffer. A linear voltammetric response for the first peak of ertapenem was obtained in the concentration range of 2.0 to 12 $\mu g.mL^{-1}$ and 1.0 to 12 $\mu g.mL^{-1}$ for DPV and SWV techniques, respectively. For the second peak, the linearity was obtained between the range 2.0 and 12 $\mu g.mL^{-1}$ for both methods.

The developed voltammetric methods were successfully applied to determine the quantity and the content uniformity of ertapenem in pharmaceutical formulations. Preparation of the sample was easy and did not require any previous treatments. Selectivity trials revealed that the oxidation signals of the drug were not disturbed by the presence of excipients or degradation products. The necessary statistical validation reveals that the proposed methods are free from significant systematic errors.

P-021

Pyrolytic Graphite Electrode Modified with Nano-diamonds Decorated with Silver Nanoparticles as an Efficient Sensor for Voltammetric Determination of Thioridazine

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Nowadays, carbon-based nanomaterials have attracted enormous interest due to their excellent electrical, chemical and mechanical properties, which make them suitable for developing nano-electronics and electrochemical sensors [1-3]. Recently, nano-crystalline diamond (also called nanodiamond, ND) as a novel carbon material, because of its special properties such as high surface area, biocompatibility and non- toxicity, can be used in fabrication of electrochemical sensors [4-5].

In this region, metal nanoparticles have attracted much attention too. As a result, interesting class of carbon nanostructures derivatives were formed by deposition of metallic nanoclusters on their surfaces. Furthermore, uniform dispersion of metallic nanoparticles decorated on their surfaces can yield ideal nanocatalysts for application in chemically modified electrodes [6-7].

In this work, nano-diamonds decorated with silver nanoparticles (AgNPs-NDs) was used as an effective and new modifier for electrode surface modification. The decoration of NDs with AgNPs improved colloidal dispersion of the decorated NDs in water, affording uniform and stable thin films for improving the surface properties of the working electrode. The resulting modified electrode was used for sensitive voltammetric determination of Thioridazine (TR). Because of enchantment of surface area peak current for TR increased significantly. The effect of different experimental parameters, such as deposited amount of the modifier suspension, pH, accumulation potential and time, and scan rate on the voltammetric response of TR was investigated using cyclic voltammetry. Under optimal conditions, the modified electrode showed a wide linear response to the concentration of TR in the range of 0.08–10 μM with a detection limit of 10 nM. The proposed method was successfully applied in determination of TR in biological samples with satisfactory results. The modified electrode showed excellent sensitivity, selectivity, long-term stability and remarkable reproducibility.

Keywords: Thioridazine; Nanodiamond; Ag Nanoparticles; Modified Electrode; Cyclic Voltammetry

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P-022

Electrochemical determination of Sumatriptan at a glassy carbon electrode modified with a bilayer of multi walled carbon nanotube and poly-pyrrole doped with new coccine

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The high application potential of conducting polymers (CP) in chemical and biological sensors is one of the main reasons for the intensive investigation and development of these materials [1, 2]. In this work, a promising electrochemical sensor was developed based on a layer by layer process by electropolymerization of pyrrole in the presence of new coccine (used as doping anion) on the surface of the multi-walled carbon nanotube (MWCNT) pre-coated glassy carbon electrode (GCE). The electrochemical behavior of sumatriptan was investigated on the surface of modified electrode using linear sweep voltammetry. Sumatriptan, a triptan drug including a sulfonamide group, is used in human medicine for the treatment of acute migraine episodes (vascular headaches) [3]. The results showed a remarkable increase in the anodic peak current of sumatriptan in comparison to bare GCE. The effect of experimental variables on the electrode response, such as drop size of MWCNT suspension, pH of the supporting electrolyte, accumulation time and the number of cycles in the electropolymerization process was investigated. Under optimal conditions, the modified electrode showed a linear dynamic range of 4.0×10^{-8} – 6.0×10^{-6} M with a detection limit of 2.0×10^{-8} M. The prepared electrode showed high sensitivity, selectivity, stability and good reproducibility in response to sumatriptan. This sensor was successfully applied for the accurate determination of trace amounts of sumatriptan in pharmaceutical preparations.

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P-023

Heparin Determination by Cathodic Stripping Voltammetry Method

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Heparin is an important component of biological fluids in the human and animal organisms. It is an anticoagulant possessing a broad spectrum of action, capable of retarding all phases of the blood coagulation process and reflecting (directly or indirectly) the degree of functional activity of the population of mast cells responsible for heparin production *in vivo* [1, 2]. Monitoring of the heparin content in biological fluids, drugs and other pharmaceutical products is an important problem in modem analytical chemistry.

At present, many methods had been proposed for the determination of heparin, including spectrophotometry [3], fluorometry [4], HPLC [5] and electroanalytical methods [6].

In the work the differential pulse cathodic stripping voltammetry (CSV) is applied for the determination of heparin traces using a hanging mercury drop electrode. The effects of various factors such as: preconcentration potential and time, pulse height, step potential and supporting electrolyte composition are optimized. The linear range, detection limit and repeatability of the method are determined. The proposed method was successfully applied for the determination of heparin in pharmaceutical products. The method was validated by studying the recovery of heparin from the spiked pharmaceutical samples.

Acknowledgements

This work was supported by AGH University of Science and Technology grant (Project No. 11.11.160.799).

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P-024

Electrochemical characterization of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with taurine

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This work shows for the first time a possibility of using conducting polymer (CP) films p-doped with taurine ligand (Tau = $C2H6NO3S^-$) as artificial biological membranes in order to study membrane potential formation mechanism [1].

Taurine is present both animal and human body where it acts as monodentate ligand toward cations [2]. It is engaged in several essential biological processes, including Ca^{2+} transport processes. The results obtained indicate that sensitivity toward calcium and magnesium cations can be induced by soaking polymer films doped with taurine in the solution containing these ions.

The PEDOT-Tau films electropolymerized by Cyclic Voltammetry (CV), after soaking, exhibited close-to-Nernstian response in the open-circuit. To obtain background information, important for in-deep understanding of a dynamic response, the films studied with Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDAX), X-ray Photoelectron Spectroscopy (XPS), Laser Ablation Inductively Coupled Plasma Mass Spectrometry ICP-MS (ICP-MS-LA), Atomic Force Microscopy (AFM) and Electrochemical Impedance Spectroscopy (EIS).

Acknowledgements
Johan Gadolin Scholarships at Process Chemistry Center is gratefully acknowledged for financial support.

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P-025

Biomimetic membranes based on conducting polymer films doped with ATP, ADP and AMP ligands

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Poly(3,4-ethylenedioxythiophene) films (PEDOT films) doped with biologically active ligands: adenosine triphosphate (ATP), adenosine diphoshate (ADP) or adenosine monophosphate (AMP) were deposited from the solution containing 0,1M sodium salt of ATP, ADP or AMP and 0,01M EDOT and sensitized towards calcium or magnesium ions by chemical or electrochemical methods.

It was shown earlier [1], that the conducting polymer films doped with biologically active ligands, e.g. ATP, may be used as a model biological membranes to study the mechanism of membrane potential formation, in particular to study the competitive binding of cations to biologically active ligands and to observe the resulting effect on transient membrane potential during equilibration.

In this work PEDOT films doped with ATP, ADP or AMP were used to study the influence of calcium and magnesium ions on the potential transient of such films and to allow comparison of the responses.

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P-026

Ion Amperometry at Liquid/liquid Interfaces for the Detection of Substances of Interest

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In this research, the interface between two immiscible electrolyte solutions (ITIES) was used as a method for the growth of Human Embrionic kidney 293 cells (HEK cells). The HEK cells were cultured on a liquid-liquid interface formed when aqueous culture media is overlaid onto a nontoxic, hydrophobic substrate. Figure 1 shows that the cells are spread and divided at the interface between the two immiscible phases.

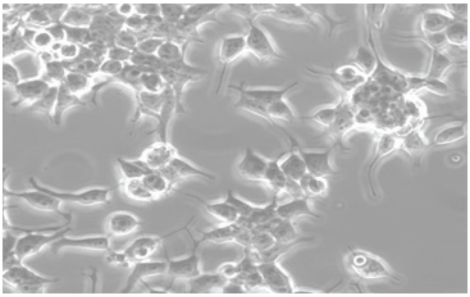

Figure 1 – Phase contrast micrograph of HEK cells at the culture media/Flurocarbon interface after 48h of incubation.

When properly stimulated the cells release potassium, in order to be validate the method used in the detection of the potassium released by the cells a study of potassium facilitated ion transfer was done using a miniaturized ITIES. The potassium detection was made using valinomycin as ionophore in a 1,2 – dichloroethane/ potassium aqueous solution interface.

The detection of two drugs, ephedrine and propranolol, was investigated in order to demonstrate a different practical utility of the system, chiral discrimination. In this case, the liquid-liquid electrochemistry provided a mean for the detection of the transfer of ionized chiral molecules facilitated by a chiral ionophore (lipophilic cyclodextrins).

These results illustrate the opportunities acquired by the use of ion amperometry at liquid-liquid interface as an alternative mean for the detection of various substances of interest.

P-027

Electrochemical Biosensing Based on Nanocomposites

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In recent years, with the combination between analytical chemistry and bioscience, the rapid development of bioanalysis and sensing research, the research and application of bioelectrochemistry and biological sensors have been a focal point in the fields of analytical chemistry. Among them, electrochemical sensors research based on functionalized carbon nanotubes, Au/ Polypyrrole/ Prussian blue nanocomposites and biological self-assembly membrane have aroused wide concern among the people. Therefore, we have constructed a series of electrochemical biological sensing interfaces which have good property , the main contents include following aspects, (1) Preparation and studies of Hydrogen peroxide biological sensors based on sol-gel/MWNTS fixing horseradish peroxidase. (2) Preparation and studies of Hydrogen peroxide biological sensors based on L—Cysteine/SWCNTS fixing horseradish peroxidase. (3) The preparation of modified electrodes based on Au/ Polypyrrole/ Prussian blue nanocomposites and its detection for the Hydrogen peroxide. (4) Epinephrine sensors based on PPY/AuNPs/SWCNT nanocomposites. (5) Physiological buffer sensor based on Prussian blue membrane nanostructures. (6) Detection of double-function sensors for porphyrin based on phosphates self-assembly membrane. (7) Molecular imprinting sensor based on indirect measurement of aspirin.

Thanks for the financial aid of the Natural Science Foundation of China. (nos. 20775060, 20875077, 20927004, 20965007 and 20945003)

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P-028

Development of catechol sensors with polypyrrole synthesized using *Quillaja Saponin*

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Introduction

The developement of catechol sensors is an active area of research[1]. In this investigation, the development of catechol sensors with polypyrrole synthesized using *Quillaja Saponin* is studied using amperometric and impedance studies.

Experimental

The polymerization of pyrrole is carried out at platinum electrodes using the surfactant *Quillaja Saponin*. The cyclic voltammetric, amperometric and impedance measurements were performed using the electrochemical workstation CH660A(CH Instruments, USA). The working electrode was Pt with a diameter of 2mm while the reference electrode was a saturated calomel electrode, Pt wire being the counter electrode in a three-electrode arrangement[2]. In the case of impedance and amperometric experiments for detection of catechol , the working electrode is represented as Pt/Ppy/KCl/Tyr where Tyr denotes *Tyrosinase*

Results and Discussion

Fig 1A provides the typical Nyquit and Bode' plots for the polypyrrole-coated electrodes at a catechol concentration of 24 μM. while Fig 1B depicts the amperometric response of Pt/Ppy/KCl/Tyr electrode in presence of catechol. The linear concentration regime is obtained from nanomolar to micromolar range indicating the specific influence of the surfactant.

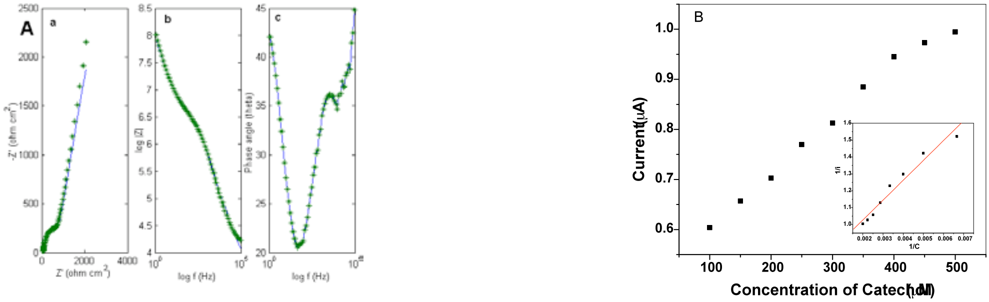

Fig 1. (A) Typical Nyquist (a) and Bode' plots (b) and (c) pertaining to Pt/Ppy/KCl/Tyr at a catechol conentration of 24 μM. The points denote the experimental values while line denotes the fitting of the data using the equivalent circuit.(B)The variation of the steady state chronoamperometric current with concentration of catechol. Inset epicts the Lieweaver-Burk plot.

Summary

The electrochemically synthesized polypyrrole in presence of the surfactant *Quillaja Saponin* is shown to be effective for detection of catechol in the nanomolar to micromolar concentrations.

P-029

Fullerene-Gold Nanoparticle Nanocomposite Electrode for the Development of Laccase-based Biosensors.

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One of the main problems affecting the development of first generation electrochemical biosensors for the analysis of real matrices is the interference of electroactive species eventually present in the sample under investigation. To solve this problem several approaches have been followed: among them, third generation biosensors based on direct electron transfer (DET) display the most interesting features to this end. In this work we present a novel Laccase electrochemical biosensing platform based on the coupling of two different materials (gold nanoparticles and fullerene) displaying interesting electrochemical features. Gold nanoparticles (AuNPs), exhibit interesting electrocatalytic behavior and have been already widely used for sensing applications; on the other hand, fullerenes are a very promising family of electroactive compounds although they have not been fully employed yet in biosensing.

The new type of nanocomposite material described in this research, relies on the ability of fullerene to be functionalized with high efficiency through reactions initiated by a zwitterionic complex: this procedure allow us to insert in the fullerene surface several alkyl thiols able to react with the gold surface of the nanoparticles as well as of the gold electrode used as support. In fact, in a first step the functionalized fullerene was bound on the gold electrode surface, after that the gold nanoparticles were bound onto the fullerene modified electrode. This two steps have been preventively studied onto a gold disk by means of an electrochemical surface plasmon resonance technique.

Finally, Laccase has been immobilized onto the gold nanoparticles surface; the resulting biosensor has been characterized putting in evidence that the synergy on electrocatalytic activity provided by the nanocomposite material, enhances the sensitivity of the biosensor opening interesting perspectives in the realization of electron transfer based biosensors.

P-030

Electrochemistry of Soluble Proteins from the Respiratory Chain Immobilized on Gold Nanoparticles

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In order to exploit the properties of redox proteins for biofuell cells and biosensors, an efficient immobilization of the enzymes on the electrodes is required.[1-3] The immobilization method must provide a suitable environment for the enzyme since this will directly affect the lifetime of the bio device. It must also allow a high loading of enzymes in order to get a good current density. Another crucial aspect is to achieve an efficient electron transfer between the electrode and the immobilized enzymes.

One of the most promising methods of immobilization is the use of gold nanoparticles.[4] Their high surface to volume ratio allows a high loading of enzymes and they act as a relay in the long-range electron transfer between the electrode and the cofactors. In addition, they are considered as quite biocompatible.

Using gold nanoparticles of about 15 nm diameter and various modifiers, we have successfully immobilized cytochrome *c* from *Horse heart*, cytochromes c_1, cytochrome c_{552} and Cu_A from *Thermus thermophilus.* The immobilization procedure has been followed by electron microscopy and Surface-Enhanced Infrared Spectroscopy. The electrochemical behavior of the immobilized enzymes has been studied by cyclic voltammetry. In particular, the electron transfer rates between the enzymes and electrode have been determined and compared. These studies have opened the way to the immobilization of larger membrane proteins from the respiratory chain and first results will be discussed.

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P-031

A Novel Sensitive Electrochemical Dna Biosensor For Assaying Of Anticancer Drug Leuprolide

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The investigations of drug-DNA interactions would provide new compounds to be tested for an effect on a biochemical target, for the design of DNA biosensors, which will further become DNA microchip systems. DNA biosensors eliminate the need for some difficult analyze technique. The anticancer drug, leuprolide (LPR) bound to double-stranded fish sperm DNA (dsDNA) which was immobilized onto the surface of an anodically activated pencil graphite electrode (PGE), was employed for designing a sensitive biosensor.

The mechanism of the interaction was investigated and confirmed by differential pulse voltammetry using two different interaction methods; at the PGE surface and in the solution phase. The decrease in the guanine oxidation peak current was used as an indicator for the interaction in acetate buffer at pH 4.80. The response was optimized with respect to accumulation time, potential, drug concentration, and reproducibility for both interaction methods.

The linear response was obtained in the range of 0.20 – 6.00 ppm LPR concentration with a detection limit of 0.06 ppm on DNA modified PGE and between 0.20 and 1.00 ppm concentration range with detection limit of 0.04 ppm for interaction in solution phase method. LPR showed an irreversible oxidation behavior at all investigated pH values on a bare PGE. Differential pulse adsorptive stripping (AdSDPV) voltammetric method was developed for the determination of LPR. Under these conditions, the current showed a linear dependence with concentration within a range of 0.005 and 0.20 ppm with a detection limit of 0.0014 ppm. Each determination method was fully validated and applied for the analysis of LPR in its pharmaceutical dosage form. The utility of this electrochemical biosensor for interaction between ds-DNA and LPR is cost effective and it provides rapid detection. The proposed electroanalytical method is experimentally convenient, sensitive, selective and rapid so that it requires only small amounts of materials.

P-032

A Hybrid Electronic Tongue for Direct Classification of Baby Liquid Foods With or Without Gluten

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People suffering from celiac disease are gluten intolerant and inadvertent ingestion of gluten proteins must be avoided. Several techniques have been proposed to detect/quantify gluten proteins in foodstuffs: immunochemical methods, mass tandem spectrometry and polymerase chain reaction as well as gluten sensors [1]. Recently, a potentiometric electronic tongue (ET) with lipo/polymeric membranes has been used to detect gliadins, which are gluten proteins, in foodstuffs [2]. However, the use of these techniques requires the previous extraction of gluten proteins. This step can be a possible drawback since it is not possible to guarantee that the extraction has a 100% yield since the protein types overlap in solubility and extractability [3]. In this work, the feasibility of a hybrid multi-sensor ET, which combines repeated cross-sensitivity and ion selective sensors (Fig. 1), to discriminate gluten-free and gluten-containing liquid baby foods has been evaluated. The device was constructed using a screen-printed technique and directly applied in the liquid infant food samples. No extraction or dilution/dissolution step was required. In total, 5 "gluten-free" and 10 "gluten-containing" liquid baby foods of different flavors were purchased at local supermarkets and analyzed. The preliminary results obtained from the principal component analysis (Fig. 2) show that the signals profiles recorded by the hybrid ET possessed valuable information allowing grouping the samples in mainly two groups. In fact, linear discriminant analysis allowed the correct classification of 95% of the samples (leave-one-out cross-validation process) being only one baby liquid food containing gluten misclassified as gluten-free. Although further studies are needed, the satisfactory preliminary results described here presumably demonstrate the ability of the hybrid ET to be used as a rapid and disposable practical tool for quality control of liquid foods for babies suffering from gluten intolerance.

Figure 1

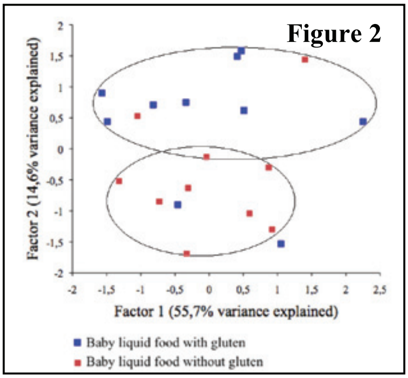

Figure 2

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P-033

Immobilization of Oligopeptides on Gold CDtrode for the Development of Biomimetic Sensor for Pesticides

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Enzymes have been used in the construction of devices to quantify substrate by catalytic reaction. The disadvantages of biological materials as instability and high production cost are well known. Therefore, the design and development of artificial oligopeptides as a mimic of the acethylcholinesterase (AChE) binding site, preserving the highly selective biological properties, was the approach used in this work. The aim of this study is the development of a biomimetic sensor, based on the immobilization of the oligopeptide on gold electrode, in order to obtain a screening analytical tool for pesticides (carbamate and organophosphate) in food samples. The oligopeptide proposed was synthesized by solid phase peptide synthesis methodology and immobilized on gold surface by the thiol group. Due to the high affinity of this group with gold, CDtrodes, electrodes constructed from gold recordable compact discs (CD-Rs), were employed. The Au-CDtrodes have shown an electrochemical performance comparable with commercial gold electrodes, presenting many advantages as simplicity of construction, low cost and if necessary, disposable.

The CD-R polymer layer was removed by concentrated HNO_3, and the gold surface was submitted to a voltammetric pretreatment of 10 cycles in 0.5 mol L^{-1} sulfuric acid solution in the potential range from +0.2 to +1.5 V at a scan rate of 100 mV s^{-1}. Electrochemical measurements were carried out in a potentiostat/ galvanostat AUTOLAB employing a conventional cell: Au-CDtrode (A_{geom} = 0.071 cm^2), Ag|AgCl|$KCl_{(sat)}$, Pt wire (A_{geom} = 4 cm^2) as working, reference and auxiliary electrodes, respectively. The Au-CDtrode was characterized by atomic force microscopy, presenting an average height of 140 nm about the recording tracks and 50.4 nm of roughness. The cleaning step and the modification of the surface with 1×10^{-3} mol L^{-1} oligopeptide by incubation for 1h at 25 ^{o}C were analyzed by diffuse reflectance infrared Fourier transform spectroscopy. A surface recovery of 68% was obtained using cyclic voltammetry.

As the oligopeptide mimics the active site of the AChE enzyme, the affinity with the organophosphate pesticide dichlorvos was monitored by square wave voltammetry, in the potential range from -0.3 to -1.4 V, with a frequency of 100 Hz, amplitude of 50 mV and scan increment of 2 mV, using 0.05 mol L^{-1} $NaClO_4$ as supporting electrolyte. The response of the peptide modified electrode presents a current peak of 10 μA at -1.2 V. After the 1×10^{-5} mol L^{-1} pesticide pre-concentration step and incubation for 30 min at 25 ^{o}C, this signal decreases significantly, suggesting the affinity reaction. The proposed strategy represents a promising tool on the development of biomimetic sensors. FAPESP (2010/04663-6), IRSES (230849).

P-034

Non-enzymatic Detection of Glucose using Silver-Modified Zeolite- Multiwalled Carbon Nanotube-Epoxy Composite Electrode

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In this paper, a silver-modified zeolite-multiwalled carbon nanotube-epoxy composite electrode (AgZ-CNT-Epoxy) was obtained, characterized and tested for non-enzymatic detection of glucose. SEM imaging has been used to provide qualitative information about distribution of multiwalled carbon nanotube and Ag-doped zeolite zones and some surface features of this composite electrode (Figure 1). The prepared AgZ-CNT-Epoxy composite electrode showed good mechanical strength and good electrical conductivity (0.14 Scm^{-1}), which was determined using the standard four probe technique. The electrocatalytic oxidation of glucose in alkaline medium directly at AgZ-CNT-Epoxy composite electrode was investigated using cyclic voltammetry (CV). A series of resultant CVs obtained directly over the concentration range 0.1 mM – 1 mM glucose is illustrated in Figure 2. The anodic current peaks corresponding to AgO formation increased progressively linearly with glucose concentration. A very unexpected and unusual oxidation peak occurred immediately after the reduction of AgO to Ag_2O on backward scanning in cathodic sense, which increased also linearly with glucose concentration. This modified electrode exhibited electrocatalytic effect towards glucose oxidation allowing its determination in aqueous solution.

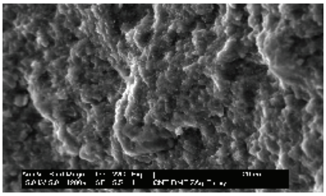

Fig.1.SEM image of AgZ-CNT-Epoxy surface

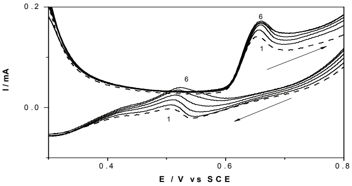

Fig.2.Detail of CVs recorded at AgZ-CNT-Epoxy in 0.1 M NaOH supporting electrolyte (curve 1) and in the presence of various glucose concentrations: curves 2-6:0.2-1 mM glucose

P-035

Graphite Electrode Modified with New Phenothiazine Derivatives as Amperometric Transducer for NADH Detection

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The adsorption of electrocatalytical active species onto carbonaceous electrode materials represents a simple and inexpensive procedure, leading to modified electrodes highly suitable for NADH electrocatalytic oxidation [1,2].

Two newly synthesized phenothiazine derivatives, 3,7-di(m-aminophenyl)-10-ethyl-phenothiazine (DAEP) and 3,7-di(m-hydroxyphenyl)-10-ethyl-phenothiazine (DHEP), were used to modify solid graphite electrodes by adsorption from DMSO solution.

Cyclic voltammetry and rotating disc electrode measurements, performed under different experimental conditions (pH, potential scan rate, rotation speed and NADH concentration) allowed to: (i) notice that both compounds undergo a quasi-reversible one electron / one proton redox process (k_s = 0.73 s^{-1} for DAEP and 0.38 s^{-1} for DHEP), occurring at a formal standard potential which is not affected by the nature of substituents at positions 3 and 7; (ii) estimate the pK_a values of the adsorbed mediators (6.9 for DAEP and 7.8 for DHEP); (iii) evaluate the second order rate constants for NADH electrocatalytic oxidation ($k_{obs,[NADH]=0}$ = 6014 M^{-1} s^{-1} for DAEP and $k_{obs,[NADH]=0}$ = 134 M^{-1} s^{-1} for DHEP).

Based on the mediators' structure, an explanation for the higher electrocatalytic efficiency noticed for DAEP mediator was attempted.

Table. Electrocatalytic parameters for NADH oxidation at G/DAEP and G/DHEP electrodes. Experimental conditions: supporting electrolyte, 0.1 M phosphate buffer (pH 7).

Compound	$k_{obs\ [NADH]=0}$ M^{-1} s^{-1}	k_{+2} s^{-1}	K_M mM	Γ nmol cm^{-2}
DAEP	6014.4	337.8	56	0.77
DHEP	134.2	101.4	755	2.99

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P-036

Multi-walled carbon nanotubes decorated with Fe_3O_4 nanoparticle for modification of glassy carbon electrode: Application to simultaneous voltammetric determination of guanine and adenine in DNA

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Guanine and Adenine are important components found in deoxyribonucleic acid and play fundamental roles in life process. The abnormal changes of the bases in organism suggest the deficiency and mutation of the immunity system and may indicate the presence of various diseases. Therefore, the determination of these bases has great significance to the bioscience and clinical diagnosis. The unique properties of nanoparticle materials (enhanced mass transport, high surface area, improved signal-to-noise ratio) can often be advantageous in electroanalytical techniques. Generally, electrocatalysts with small particle size and high dispersion will result in high electrocatalytical activity. So, Controlling the size and distribution of nanoparticles on a substrate remains one of the main challenges of materials science. Carbon nanotubes properties (high surface area, unique physical properties, morphology and high electrical conductivity), can make them extremely attractive as supports for heterogeneous catalysts. Due to these excellent properties, we synthesized a composite of MWCNTs decorated with Fe_3O_4 nanoparticles. The prepared modified electrode (Fe_3O_4/CNT/GC) offers dramatic improvements in the stability and sensitivity of simultaneous voltammetric measurements of guanine and adenine in pH 7.0 phosphate buffer solution compared to individual CNT/GCE or bare GCE. The surface morphology and nature of the composite film deposited on glassy carbon electrode has been characterized by transmission electron microscopy (TEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques. A remarkable enhancement in microscopic area of the electrode together with the catalytic role of the composite modifier resulted in a considerable increase of the peak current, and negative shift in the oxidation potentials. The mechanism of the electrocatalytic process on the surface of the modified electrode was analyzed by obtaining the cyclic voltammograms at various potential sweep rates and pHs of the buffer solutions. A wide linear dynamic range of 0.02μM-10μM with a detection limit of 3nM for guanine and A linear dynamic range 0.08μM - 60μM with a detection limit of 12nM for adenine were obtained. The modified electrode was successfully applied for highly sensitive simultaneous determination of trace amounts of Adenien and Guanine in DNA.

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P-037

Metal and Nanoparticle Modification of Screen Printed Electrode Sensors for Amino Acid Determination

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Amino acids are often added to food samples during their preparation in order to correct for possible dietary deficiencies [1]. So, nowadays the determination of amino acids is important, because of the burgeoning interest and concern with the food that is consumed. Over the past decade, numerous procedures involving high-performance liquid chromatography HPLC have been successfully developed and implemented for the determination of amino acids, but in recent years a detection methodology that does not require derivatization is preferred, when available, for convenience and simplicity.

One of the possibilities for the rapid determination of amino acids is using electrochemical methods. Since amino acids have at least two active functional groups (depending on pH): $-NH_2$ and $-COOH$, they have the ability to complex some transition metals (e.g. nicke1 [2] and copper [3]). One of the easiest metal ions to complex is the Cu(II) ion, which can form different complexes depending on the pH, besides complexing with ligand (amino acid), as well as with H^+, in acidic solution, or OH^-, in alkaline solution, at the same time [4].

The aim of this work was to study and optimize different metal and nanoparticle modified electrodes in a variety of media as potential sensors for the electrochemical detection of the amino acids tryptophan and tyrosine, in the presence and in the absence of copper.

Screen-printed electrodes (SPE), being one of the most interesting alternatives in the design of electrochemical sensors, reported as sensors for biomedical, environmental and industrial analysis, were used in this work as the substrate for different modifications (copper, carbon nanotubes, carbon black and gold) in order to improve amino acid determination. The results of these studies will be reported.

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P-038

Electrochemical Switching of the Flavoprotein Dodecin on Surfaces

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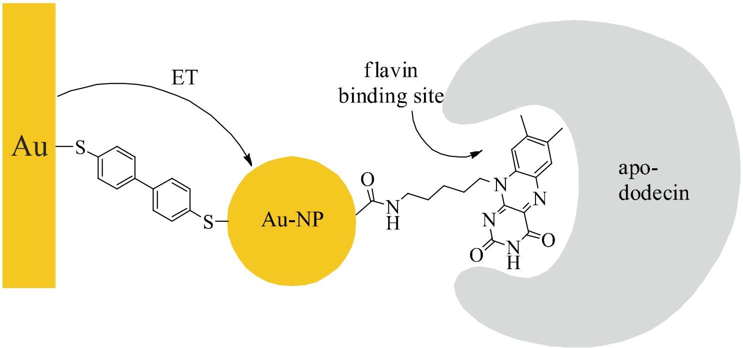
Dodecin from *Halobacterium salinarum* is a dodecameric, hollow-spherical flavoprotein which contains six flavin binding sites. In each binding site, two flavins are arranged in an aromatic tetrade between two tryptophan residues. Dodecin binds not only native but also artificial flavins with high binding affinities. Reduction of the flavin ligand induces the dissociation of the holocomplex into apododecin and free flavin. Inspired by the binding mode and the redox characteristics of dodecin, we are developing electrochemically active flavin modified electrode surfaces (electrode – molecular wire - flavin) which are able to bind or release apododecin triggered by the redox potential. Possible applications range from the control or transport of single molecular assemblies containing apododecin, up to the development of bioelectrochemical data storage devices with an electrochemical input (write) and an optical (fluorescence sensitive) output (read). Starting with electrode surfaces of some mm^2, our further interest will be the miniaturization of this setup down to the single molecule level. In first experiments we employed an artificial flavin linked to a goldnanoparticle (Au-NP) and [1,1'-biphenyl]-4,4'-dithiol as a potential molecular wire-like system as shown below.[1] By surface plasmon resonance (SPR) and by faradaic impedance spectroscopy the stepwise surface modification as well as the binding and the release of apododecin upon reduction of the flavin are investigated. For this purpose a homemade cell to do SPR and impedance spectroscopy measurements in the same setup was developed



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P-039

Electrochemical study of lamotrigine at pyrolytic graphite electrode: pyrolytic graphite electrode versus modified glassy carbon electrode

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Lamotrigine (LTG), 3,5-diamino-6-(2,3-dichlorophenyl)-1,2,4-triazine is a new-generation antiepileptic drug registered for treatment of patients with refractory partial seizures. Lamotrigine is thought to act at voltage-sensitive neuronal membranes and inhibit the release of excitatory amino acid neurotransmitters, in particular glutamate and aspartate, which play an important role in the generation and spread of epileptic seizures[1,2]. The electrochemical behavior of Lamotrigin (lamot) at the pyrolytic graphite electrode was investigated in detail by the means of cyclic voltammetry. During the electrochemical reduction of Lamot, an irreversible cathodic peak was appeared. Cyclic voltammetric studies indicated that the reduction process has an irreversible and adsorption-like behavior. The observed reduction peak was attributed to a two electrons-two protons process referring to the reduction of N═N group in the ring to the corresponding HN─NH. The prepared electrode showed an excellent response toward the electro-reduction of Lamot leading to a significant improvement in sensitivity as compared to the Carbon nanotube, carbon nanoparticles and carbon nano diamond modified glassy carbon electrodes. Lamot was determined by this simple bare pyrolytic graphite electrode in a wide dynamic range of 0.08-100 μM and low detection limit of 60 nM.

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P-040

Arrays of Chemically Modified Ultramicroelectrodes for Multicomponent Bioanalysis

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Selective simultaneous determination of bioanalytes in complex mixtures is of great interest for researchers and finds applications in analytical chemistry, medicine and environmental monitoring. The simultaneous detection of multiple analytes can be successfully carried out using the array of electrodes and amperometry as a detection technique because of its high sensitivity and rapidity. Arrays of micro- and nanodimensions have a great potential to be applied both for intra- and extracellular measurements. Chemical modification of the electrodes can improve the performance of the array. For instance, electrodes individually modified with different ligands can be used for multianalyte detection. An array of electrodes modified with the same ligand could be applied for obtaining the spatially resolved image of biocomponents released from a cell, e.g. release of insulin from pancreatic β-cells. Modification helps to increase the sensitivity of detection, minimizes the possible interference from other electrochemically active components, and makes it possible to detect components which are generally electrochemically inactive.

The purpose of this research is to develop different types of micro- and ultramicroelectrode arrays for the simultaneous measurement and monitoring of bioactive compounds (e.g., oxygen, glucose, insulin, glutamate). The electrodes in the array are individually addressable and chemically modified. The research has been started from the development of a two microelectrode array for simultaneous detection of glucose and insulin. The array is fabricated by inserting a carbon fiber into each barrel of a multibarrel glass capillary followed by pulling the capillary to form a sharp tip containing two disk-shaped electrodes. The surface for glucose sensing was modified with glucose oxidase entrapped into a polymer film grown by cycling the enzyme and monomer containing solution at certain potential range or carrying out potentiostatic electropolymerization of the monomer and enzyme mixture. The performance of the electrode can be improved by including the electroactive mediators which facilitate the electron transfer between the immobilized biocatalyst and the electrode surface. Insulin can be electrocatalytically oxidized on a surface modified with a mixture of ruthenium salts electrodeposited by cycling between -0.2 and 1.1 V vs Ag/AgCl. The electrochemical properties of the array and its surface structure were characterized by cyclic voltammetry, amperometry and scanning electron microscopy. The modified electrodes in the array were tested on glucose and insulin solutions. The expanded array containing 7 barrel electrodes for the detection of larger number of bioanalytes is under development. The future plans include the fabrication of up to 25 individually addressable microelectrodes using photolithographic technique. Total working surface of such arrays is 15-30 μm. They can be applied for monitoring of the analyte released from a single cell.

P-041

A New Biosensor Based on Schiff-base Iron (III) Complexes Modified Carbon Paste Electrode for Simultaneous Determination of Anti-inflammatory Drugs

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A new chemically modified electrode is constructed based on Fe (III) Schiff base modified carbon paste (Fe (III)-SBMCP) electrode. The electrode was evaluated as a sensor for sub-micromolar determination of Mefenamic acid and Indomethacin in aqueous solutions. The measurements were carried out by application of the differential pulse voltammetry (DPV) method in phosphate buffer solution with pH 3.5. Fe (III) loaded in Schiff base can increase anodic peak currents by adsorption of Mefenamic acid and Indomethacin on electrode surface. The prepared electrode shows voltammetric responses with high sensitivity and selectivity for Mefenamic acid and Indomethacin in optimal conditions, which makes it very suitable for simultaneous determination of these compounds. A linear relationship was found for Indomethacin in the 0.2-150 $\mu mol.L^{-1}$ range containing 10µM Mefenamic acid with a calibration equation of Ip (nA) = 28.593c ($\mu mol.L^{-1}$) + 21.79 ($R^2 = 0.9990$) and a detection limit of 0.08 $\mu mol.L^{-1}$.

Keywords: Schiff base, Mefenamic acid, Indomethacin, Modified electrode.

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P-042

Electrochemical Determination of Ibuprofen using Silver-Modified Zeolite-Carbon based Electrode

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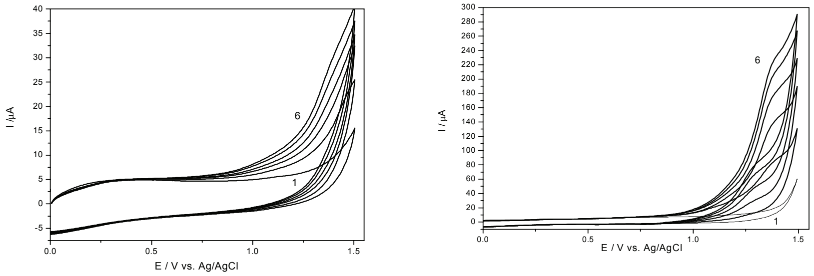
The electrochemical bahaviour of ibuprofen (IBP) was investigated at two types of composite electrodes, *i.e.*, silver-modified zeolite-multiwalled carbon nanotube-epoxy (AgZCNT) and silver-modified zeolite-expanded graphite-epoxy (AgZEG) composites electrodes, in comparison with comercial glassy carbon (GC) electrode. All electrochemical measurements were carried out using a potentiostat/galvanostat PGSTAT 30 (Eco Chemie, The Netherlands) controlled with GPES 4.9 software and a three-electrode cell, with a saturated calomel electrode as reference electrode, a platinum counter electrode and composites and respective, GC working electrodes. The electrochemical investigation of ibuprofen oxidation and detection on the tested electrodes was achieved using cyclic voltammetry (CV), chronoamperometry (CA) and pulsed voltammetric/amprometric techniques. For example, two series of CVs recorded at AgZEG and GC electrodes, respectively are shown in Figure 1. Some aspects regarding the mechanism of IBP electrooxidation on the tested electrodes are discussed. In comparison with GC electrode, both composite electrodes exhibited an electrocatalytic effect towards ibuprofen oxidation allowing its determination in aqueous solution with improved electroanalytical perfomance. The electrochemical detection of IBP using composite electrodes revealed a good accuracy based on the comparison with spectrophotometric results.



b)

a)

Fig.1.CVs recorded in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) and in the presence of various IBP concentration: curves 2-6:10-50 mgL^{-1} IBP at: a-GC electrode; b-AgZEG composite electrode

P-043

Mixed Metal Oxide Composite Materials for Sensitive Sensing of Monosaccharides

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New hybrid materials based on mixed metal oxide nanoparticles and carbon nanotubes materials (CNT) homogenously dispersed in a Nafion polymer were synthesized for electrocatalytic sensors application. Ni and Co mixed oxides exhibit interesting and improved electrocatalytic activities and the possibility of utilizing these materials as anode electrodes for the oxidation of carbohydrates is evaluated in the present work. A screen-printed electrode body is used as platform for immobilization of the nanocomposite to build the CNT-Ni-Co-oxide electrodes.

The electrochemical performance of these composite based sensors was investigated by electrochemical methods, in terms of sensitivity, detection limit and stability towards carbohydrates detection in alkaline media. Cyclic voltammograms of the modified electrode show a stable and well defined redox couple in alkaline media due to the synergy of Ni(II)/Ni(III) system with Co(II)/Co(III). The modified electrode shows excellent electrocatalytic activity toward monosaccharides oxidation at reduced potential (250-300 mV *vs* Ag/AgCl) in alkaline solutions. Six monosacharides were determined amperometrically at the surface of this new modified electrode with high sensitivity over a wide range of concentrations, from 0.02 up to 12.12 mM. Low detection limit of 5 μM could be obtained.

The electrochemical activities of the electrodes depend on both the catalytic properties of the material and the electrode surface area. SWNT played an important role, providing an electro-conductive network and having a large active surface area, helping the metal oxide to be better dispersed and exposed toward solution. The electrocatalytic properties toward carbohydrates detection are improved when metal oxides are composited with carbon nanotubes material. The morphological features of CNT-Ni-Co-oxide/Nafion composite were characterized by atomic force microscopy (AFM).

Such performance characteristics compare favorably with those of previously reported metal oxide-modified electrodes and/or CNT-modified electrodes for carbohydrates in alkaline solution, and indicate great promise for measurements of sugars in flow systems.

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P-044

Electrocatalytic Determination of Ascorbic Acid by Gold-Cysteamine-Lysine-Cu^{2+} Self Assembled Monolayer Modified Electrode

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Electrocatalytic activity of Cu^{2+} immobilized on the topside of Gold-cysteamine-glutar aldehyde-Lysine (Au-CA-GA-Lys) self assembled monolayer (SAM) electrode investigated by differential pulse voltammetry (DPV) and cyclic voltammetry (CV) method. A new gold SAM electrode constructed. This electrode illustrated a selective and reproducible adsorption for Cu^{2+} . Preparation steps of the modified electrode were studied by CV. In the absence of Cu^{2+} , DPV redox peak for ascorbic acid is observed at about 400 mv with anodic current equal to 0.5 µA vs.Ag/AgCl for 1.0×10^{-4} M of ascorbic acid. At presence of Cu^{2+} on the modified electrode, anodic peak observed at 300 mv vs.Ag/AgCl with 4.5 µA for 1×10^{-6} M of ascorbic acid. This electrocatalytic acitivity of copper ion could be apply for determination of trace concentration of ascorbic acid. The differential pulse voltammetric response of the SAM modified electrode was linear against the concentration of the ascorbic acid in the ranges of 1×10^{-10} - 1×10^{-8} and 5×10^{-8} - 1×10^{-6} with R^2= 0.9978 and R^2= 0.9981 respectively at pH=6.0. RSD were determined as 3.6% by DPV.

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P-045

Application of Recombinant Human Arginase I in Analytical Biotechnology

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For enzymotherapy of some malignant diseases (melanoma, hepatocarcinoma) is very perspective the use of arginine-catabolizing enzymes. Proliferation of some cancer cells are strongly depended on arginin concentration. Monitoring of arginin content in serum blood is very essential for treatment control of some cancers.

The progress of nanotechnology opens the possibility to create bioselective elements based on nanoparticles, which have unique properties not inherent to microsized objects. Nanosized materials have high surface, which is very important for the immobilization of enzymes.

The goal of this work is the development of a new biosensor for L-arginine assay based on recombinant arginase I (EC 3.5.3.1; L-arginine amidinohydrolase) isolated from overproducing yeast strain *Hansenula polymorpha* NCYC 495 and immobilized on gold nanoparticles (nAu). nAu were synthesized by reduction of $HAuCI_4$ and functionalized using 16-mercaptohexadecanoic acid. The enzyme was immobilized on modified nAu using carbodiimide-pentafluorophenol method. The yield of arginase-nAu was 93 % of initial enzyme activity. Arginase-nAu were characterized by scanning electron microscopy (CEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray spectroscopy. Storage stability of arginase-nAu was compared to the control enzyme in solution.

Potentiometric bi-enzyme biosensor selective to L-arginine was developed. The bioselective layers include arginase-nAu or arginase I (without nAu) and commercial urease immobilized in alginate membrane on the surface of ammonium-selective electrode. Some physico-chemical (t°-, pH-optimum) and enzymological (K_M value, sensitivity, selectivity and storage stability) characteristics of the developed potentiometric sensor were investigated. The biosensor exhibits a good response to the target analyte with the linear range from 0.1 to 40 mM and detection limit below 10^{-5} M of arginine. Moreover, biosensor was sufficiently stable and gives a fast response to analyte ($t_{95\%}$ varies from 3 to 5 min). The constructed biosensor was tested on the real samples of pharmaceutical products (Tivortin, Cytrarginine, Aminoplazmal 10% E). A good correlation between results obtained by biosensor assay when compared to the arginine content declared by commercial producers.

P-046

Novel Bio-inspired Sensory Material for Implantable Tissue Applications

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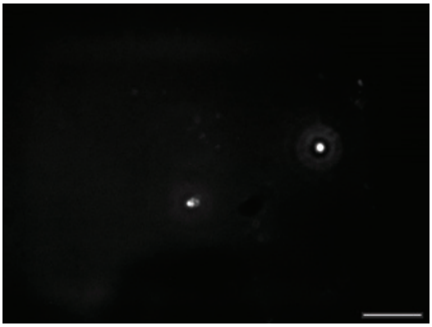
We describe the synthesis of a novel poly(vinyl alcohol) [PVA] hydrogel doped with liposomes, which is a candidate for synthetic implantable tissue. Cross-linking in the hydrogel has been achieved by freeze-thaw cycles. Thus, uniquely, the synthesis of the hydrogel involves no chemical cross-linkers, many of which are potentially carcinogens, or a temperature or chemical / pH trigger for the gelation process, which helps preserve the chemical environment within the liposomes. The integrity of the liposomes during the freeze-thaw cycles has been ensured by the use of a cryoprotectant (trehalose). Also, this method is considerably more advantageous than photoinitiated cross-linking not only as it avoids the use of potentially toxic initiators but also because the latter technique cannot be effectively applied to thick samples.

Liposomes, which are closed sacs formed by phospholipid bilayers, may be regarded as prototype cells. The incorporation of ion channels, which can produce stimulus-initiated ionic currents, in the liposomal membrane enables the mimicking of the sensory action of the cell membrane. The liposome-doped hydrogels are considerably more robust and stable than similar systems that have been extensively studied for sensory applications, such as free-standing as well as supported bilayer lipid membranes (BLMs). The hydrogels have been characterised by scanning electron microscopy (SEM), transmission electron microscopy (TEM), fluorescence microscopy, time-resolved fluorescence spectroscopy, cyclic voltammetry and electrochemical impedance spectroscopy.



Fluorescence micrograph of liposomes containing 5-carboxyfluorescein embedded in hydrogel matrix (the scale bar corresponds to 40 microns).

P-047

Analysis of Bienzyme-type Lactose Biosensor Response by Wavelet Transformation

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Lactose sensor is important to diagnose lactose intolerance patients. In the present study, we prepared bienzyme lactose sensor based on *β*-galactosidase and glucose oxidase[1)]. Lactose is disaccharide, and hydrolyzed by *β*-galactosidase to glucose and galactose. Thus, the lactose concentration can be determined by measuring the generated glucose concentration. However, if a sample contains lactose and glucose, it is not easy to distinguish the lactose and glucose responses. The wavelet transformation (WT) has been shown a powerful tool for the deconvolution of the electrochemical signals[2)]. The WT can decompose a signal as a function of the frequency in time domain.

The several signals with different time constants can be distinguish by using the WT. In the present study, the bienzyme lactose sensor responses were analyzed by the WT for simultaneous determination of lactose and glucose concentration.

Figure 1 shows current changes of the lactose biosensor in response to addition of (a) 1 mM lactose, (b) 0.1 mM glucose, (c) 1 mM lactose and 0.1 mM glucose solutions, respectively. As you can see, the reaction time constant of glucose is about four times larger than that of lactose. Figure 2 shows power spectrum density (*PSD*) signal of the lactose biosensor response with time and pseudo-frequency calculated by WT. As shown in Fig.2, the *PSD* signal related to the response of lactose was detected in low frequency range around 0.1 Hz. On the contrary, the *PSD* signal related to the response of glucose was detected in high frequency range around 20 Hz. These results indicated that simultaneous detection of lactose and glucose can be achieved by combination of bienzyme-type lactose biosensor with wavelet transformation.

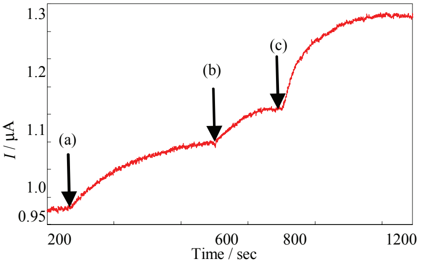

Fig1. Current changes of the lactose biosensor in response to addition of (a) 1 mM lactose, (b) 0.1 mM glucose, (c) 1 mM lactose and 0.1 mM glucose solutions, respectively.

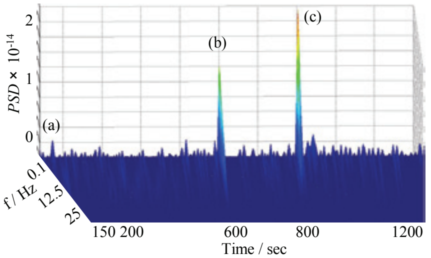

Fig2. PSD signal of the lactose biosensor response with time and pseudo-frequency calculated by WT (a) 1 mM lactose, (b) 0.1 mM glucose, (c) 1 mM lactose and 0.1 mM glucose solutions, respectively.

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P-048

Electrochemical microdevices as a promising analytical tool for in vivo exploration of oxidative stress

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Electrochemical devices represent a powerful tool to explore directly and easily oxidative stress on human skin. Among the involved species, the low molecular weight antioxidants (LMWA) are able to transfer electrons to reduce and eliminate pro-oxidants, molecules responsible for oxidative stress. Cyclic voltammetry was performed to detect LMWA and to evaluate the antioxidant capacity of skin [1]. However, the method used suffered from two major drawbacks. Firstly, the measurements involved handmade fabricated microelectrodes. This production way is time-consuming and each microelectrode must be characterized to check the active surface. Secondly, the device, composed of a working microelectrode, a commercial reference electrode and a macroscopic counter electrode, was bulky and complex for routine analysis. Now, thanks to microtechnologies, generic microelectrodes and electrochemical microdevices can be mass fabricated with multiple geometries. Nevertheless, to obtain reliable and reproducible results, the electrochemical measurements require a prior knowledge of the microelectrodes materials, and more especially of the surface states and properties. Integrated electrochemical microdevices, involving the working, counter and reference electrodes, were fabricated thanks to "Silicon & Polymers" microtechnologies. The thin film metallic materials used, i.e. gold, platinum and silver, were characterized by cyclic voltammetry to study the quality and the definition of active surface. Finally, the silver electrode was oxidized to obtain the integrated reference electrode. To explore the global antioxidant capacity of the skin, the microdevices were directly placed on the inside of the forearm (Fig. 1.). The recorded cyclic voltammogramms (Fig. 2.) showed well defined anodic current, induced partially by the electrochemical oxidation of the antioxidant species. Such current-potential curves were compared to those obtained with electrochemical standard devices, evidencing a good agreement between the different results.

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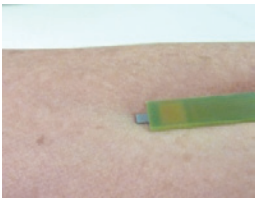

Fig.1. Electrochemical microdevice directly on the skin

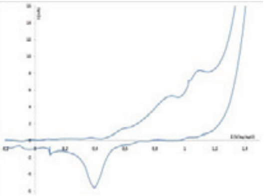

Fig.2. Cyclic voltammogramm obtained directly on the forearm with microdevice

P-049

Amperometric Detection of Catechol at Graphite Electrode Modified with Pt Nanoparticles

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In last years many research effort have been performed in the field of electroanalytical chemistry in order to improve the design of electrochemical biosensors, looking for better analytical characteristics in terms of sensitivity, selectivity, reliability, simplicity and low cost. Additionally, the exponential growth observed in the fields of nanoscience and nanotechnology, results into a rapid advance of using of nanomaterials (i.e. nanometer-sized particles) in the areas of bio-electro-analysis and new electrode materials. At the present it is well-known that the performance of biosensors depends significantly on the strength of interactions existing between the immobilized biomolecules and the electrode material. In this context, the use of nanomaterials for the construction of biosensing devices constitutes one of the most exciting approaches [1-3].

In this context, the electrochemical investigation of two new modified electrodes based on Pt-nanopaticles (Pt-NPs), deposited on graphite powder entrapped either in polypyrrol (pPy) or in Nafion® polymeric films was performed under different experimental condition (scan rate, pH and catechol concentration). The voltammetric response of the modified electrodes towards catechol was significantly enhanced by the presence of Pt-nanopaticles. The electroanalytical parameters for both modified electrodes, compared with those corresponding to the unmodified electrodes, recommend them as amperometric transducers for tyrosinase based amperometric biosensors.

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P-050

Gelatin on a gold electrode: its electrochemistry and its ability to entrap a redox enzyme

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Bio-electronic devices, that employ enzymes as bioactive interfaces, can provide real-time reliable information about the chemical composition of their surrounding environment. An improved immobilization of the enzyme onto the electrode surface can be obtained by incorporating this biological recognition element into a biocompatible matrix. In this strategy, the preservation of the native configuration of the enzymes and therefore the enzymatic activity can be ensured.

The embedding matrix, under investigation in this work, is the water soluble protein gelatin, an example of a physically crosslinked hydrogel. There are different types of gelatin available, with type A and type B gelatin being the most common. Although different research groups have reported on the use of gelatin as immobilization matrix, the electrochemical behaviour of gelatin studied at electrode surfaces has not been published yet to our knowledge.

In the presented work, the electrochemical behaviour of gelatin coated gold electrodes in physiological pH conditions is studied in a potential window -1.5 till 1.0 V vs SCE (saturated calomel reference electrode) by performing cyclic voltammetry. Redox processes due to the gold surface, the used HEPES (2-[4-(2-hydroxyethyl)-piperazinyl]ethanesulfonic acid) buffer solution and the gelatin layer are identified. A similar electrochemical behaviour is observed for gelatin A and gelatin B. The deposition of gelatin onto the gold surface is confirmed by attenuated total reflection-infrared (ATR-IR) spectroscopic analyses.

To avoid the interference of the above mentioned redox reactions, applying a reduced potential window is necessary to study the immobilization of a redoxactive enzyme in the gelatin matrix. The challenge of the ongoing research is to identify and clarify the redox processes occurring at the gold electrodes, modified with a gelatin layer, containing an enzyme. The selected enzyme currently under study is alcohol dehydrogenase.

P-051

Electrochemical Detection of Purine Metabolites in Human Urine

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A sensitive electrochemical method was developed for simultaneous determination of uric acid (UA), xanthine (XAN), hypoxanthine (HYP) (products of purine catabolism in human), allopurinol (ALO), and oxypurinol (OXY) (a drug used in treatment of purine catabolism disorders and its metabolite, respectively). It is demonstrated that differential pulse voltammetry in connection with a special prepared electrode can serve as a simple and efficient tool for monitoring transformation of purine catabolites (HYP - XAN - UA) catalyzed by xanthine oxidase (XO) as well as inhibition of this pathway by ALO. The mechanically treated electrodes have been tested in analysis of real clinical samples of human urine.

Acknowledgements.
This work was supported by the Academy of Sciences of the Czech Republic (KAN200040651 to S.H.), the Czech Science Foundation (205/10/2378 to S.H., 202/08/1688 to V.V.), the Grant Agency of the Academy of Sciences of the Czech Republic (A400040804 to F.J.) the Ministry of Education, Youth and Sports of the Czech Republic (LC06035 to M.F.), and institutional research plans (AV0Z50040507, AV0Z50040702).

P-052

Methods for DNA Isolation and Detection of Fungal DNA

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Aflatoxins B1 and B2 are secondary metabolites produced by the aflatoxigenic species of the filamentous fungi *Aspergillus flavus* and *A. parasiticus* when they infect corn, cotton, peanuts, and tree nuts. These compounds are known to be toxic and carcinogenic to animals and humans. A positive correlation between aflatoxin contamination of agricultural commodities and primary human hepatocellular carcinoma has been documented. For this reason, efforts to reduce and eventually eliminate aflatoxin contamination from food and feed have been undertaken by scientists [1].

Convectional methods for identifying and detection fungi rely on microscopic or culture techniques, which are time consuming. DNA-based detection (method like PCR) is more sensitive, specific and had been employed for the detection of aflatoxinogenic fungi [2]. We are focused on the detection of *Aspergillus* species by using plate techniques, by molecular biological methods (PCR) and electrochemical detection of DNA hybridization gene encoding of aflatoxin production.

In this contribution, we compared a few DNA extraction methods for *Aspergillus* species and tested the resulting DNA as to its suitability for PCR and for electrochemical detection of DNA. We detected the specific section of gene encoding the production of aflatoxin B1. For the electrochemical detection were used different carbon electrodes (carbon paste electrode, screen printed carbon electrode, glassy carbon electrode and 3-electrode sensor from BVT Technologies). Specific sequence of DNA was immobilized onto a surface of the carbon electrode. Unoccupied surface was blocked and hybridization between the target DNA and biotin-DNA probe followed. Then the conjugate of streptavidin with alkaline phosphatase was added and bound to the biotin labelled probe. The electrode was placed into voltammetric cell containing buffer with substrate for alkaline phosphatase. The product of enzymatic reaction quantified voltammetric technique (DPV, SWV, LSV). Numerous variables of the assay protocol were characterized and optimized. Then, the procedure was used for the detection of pure culture of *Aspergillus* species and DNA of *Aspergillus* species isolated from real samples of feed and foodstuffs.

Acknowledgments: This work was supported by the Ministry of Education, Youth, and Sports of the Czech Republic (projects MSM0021627502 and LC06035).

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P-053

A Cost-effective Carbon Black /Graphite Composite Electrode (CB/CPE) for Sensitive Detection of Dienestrol Based on the Enhancement Effect of Cetyltrimethylammonium Bromide (CTAB)

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Dienestrol(DIES) is a synthetic non-steroidal estrogen used as growth promoters in culturing. In the last decade, the dienestrol residue in related animal products has attracted attention due to its high estrogenic potency and toxic effects on public health.The use of DIES is strictly banned in the EU by Directive 96/22/EC and Ministry of agriculture of China. Different methods including chromatography have been developed over years for monitoring the illegal use of DIES. However, it is always difficult to rapidly and precisely monitor for abuse of DIES especially in tissue samples due to the complexity of biological matrices and the lower accumulate levels. The carbon paste electrode has been widely applied in the electroanalysis owing to its ease of fabrication and modification, and renewable surface. Various carbon materials have been used for the construction of CPE to improve sensitivity, selectivity and stability, Carbon black, known for its abundance defect sites and high surface area, is commonly applied in gaseous phases analysis, fuel cell and lithium battery.As far as we know, few applications have been reported using CB as an sensing material for sensors. A simple and low-cost dienestrol sensor was prepared and investigated based on CB/CPE in the presence of CTAB below CMC. Higher sensitivity and stability, better electron transfer and electrocatalytic properties than the CPE towards DIES were observed by FSEM, EIS and CV, which were attributed to the high surface-area-to-volume ratio of CB. Moreover, abundance CTAB molecules adsorbed on the CB/CPE surface via hydrophobic interaction, altered the structure of electrode/solution interface and enriched DIES on the electrode surface. The oxidation peak current of DIES increased greatly and the oxidation potential lowered, indicating the electron transfer between DIES and the electrode becomes easily. A new electroanalytical method for DIES has been established by DPV, and the linear range was from 1.0×10^{-8} to 1.1×10^{-5} $\mathrm{molL^{-1}}$ with the detection limit of 3.7×10^{-9} $\mathrm{molL^{-1}}$ (S/N=3). The proposed sensor was successfully applied to fish muscle samples analysis.

P-054

Direct Electrochemistry of Glucose Oxidase on a Mn_3O_4-Nafion Composite Film Modified Electrode

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In recent years, transition metal oxide nanomaterials have attracted considerable attention in the area of electrochemical biosensor. Among various kinds of transition metal oxide nanomaterials, manganese oxides have been the target of many studies because of its outstanding structural flexibility properties. Direct electron transfer between proteins and electrodes has also attracted considerable attention since it can serve as a model system to understand electron transfer mechanisms in biological systems, and also provide a foundation for the construction of electrochemical biosensors. As one of manganese oxides, Mn_3O_4 has been the key topics because of their potential applications in electrochemical areas, including Li-ion batteries, electrochemical supercapacitors [1, 2]. However, as far as we know, there is no report on the direct electron transfer based on Mn_3O_4 nanomaterials.

In this study, we first reported an application of Mn_3O_4 octahedral nanoparticles (Fig. 1) prepared by a simple hydrothermal method in the fabrication of an electrochemical biosensor. The direct electrochemistry of glucose oxidase (GOD) immobilized in the modified electrode based on a composite film of Mn_3O_4 octahedral nanoparticles and Nafion has been investigated with a fast electron transfer rate of $18.6\ s^{-1}$ (Fig. 2). Considering lower cost and ready preparation of Mn_3O_4, the Mn3O4 based modified electrode should have wide applications in third-generation biosensors, bioelectronics and electrocatalysis.

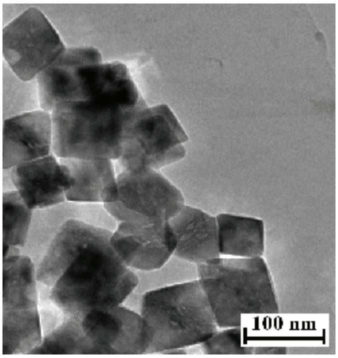

Fig. 1. TEM image of Mn_3O_4 nanoparticles

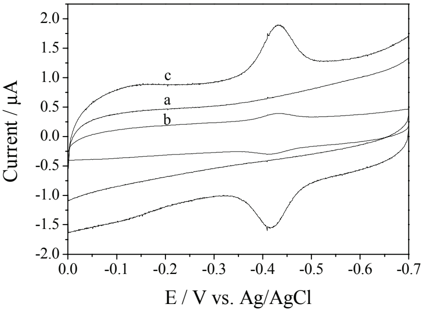

Fig. 2. CV curves of Mn_3O_4-Nafion/GCE (a), GOD-Nafion/GCE(b), GOD-Mn_3O_4-Nafion/GCE (c) in 0.1 M PBS (pH 7).

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P-055

Electro-responsive Properties of Star Shaped SNS Derivative

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Building super-structured CPs is of great interest because of the novel properties that could arise from such structures.[8–11] Branched conducting polymers with electronically-connected nodes are excellent candidates among this family of super structured CPs; with such polymers, there should be no need for inter-chain coupling or inter-chain electronic transfer to ensure high electronic conductivity. Moreover, this type of material possesses a three dimensional structure which could also improve the conductivity.[1]

In this work, we synthesized a new star-shaped SNS derivative (2,4,6-tris(4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)butylamine)-1,3,5-triazine) (Fig.1). Electrochemical and electrochromic properties of SNS derivative were investigated.

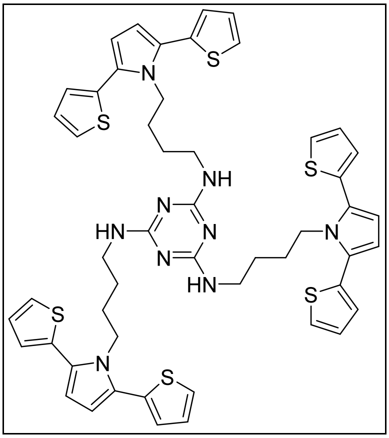

Fig.1 Star-shaped SNS derivative

Reference:
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P-056

Compact-Sized LB Film Taste Sensor

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A single-channel compact-sized taste sensor using a polyion-complex Langmuir-Blodgett (LB) film is reported. A sensing film consisting of dioctadecyldimethyl ammonium bromide（DOABr） was deposited in 20 layers on an evaporated Au film with potassium polyvinyl sulfate （PVSK） as an under layer. The measuring parameters were the maximum potential change depending on the adsorption effect and the stability potential change depending on the disadsorption effect. The sensor holder is easy to carry and is used to measure only with dipping taste solutions. Five basic taste substances were discriminated completely with these parameters.

Figure1shows a schematic of the new type of sensor holder used for measuring taste substances. The holder is made of a poly dimethyl siloxane (PDMS) resin plate and a taste sensor with glass plate is attached to the other side of the unit The holder were dipped into sample solutions each containing one of five basic taste materials. The solutions flowed at a suitable rate into a sensor chamber through a small hole 5 mm in diameter. A salt bridge was also attached by connecting a reference electrode to one side of the holder and connected to KCL saturated solution by measuring the other reference electrode in the solution. Figure 2 shows a taste map for the five basic taste substances that had a low concentration of 5 mM. Five basic substances were clearly discriminated with small variance by using two of the maximum potential change and the stability potential change as measuring parameters.

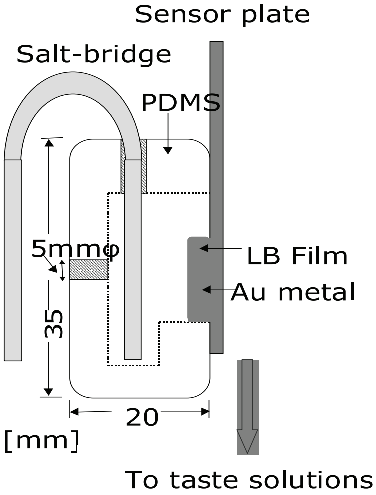

Fig. 1 New taste sensor holder

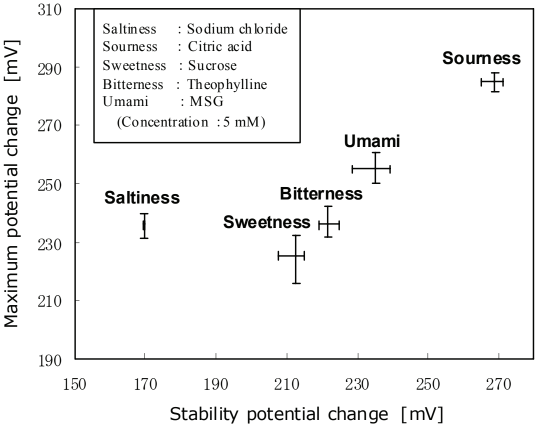

Fig. 2 Taste map for five basic tastes

P-057

AuQCM and Modified AuQCM Electrodes as Substrates for Phenazine Monomer Polymerization

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The electrochemical quartz crystal microbalance (EQCM) is a powerful tool that can be successfully employed to investigate electroactive films deposition mechanisms at quartz crystal based substrates, enabling the monitoring of both mass and current change during the deposition process.

Neutral red (NR) and methylene blue (MB), as electroactive phenazine monomers, can be electropolymerized, the corresponding polymers being widely used in sensors and biosensors. Interest has focussed on investigating how counterions and protons are involved in the redox process of the phenazine polymer, monitoring the mass change correlated to the ion exchange during the redox process [1]. The polymerization process of phenazine monomers is complex, and is still unclear, the aim of this work being to investigate the electropolymerization process by potential cycling of the monomers MB and NR on different substrates based on gold piezoelectric quartz crystals (AuQCM), with simultaneous gravimetric monitoring.

MB monomer was deposited at AuQCM and nanostructured ultrathin sputtered AuQCM (AuQCM/C), prepared as described in [2], and NR on AuQCM and on layer by layer films of hyaluronic acid with myoglobin deposited on AuQCM (AuQCM-$\{HA/Mb\}_6$, made following the procedure in [3]. The purpose was to investigate how the monomer chemical structure together with electrode morphology and surface roughness can influence the electropolymerization mechanism and properties of the phenazine-modified electrodes. The polymerization process of MB and NR differ which can be attributed to their different chemical structures and hydrophilicity. The substrates also influence the polymerization, ascribed to dissimilar monomer interaction with and adhesion at the electrode surface, which initiate the process. Cyclic voltammetry and electrochemical impedance spectroscopy were used to analyze the electrochemical properties of the PNR-modified electrodes and were compared with the unmodified AuQCM.

By comparing the results obtained at different AuQCM based substrates, valuable information can be obtained for future application of these modified electrodes in sensor and biosensor devices.

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P-058

Theory of Large-Amplitude AC Voltammetry for Reversible Redox Systems

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Ac voltammetry [1] is a powerful technique for interrogating electrochemical systems using an applied voltage. The voltage input consists of a dc ramp, $E_{dc}(t)=E_{in}-\upsilon t$, with a superimposed sinusoidal excitation, $E_{ac}(t)=-\Delta E\sin(\omega t)$. Existing theoretical results for the current response assume small amplitude sinusoidal excitations and the "slow scan limit approximation'' [2], where the frequency, ω, of the sine-wave is on a much faster time-scale than the rate of the dc ramp, υ. However, there are no theoretical estimates of the limits of accuracy of the slow scan limit approximation and the assumption of small amplitude sinusoidal excitations is very restrictive. Here we derive theoretical results valid for sinusoidal excitations of any magnitude, and include rigorous estimates for the error induced by the slow scan limit approximation. We also show how the Hanning window [3] can be used in conjunction with the FFT to remove the effects of spectral leakage and isolate the purely faradaic higher harmonics in the presence of large capacitance, as shown by the distinct peaks in the power spectrum in Figure 1. Using these results, we detail protocols for deriving the parameters describing the underlying electrochemical system from the experimental current response. The half-wave potential, $E^r_{1/2}$, can be deduced easily from the symmetry of the harmonic envelopes, as shown in Figure 2, while other parameters can be deduced from different features of the harmonic envelopes and the dc response. These simple protocols will greatly enhance the capability and applicability of this technique.

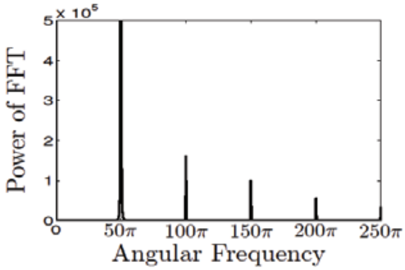

Figure 1: Power spectrum of FFT using Hanning window.

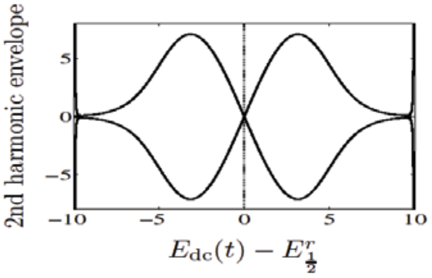

Figure 2: Envelope of 2nd harmonic with symmetry about $E_{dc}(t)=E^r_{1/2}$.

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P-059

A Mechanism Research of Charge Transfer Resistance by the Use of Conductive Atomic Force Microscopy and Electrochemical Method

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Electrochemical impedance spectroscopy (EIS) has been widely used in applications such as corrosion and biosensor over these decades. For the development of electrochemical sensor, the condition and property of electrode surface play a crucial role. The factors of how the surface property affects the electrochemical response have been studied for years; however, a more detailed research of the mechanism is still required. In a faradaic EIS, a Randles model is often used to fit the measured impedance data and the circuit element of charge transfer resistance (R_{ct}) dedicates the most of the impedance change. Apart from the energy potential of the redox pair, steric hindrance and electrostatic force are the two well known factors responded for the R_{ct} change. To further investigate how these two factors affect the R_{ct} element, we used both conductive atomic force microscopy (CAFM) and electrochemical method as tools. In this study, two novel conductive linkers, $HS\text{-}C_8H_7S_2\text{-}(CH_2)_n\text{-}COOH$ (n=3, 6), were used to form the self-assembled monolayers (SAMs) on the gold electrode. Besides, another two conventional thiol linkers, $HS\text{-}(CH_2)_{12}\text{-}COOH$ (12MCA) and $HS\text{-}(CH_2)_2\text{-}NH_2$ (Cysteamine) were also used for comparison. From the results of CAFM, it can be found that the conductivity of both conductive linkers is significantly higher than conventional thiol linkers. By the help of these conductive linkers, the steric hindrance effect of the conventional thoil linkers can be reduced greatly, especially for $HS\text{-}C_8H_7S_2\text{-}(CH_2)_3\text{-}COOH$ whose resistance is in the same order as that of the bare gold electrode. However, from EIS experiments performed in pH 7.2 PBS with 1 mM $Fe(CN)_6^{3-/4-}$, which is the condition usually applied in measurement of antibody-antigen interaction, we found that both conductive and non-conductive linkers with carboxyl functional groups shows the same orders of R_{ct}, which are around 1 MΩ. This is due to the deprotonation of carboxyl groups in high pH condition and induces large repulsive electrostatic force. In contrast, the R_{ct} of cysteamine is nearly the same with bare electrode because of the protonation of NH_2 group. This result indicates that the steric hindrance plays a much minor role between these two effects. This fundamental understanding can be very helpful in various kinds of surface researches and EIS biosensor development. For example, for faradiac type biosensors, conductive SAMs has recently been developed to lower the impedance baseline. Once the impedance baseline is lower, the measured current can be three orders higher than in the use of conventional long chain thiol linker, and further improve the sensor sensitivity and detection limit. By this understanding, we can further design a series of conductive linker to improve the sensor performance.

P-060

Salt Matrix Voltammetry

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The triple phase interface between electrode | ammonium chloride salt crystal | gas is investigated. It is shown that through microscopic contacts between the salt crystals and the electrode it is possible to carry out voltammetry and electroanalysis. Humidity plays an important role in this process due to the existence of a thin layer of water on the salt crystals therefore allowing a current to pass. The negative portion of the potential window is controlled by the amount of oxygen present in the system. Removal of the oxygen by means of passing argon gas through the electrochemical cell increases the size of the potential window allowing the possibility for gas sensing applications. Electro-deposition of copper is also investigated and it is shown that copper deposits are only weakly bound to the electrode surface.

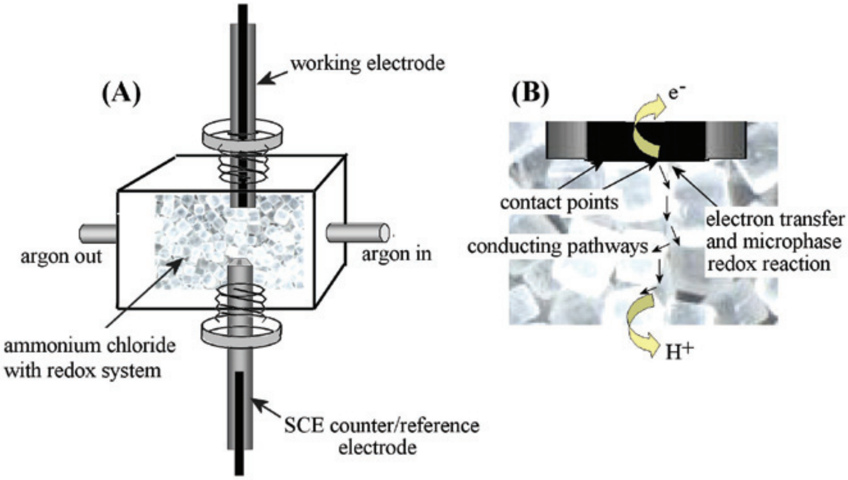

Figure 1. Schematic drawing of the electrochemical cell with an SCE counter/reference electrode and a gold disc working electrode. A redox system is immobilised onto the ammonium chloride crystals and gas such as argon is passed through the cell with defined relative humidity. (B) Schematic drawing of the redox process at the salt | electrode | gas triple phase boundary based on ion mobility across the salt crystal surface.

P-061

Wall Electric Polarization as a Stability Modifier for Wall-bounded Water Flow

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Stability modifiers, which are used to effect a desired change in wall-bounded flows, are those methods of flow control that alter the shape of velocity profile to minimize the linear growth of unstable waves in boundary layers [1]. Increase of net energy gain in two Norwegian hydroelectric power stations has proved that positive electric polarization of the wall is an efficient method for reduction skin-friction drag in water boundary layers [2]. Hypotheses for this reduction include the change of interfacial water properties during polarization of the wall [2, 3]. However, the precise mechanism of this effect is not clear yet what hampers to efficiently realize its potential benefits. Here we show that the measured averaged viscosity and density values of interfacial water on gold electrode decreases and increases, respectively, when the electrode potential is shifted towards the potential of zero charge. We found that the polarization of the wall towards pzc lowers the viscosity near the surface and makes the viscosity gradient along a normal from the wall surface less negative. That increases water flow velocity gradient near the wall and minimizes the linear growth of unstable waves, i.e. the wall electric polarization is likely to function as a stability modifier for wall-bounded water flow. The electric polarization is simple and low energy consuming what is a great advantage over the other stability modifiers such as wall heating or cooling, wall motion, suction, shaping. We anticipate our results to be starting point for more sophisticated and effective use of applied potential to actively manipulate a wall-bounded liquid flow field to effect a desired change.

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P-062

On-Chip Electric Field Driven Electrochemical Detection using Boron-Doped Diamond Microelectrodes

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The miniaturisation of electrochemical devices has been gaining renewed attention as a consequence of the rapid development within the field of lab-on-a-chip systems[1]. This owing to the fact that electrochemical devices can be readily miniaturised without loss of performance through the use of standard microfabrication techniques.

The main on-chip application of electrochemistry entails electrochemical detection (ED) in capillary electrophoresis (CE)[1,2]. The main problems associated with this application are interferences due to the presence of the CE electric field[3,4] and uncertainties in the positioning of the electrodes[1,2]. Klett et al.[5] demonstrated that the influence of the separation electric field on ED can be eliminated by ensuring that the detection and reference electrodes are positioned on an equipotential surface. It has also been shown[6] that the separation electric field can be used for detection by measuring the current between two microband electrodes in the end column detection mode. The electric field can then be use to drive amperometric detection anywhere within a microfabricated flow channel containing an array of microband electrodes[7].

Our present study[8] aims at the development of electric field driven ED techniques for inclusion in chip-based devices. Following the procedure described elsewhere[7] it will demonstrate that by using a different and more stable electrode material, the external electric field can be employed to drive amperometric detection between two electrodes in an array of 20 boron-doped diamond microband electrodes. This enables the ED of electroactive species such as ferro/ferricyanide, ascorbic acid and dopamine.

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E.O. Jorge would like to thank the Portuguese FCT for the financial support.

P-063

Conductometric Hydrogen Gas Sensor Based on Electrochemically Deposited Polypyrrole Nanowires

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Nanostrucrued conducting polymers and their nanocomposites are considered attractive materials for gas sensing due to their high surface to volume ratios and room temperature operation [1,2]. Controllable deposition of polypyrrole (PPy) nanowires can be achieved through electropolymerization [3]. In this work, PPy nanowires were electrodeposited on an conductometric interdigitated transducer and characterized with scanning electron microscopy (SEM) as shown in Fig. 1, as well as Raman spectroscopy (Fig. 2). The sensor was tested towards different concentrations of H_2 gas, at room temperature (Fig. 3).

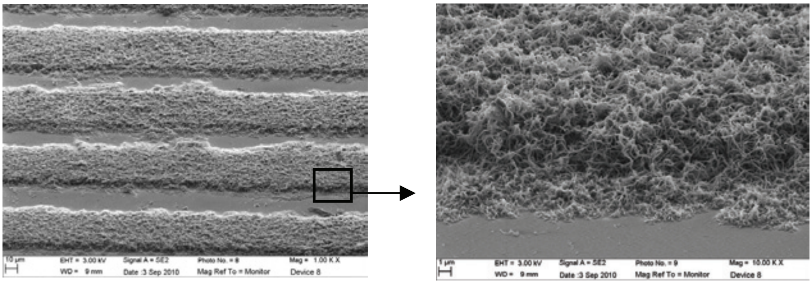
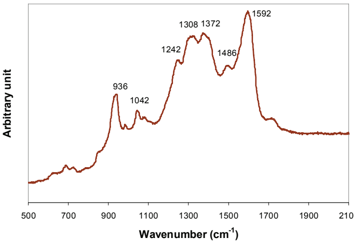


Fig. 1. SEM images of the sensor's surface.



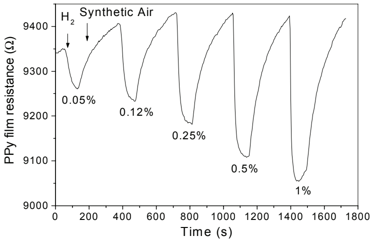


Fig. 2. Raman spectrum of PPy.

Fig .3. H_2 gas sensor dynamic response.

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P-064

The stabilization of charged states at phenazine-like units in polyaniline under p-doping: An *in situ* ESR-UV/vis/NIR and ATR-FTIR spectroelectrochemical study

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Since the early works on polyaniline (PANI) structures [1,2] it is obvious that phenazine rings have to be considered as a part of the polyaniline chain. The role of phenazine-like units on the stabilization of charged states in PANI was studied by *in situ* FTIR and ESR-UV/vis/NIR spectroelectrochemistry. The comparative FTIR studies of electrochemically prepared PANI and its copolymers with different ratios of phenosafranine monomer give evidence on the existence of phenazine-like units in PANI. During p-doping of PANI *in situ* FTIR spectra with characteristic vibrations of linear structures are observed together with a new peak at 1540 cm^{-1} attributed to the changes induced in the phenazine-like units (Fig.). The potential dependence of IR bands at 1572, 1476, 1318, 1250 and 1145 cm^{-1} observed during oxidation was compared to that of the ESR and the absorption data [3] and points to the diamagnetic species like π-dimers formed at higher oxidation level of PANI. By the potential dependence of the IR line at 1540 cm^{-1} it was shown that the part of π-dimers in the polymer is stabilized at the link of the phenazine unit to the linear PANI segment while the linear aniline segment stabilizes the polaron and the polaron pair in the PANI structure in the initial oxidation [4]. By the combination of *in situ* ATR-FTIR and *in situ* ESR-UV/vis/NIR spectroelectrochemistry on the role of the phenazine structure in the stabilization of charged states during p-doping of polyaniline can be clarified.

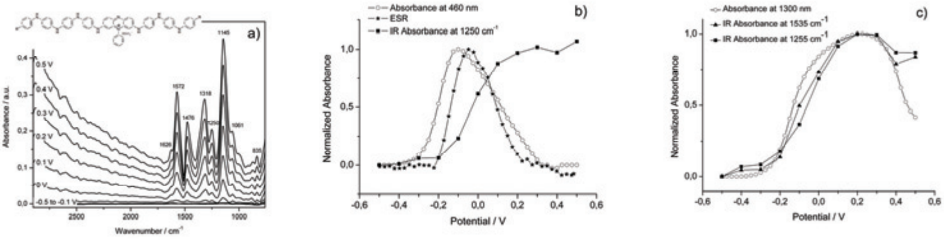

Fig. (a) *In situ* ATR-FTIR spectra during the anodic oxidation of PANI. Potential dependence of the spectroscopic data during oxidation of PANI (b) and its copolymer (c).

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P-065

Electroreduction and Sensing of Dissolved O_2 and H_2O_2 on a Polypyrrole/Magnetite Hybrid Electrode

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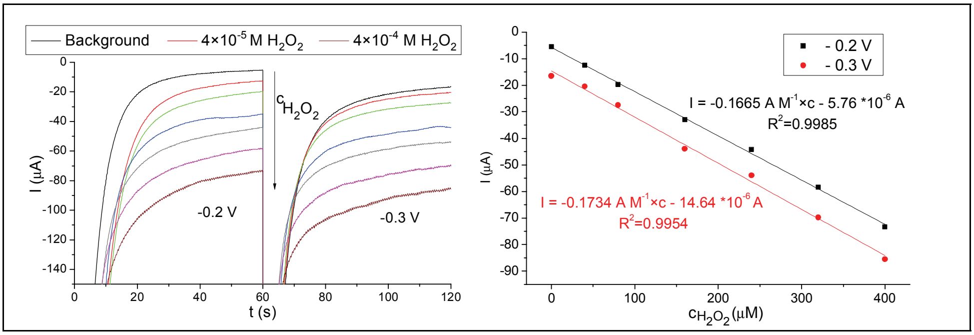
Conducting polymer based magnetic (nano)composite electrodes are still in the focus of research and development, because these materials show both high electric conductivity and magnetic susceptibility and can be used for instance as electrocatalyst in several electrochemical processes.

Although polypyrrole and PEDOT [1] layers are proved to be active in the electrocatalytic oxygen-reduction reaction alone, they are often combined with different ferrites to enhance the activity. Magnetite (Fe_3O_4) nanolayers are prominent candidates for electrocatalytic applications due to the redox switching between Fe^{3+}/Fe^{2+}. This behavior can be exploited in different processes, such as the O_2 or H_2O_2 reduction.

Magnetite/Polypyrrole hybrid layers were electrochemically deposited on gold electrode by exploiting the chemical interaction between the nanoparticles and the conducting electrolyte (K-tetraoxalate) [2]. These electrodes showed sensitivity during the electrochemical measurements toward the dissolved molecular oxygene, which effect could be enhanced by illumination with white light, where the photocurrent was the consequence of the electrochemical decomposition of the intermediers, primarly the hydrogen-peroxide.

To justify this theorem independent measurements were carried out which aimed at the electrochemical decomposition of hydrogen-peroxide. Our chronoamperometric experiments proved, that the hybrid electrode can detect really small, even 40 µM of concentration H_2O_2 in aqueous phosphate buffer (c=0.5M, pH=7), and can be calibrated with excellent linearity. This brings up the opportunity of its application in electrochemical sensors.



Based on our results, further studies on the detection of H_2O_2 in the presence of oxygen are in progress, and will be presented.

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P-066

Electro-catalytically Propelled Nanomotors for Chemical Sensing Approaches

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Nanomotors open new opportunities for both microfluidics and chemical sensing. Such flow systems can be considered nanofluidic chips where the solid phase is moved instead of the liquid. The movement of electro-catalytically propelled nanomotors can be controlled by several means:

First we illustrate how to influence the movement of bimetallic nanowire motors by applying short heat pulses to accelerate them or to slow them down. The accelerated motion observed during the heat pulses is attributed to both the thermal activation of the redox reactions of the hydrogen peroxide fuel at the platinum and gold segments and to the decreased viscosity of the aqueous medium at elevated temperatures. The thermally influenced motion during repetitive temperature pulses is highly reversible and fast.[1]

We also report on the electrochemically controlled movement of bimetallic nanomotors. By placing a gold microwire electrode in close proximity to the plane of the nanomotors and applying different potentials, we achieved a cyclic 'on' and 'off' electrochemical activation of the nanomotor motion. These effects can be attributed to the depletion of hydrogen peroxide or formation of dissolved oxygen during either negative or positive polarization.[2]

Furthermore, we exhibit the first example of motion-based chemical sensing based upon bimetallic nanomotors. We performed highly selective and sensitive detection of silver(I) based upon the dramatic acceleration of Au-Pt nanomotors in the presence of this analyte. Remarkable specificity was observed in comparison to ten other metal ions. The surprising effect of silver ions upon the speed of Au-Pt nanomotors is attributed to the electroless deposition of silver onto the wires in the presence of the fuel hydrogen peroxide.[3] A similar effect had been observed when using Au-Ag alloys as the second component of the nanomotors. This composition obviously leads to enhanced electrochemical reactivity at the nanomotor surface.

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P-067

Electroanalytical Behavior of Rutin at Screen-Printed Electrodes

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Electroactive groups in the structure of rutin could turn electroanalytical techniques an interesting alternative for the determination of this analyte. However, the capacity of rutin or its oxidation products to adsorb strongly on the working electrode surface[1] may limit the application of these methods for the determination of this flavonoid, which can be circumvented with the use of disposable electrodes. This study aimed to determine the electroanalytical behavior of rutin using screen-printed electrodes as working electrodes. It was found that the electrochemical profile of rutin is consistent with that observed in other types of carbon electrodes in previous works[1,2], in an adsorption-involved and a pH-dependent oxidation process. The replacement of electrodes between the analysis ensured rapid analysis, good reproducibility and repeatability, adequate linearity (r = 0.998) and low detection limit (62.22 µg mL^{-1}), as can be seen in Figure 1:

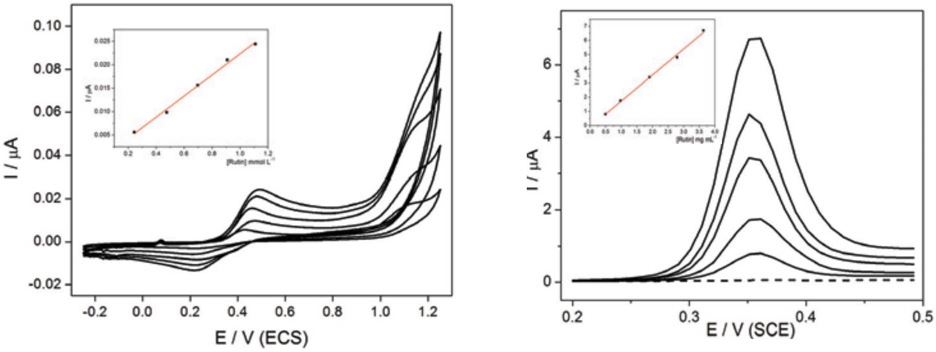

Figure 1 – Cyclic voltammograms (left) and differential pulse voltammograms (right) of five successive additions of rutin standard solution and their respective calibration curves at screen printed carbon electrodes (Phosphate buffer 0.1 molL^{-1}, pH 5.0-6.0)

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P-068

Determination of Tl(I) by Square Wave Anodic Stripping Voltammetry with Bismuth Film Modified Electrodes

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During the last decade, bismuth film electrodes (BiFEs) have become attractive in electroanalytical research as substitutes for mercury electrodes in stripping voltammetry. A Bi film on a solid electrode substrate has similar electrochemical properties to mercury films in terms of potential window and ability to electrodeposit other substances on its surface, due to the ease of the nucleation process, by formation of intermetallic compounds or fused alloys [1,2]. The sensitivity of Bi electrodes depends on BiF deposition conditions and electrode substrate, electrolyte medium, and deposition time [2].

Thallium is a toxic metal, most used in the electronic and pharmaceutical industries, so that is important to monitor the quantities of Tl in industrial residues and in quality control in the pharmaceutical industry. Anodic stripping voltammetry at BiFE has been applied for heavy metal determination, in particular Cd and Pb [2]. However, other metal ions, such as Tl(I), In(III), Cu(II) and Hg(II) [3,4] can also be determined using square wave anodic stripping voltammetry (SWASV).

In this work, electrodes modified with BiF were applied to the determination of Tl(I), as well as Zn(II) and Pb(II) in acetate buffer pH 4.0, by SWASV, separately and as mixtures. The bismuth films were electrochemically deposited *in situ* onto glassy carbon and carbon film electrodes (GCE and CFE). The BiFE was also tested for the determination of these heavy metals in tap water and juice samples.

It was found that the sensitivity to Tl on Bi film electrodes does not depend on the presence of the other ions. The sensitivity was better at carbon film electrode substrates, 0.183 μA cm^{-2} nmol^{-1} L, although the limit of detection, ~2 nmol L^{-1}, did not depend on the electrode substrate.

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P-069

Development of a Simple and Fast Voltammetric Procedure for Determination of Trace Quantity of Bi (III) in Natural Water Samples

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In recent years bismuth has become environmentally significant element because its chemical and physical properties have led to its use in various areas of life (e.g., semiconductors, cosmetic preparation, medicines, alloys, metallurgical additives and recycling of uranium nuclear fuels). As a consequence, bismuth determination in environmental and biological materials is desirable and important.

The main aim of this work was to set a new electrochemical method for the determination of trace amounts of bismuth based on adsorptive stripping voltammetry at a hanging mercury drop electrode (HMDE) using cupferron as a complexing agent. This technique is favor among the different electrochemical methods because of high speed of operation, excellent sensitivity and precision. The effects of various parameters were studied in order to obtain optimal conditions. The accumulation of Bi(III)-cupferron complex was carried out at +0.05 V for 30 s from the stirred solution and then, after the equilibration time of 5 s, the voltammogram was recorded by applying the potential scan from +0.05 to -0.4V. Although a various number of the procedures for Bi (III) determination have been proposed, only in some procedures the interferences from organic matter were taken into account. The most common interfering compounds are surfactants and humic substances. It is known that they are easily adsorbed at the HMDE surface and disturb the voltammetric signal of the determinated metals. There are no propositions of procedures where the effect of these interferences has been precisely examined and eliminated. All kinds of surfactants such as anionic (SDS), cationic (CTAB), nonionic surfactant Triton X-100, and a humic acid (HA) were tested in proposed procedure. As it was assumed, these compounds caused significant suppress the AdSV response. In this work, to develop elimination of these substances, the adsorptive properties of Amberlite XAD-7 resin were exploited. The addition of resin eliminates the unwanted negative influence of the cationic and anionic surfactants on bismuth peak heights, even 10 ppm of these surfactants do not affect the voltammetric signal. In the case of Triton X-100 the concentration of 5 ppm causes a decrease of the voltammetric signal to 50 % of its original value.

The novelty of the procedure investigated in this study lies in the fact that bismuth speciation can be performed directly in natural water samples containing organic substances without matrix removal or any sample pretreatment. The experimental results of the analysis of the samples collected from Bystrzyca river and Lake Zemborzyce gave good recoveries. It holds great promise for exploiting this method for environmental and industrial monitoring of Bi (III).

P-070

Sensitive Adsorptive Stripping Voltammetric Method for Direct Determination of Trace Concentrations of Lead in the Presence of Cupferron in Natural Water Samples

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Heavy metals are essential pollution of water samples as being dangerous for human health. Among them lead is of particular interest because of its toxicity and widespread presence in the environment. Even small amounts of lead that enter the environment can result in its elevated concentrations and consequently in its accumulation. Therefore, the great emphasis is laid on the monitoring of lead in environment.

In the last years, a variety of techniques have been developed for trace determination of lead in water samples, among them adsorptive stripping voltammetry (AdSV) has been recognized as a powerful tool owing to its sensitivity connected with relatively inexpensive instrumentation. The use of several complexing agents, e.g., oxine, a combination of dimethylglyoxime and oxine, xylenol orange for the adsorptive collection of complexes with lead on the hanging mercury drop electrode (HMDE) has been previously described. In these procedures it was ascertained that organic matter present in natural samples caused interferences so UV-digestion of samples had to be employed before Pb(II) determination. Among those procedures, only in two cases the problem connected with organic matrix of natural water samples was examined more precisely and it was found that just as little amount of Triton X-100 (nonionic surfactant) and SDS (anionic surfactant) as 0.02 ppm reduced the peak current of Pb(II) to 88 % of the initial value and 0.5 ppm of Triton X-100 caused the complete suppress of peak for Pb(II).

In this communication, the possibility of direct AdSV determination of Pb(II) in natural samples without need of UV-digestion is described. This procedure is based on the adsorptive accumulation of Pb(II) complexes with cupferron (N-nitroso-N-phenylhydroxylamine) using hanging mercury drop electrode (HMDE). In standard condition the presence of even 5 ppm and 3 ppm of SDS and Triton X-100, respectively does not influence the peak current of Pb(II). The effect of cationic surfactant was also tested and it was stated that CTAB representing cationic surfactant does not decrease Pb(II) peak current even at its concentration equal to 30 ppm. There are no procedures of Pb(II) determination using AdSV where the effect of humic substances (HS) has been investigated. In the presented communication such experiments was executed and it was found that 1 ppm of HS does not disturb Pb(II) signal whereas 2 ppm of HS decreases it to 74 % of initial value.

The presented procedure was successfully applied to determine lead in natural waste water samples such as a river water samples. Major advantage of the proposed procedure is a considerable reduction of analysis time, whole time of measurement is about 5 min. whereas in the procedures described previously UV irradiation even for 2 h is recommended before analysis in order to destroy organic matter.

P-071

All-solid-state lead(II) electrochemical sensors based on electronically conducting polymer and *p*-tert-butylcalix[4]thiomides as ionphores.

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Monitoring of the activity of chemical or biochemical species in the environment is an important issue in time of growing industry and technology [1]. The selective binders and carriers used in analytical sensors are often based on the calixarene structure due to specific properties of this macrocyclic molecules [2]. We present here three derivatives of *p*-tert-butylcalix[4]thiomides **1**, **2** and **3** **(**Figure 1.) which differ by the type of carried thioamide group. Compounds **1** – **3** were applied as ionophores in solid-contact ion-selective membrane electrodes with conducting polymer as ion-to-electron transducer. Potentiometric measurements were carried out to study the analytical performance of the electrodes. The potentiometric response of the electrodes were studied for a series of cations to determine potentiometric selectivity coefficients. The obtained analytical parameters of the solid state-ISE were compared to the results with ion selective electrodes with internal filling solution.

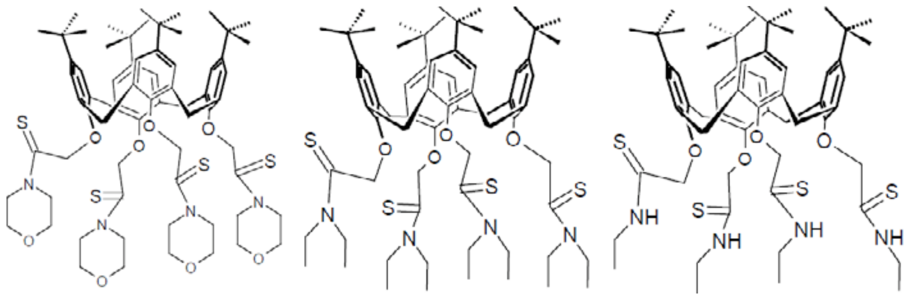

Figure 1. The studied compounds **1** – **3**

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P-072

Water uptake of ion-selective membranes measured with the oven based coulometric Karl Fischer titration method

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In solid-contact and coated-wire ion-selective electrodes (SCISEs; CWEs), thin aqueous layers or scattered islands of water can be formed at the substrate/solid-contact (SC) or the SC/ion-selective membrane (ISM) interfaces due to the water uptake of the outer ion-selective membrane (ISM). The diffusion of interfering ions through the ISM into the aqueous layer or the water pools may lead to drifting potentials and it is therefore essential to use hydrophobic ISM membranes to decrease the water uptake of the CWEs and SCISEs.[1] The aqueous water layer test was proposed by Fibbioli et al. to prove the presence of the water layer in CWEs and SCISEs.[2] In the case of the SCISE, the water uptake can affect the limit of detection (LOD) and also result in decreased adhesion of the ISM/solid-contact (SC) and the SC/substrate interface.

The water uptake of ISMs has previously been studied by the FTIR-ATR technique and it was shown that the water uptake of plasticized poly(vinyl chloride) (PVC) membranes were much higher than for silicone rubber (SR; RTV 3140).[3,4] It was also recently shown that a Ca^{2+}-selective SCISE based on polyaniline nanoparticles and silicone rubber was beneficial in obtaining a LOD of 2×10^{-9} M. The water uptake of SCISEs was also recently studied by Veder et al.[5]

This work will focus on the quantification of the water uptake of plasticized PVC and SR based ISMs measured by the oven based coulometric Karl Fisher (KF) titration method. Two different membranes types were studied: 1) Membranes consisting of only the membrane matrix (plasticized PVC and SR; 2) Membranes containing the membrane matrix, 0.8 wt% Ca^{2+}-ionophore (ETH5234) and 0.45 wt% lipophilic salt (potassium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (KTFPB). The membranes were asymmetrically (from one side) and symmetrically (from both sides) contacted with deionized water and $CaCl_2$ electrolyte solution for 0-48 hours. The water content of the PVC and SR membranes determined with the coulometric KF-method is compared to water uptake measured for the same membrane types with the FTIR-ATR technique.

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P-073

Electrochemical sensors for analysis in chemical processes

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The process analysis uses online- as well as atline- analytical methods. Online-analyses are applied directly and without sampling in a current production or manufacturing process on site. Atline-methods comprise manual or (semi-) automated sampling and measurement near by the production chamber [1]. In particular, the online- process analytics becomes increasingly important, for example in chemical and pharmaceutical manufacturing, in agriculture or in environmental protection. Many processes are characterized by high pressures and temperatures resulting in on-site measuring systems with particular high demands. Because of this issue it is necessary to consider during a development the material resistance and leakage problems in addition to basic sensory functions.

The poster presents suitable electrochemical sensors for the determination of redox potential and conductivity (see *Figure 1*) at temperatures > 150 °C and pressures up to 150 bar. The sensing elements exposed to the process media are made of special screen-printed sensors and guarantee a high and long-term stability. The tightness of the sensor heads to the ambient medium could be achieved by a newly developed embedding of the screen-printed sensors.

The determination of the redox potential as a typical example for the use of potentiometric sensors requires an electrochemical reference electrode. The extreme conditions need a solid-state design. *Figure 2* shows the set-up of the newly developed half-cell based on an polymer filled with a solid-state electrolyte [2].

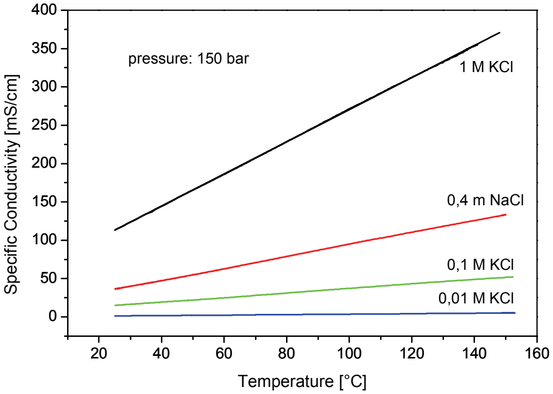

Figure 1: Specific Conductivity of aqueous KCl / NaCl – solutions up to 150 °C measured with a screen-printed conductivity sensor

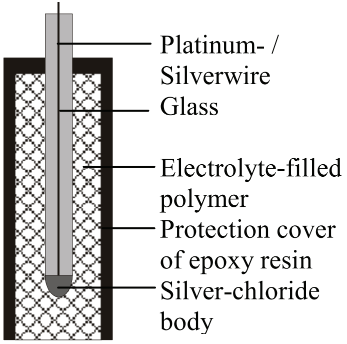

Figure 2: Schematic drawing of the reference half-cell

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P-074

Improved Internal Reference Oxygen Sensor with Composite Ceramic Sensing Electrode

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Oxygen sensors are widely used in industries for combustion control and environment pO_2 monitoring. The typical potentiometric oxygen sensor, usually operated at high temperature such as 750 °C, employs air as reference gas and Pt as both electrodes. This type of sensor needs a duct to deliver reference air. This limits miniaturization and application adaptability of the sensor. Using Pt as electrodes and applying the sensor at high temperature also implies high fabrication and operation cost.

We developed an internal reference oxygen sensor (IROS), which is free of reference air and uses the equilibrium pO_2 of Ni/NiO as internal reference (IR). The sensor uses composite ceramics as the sensing electrode instead of the precious metal Pt. The sensor voltage agrees with theoretical voltage down to 400 °C, even lower (Fig. 1) for some of the ceramic electrodes. Within 200 hrs operation, including thermal (260 - 660 °C) and pO_2 (varying from < 7e-3 atm to 1 atm) cycling, no voltage drop occurred for the cell with composite ceramic as sensing electrode. If the NiO starting material in the IROS is not reduced sufficiently before operation, its voltage will drop too early during long term operation due to the unavoidable tiny leakage of oxygen into the IR. However the degradation is recoverable by reducing the NiO again. After the recovery, the cell again had theoretical response voltage and worked stably (Fig. 2). The time constants of the sensor were characterized with electrochemical impedance spectroscopy.

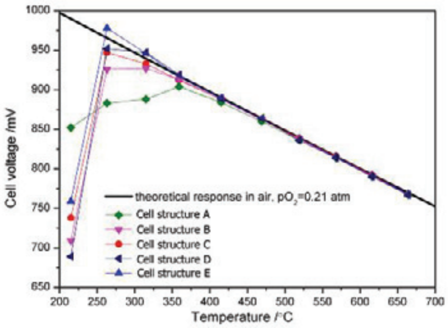

Fig. 1. Measured cell voltage versus temperature, showing good agreement of measured voltage with theoretical voltage down to below 400°C.

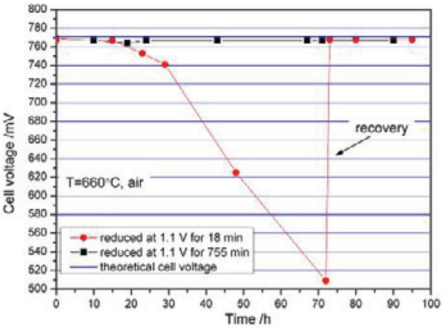

Fig. 2. Measured cell voltage versus time showing the recoverable degradation.

P-075

Fabrication of Microelectrochemical Cell by Screen Printing

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There has been a considerable recent interest in the micro-electrochemical cells owing to their promise for a wide range of future technological applications [1]. In this work, the micro-electrochemical cell was fabricated by screen printing. Screen-printing has the following characteristics: drawing precise pattern of micron order, a wide variety of inks, printing thick film and low cost. As mentioned above, we think that screen-printing is adequate to fabricate the micro-electrochemical cell.

Figure 1 shows the micro-electrochemical cell. Two glass slides (glass slide A, and B) are used as substrates. A flow channel was formed on the glass slide A by printing a glass paste. Carbon working and counter electrodes were formed on the glass slide B. Ag/AgCl reference electrode was also formed on the glass slide B. Glass slide A has two holes to inject and eject a solution. The glass slides were sealed by using ultraviolet curing UV ink which printed on the each glass slides.

Figure 2 is the cyclic voltammogram (CV) obtained by the micro-electrochemical cell at different flow rates. The concentration of $K_3Fe(CN)_6$ is 10 mM and the potential scan rate is 20 mV / s. Diffusion limit current was observed below -0.2 V and these current depended on the flow rate. In the present paper, we discuss the characteristics of the microelectrochemical cell.

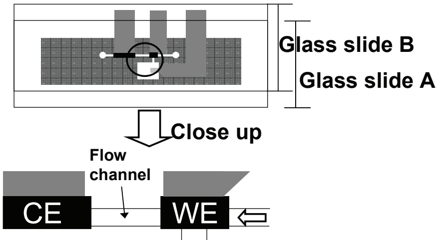

Fig. 1 Schematic illustration of the micro-electrochemical cell

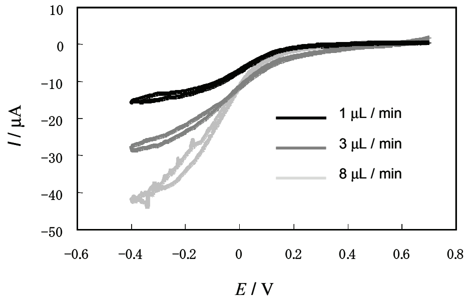

Fig. 2. CV obtained by the microelectrochemical cell at different flow rates in 10 mM $K_3Fe(CN)_6$ solution. The scan rate was 20 mV/s.

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P-076

Calcium Ion-selective Electrode for Measurements in the Presence of Dodecylsulfate

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Water hardness ions reduce the efficiency of surfactants as detergents. Therefore, control of water hardness ions, e.g. Ca^{2+} in the presence of surfactants is of practical relevance. Ion concentration in various samples is routinely measured by ion-selective electrodes (ISEs), which are supposed to obey the Nernst law. The target ion activity in calibrators is related to the ion total content and the ionic strength of the calibrator by e.g. the Debye-Huckel theory. However, use of ISEs, in particular of Ca^{2+}-ISEs in the presence of surfactants is problematic because of 2 major obstacles: (i) surfactants, being relatively lipophilic, interfere with the response of ionophore based ISEs, and (ii) metal ions, e.g. Ca^{2+} interact with surfactant ions and micelles, so the metal ion activity cannot be directly related to its total content.

In this work we tried to find a formulation for a Ca^{2+}-ISE membrane capable of working in the presence of a typical surfactant: sodium dodecylsulfate (SDS), and, in parallel, to find a way of estimation of Ca^{2+} ion activity in mixed aqueous solutions containing SDS and $CaCl_2$. PVC membranes of 11 formulations with various Ca^{2+}-selective ionophores and ion-exchangers and different plasticizers have been studied together with a DS^--selective electrode based on tetradecylammonium, and a Na^+-selective glass electrode. The correction for $CaDS_2$ precipitation was made using the DS^- ion activity measured with the DS^--ISE. The content of Ca^{2+} ions in the DS^- micelles was estimated using Na^+ ion activity measured with the Na^+-ISE, and assuming different values of Ca^{2+}/Na^+ exchange constant between micelles and solution phase ($K_{Ca/Na}$). The $K_{Ca/Na}$ value was therefore an adjustable parameter, which, when true, must be constant.

The results suggest that all the membranes studied can be divided into 3 groups. Group 1 includes membranes with low-selective ion-exchangers: thenoyltrifluoroacetone and potassium tetrakis(p-chlorophenyl)borate. These ISEs showed strong interference from Na^+ and, possibly, also $CaDS^+$. Group 2 includes membranes based on neutral ionophores ETH 129 and ETH 1001, and also a membrane based on charged ionophore calcium bis(tetramethylbutylphenyl)phosphate (CaR_2) in dioctylphenylphosphonate. These ISEs showed strong interference from DS^- ions. Group 3 consists of moderately selective membranes which showed promising results in pre-micellar solutions. Among these membranes, the one based on CaR_2 in trioctylphosphate showed near-Nernstian response also in micellar solutions when the assumed value of the adjustable parameter was constant: $K_{Ca/Na} = 200$, whatever was the total content of $CaCl_2$. Thus Ca^{2+}-ISEs with this membrane appear promising for Ca^{2+} control in the presence of surfactants.

P-077

Immobilization of Pyrroloquinoline Quinone on Carbon Nanotubes

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Pyrroloquinoline quinone (PQQ) is the cofactor of many alcohol or sugar oxidising enzymes, which are candidates for biosensors. Because of its fast redox kinetics, it can also be used as a mediator for less reactive biomolecules. It is then vital to study the electrochemistry of PQQ to understand how these enzymes and molecules work in sensor applications. However, PQQ does not react readily on metal or carbon electrodes and surface modification is usually required [1]. In this study, we present a simple way of immobilizing PQQ on carbon nanotubes.

Few-walled carbon nanotubes (FWCNT, diameter 10 nm) were drop-casted on a glassy carbon electrode. Then the electrode was dipped in PQQ solution. After dipping, the electrochemical response of the electrode was studied by cyclic voltammetry (CV). The results at different pH values are presented in Figure 1. The response is strong and reversible over a wide pH range compared to some other techniques [2]. Stability of the electrodes was also studied and different immobilization substrates were compared.

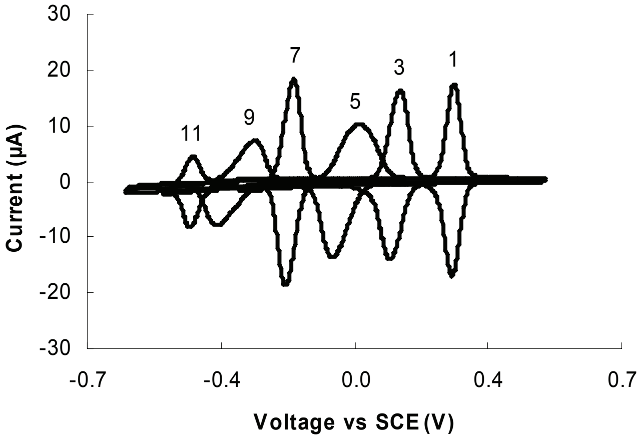

Figure 1. CVs measured from the PQQ-FWCNT electrodes at pH 1-11 (at 10 mV/s).

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P-078

Design of New Electrocatalytic Nanocomposite Electrode Materials for Voltammetric Sensors

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Miniaturisation of electrode systems is today an unquestionable trend in electroanalytical chemistry. Development of electrochemical sensors on the base of metal nanoparticles is one of novel and perspective way for fabrication of miniaturized electrode systems. Modification of electrode surfaces by catalytically active metal deposits with nanosize dimensions allow to obtain ensembles of nanoelectrodes. It also leads to improvement of electroanalytical properties of such systems in comparison to traditional macroelectrodes and , in most cases, allows to decrease of the cost of electrodes, especially made from noble metals.

In this work, we investigate the performance of a novel electrode materials based on a set of gold and palladium ensembles in PEDOT matrix. For fabrication of metal ensembles we used an electroless deposition of gold and palladium nanoparticles in PEDOT films on GC substrates. The density of particles on the electrode surfaces and into volume of polymer films was varied by time of deposition and concentration of metal ions into solutions. The structural morphology and chemical composition of electrodes were characterized by SEM, TEM and EDX-analysis.

Electrochemical behavior of nanoparticles array electrodes was studied in solutions of phosphate buffer (0.2M PBS) in the absence and presence of hydrogen peroxide with different concentrations. It was found that in both cases the electroreduction process predominantly proceed on palladium or gold nanopartiles. The obtained kinetic data show that with an increase of density of Au particles on the glassy carbon surface and in composite films the limiting currents of electroreduction are increased and reach a saturation at highest Au-loading. Similar behavior with much more expressed catalytic activity in respect H_2O_2 electroreduction was observed in the case of Pd/PEDOT/GC electrodes. The porous network structure of PEDOT support an effective dispersion of Pd and Au particles and facilitates an easy access of reagents to the catalytic sites. Amperometric method was used to examine the sensitivity of different sizes of AuNPs and PdNPs immobilized electrodes towards the detection of H2O2. The comparison between all investigated systems was made. The authors are thankful to the Russian Fund for Basic Research for financial support of this work (grant № 10-03-00793) and Saint-Petersburg State University for a research grant 12.15.313.2010.

P-079

Rapidly renewable metal annular band electrodes

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Metallic and amalgam electrodes are widely used in electrochemistry for several dozen years [1,2]. Voltammetric measurements require application of the electrodes which are characterized by the perfectly repeatable and reproducible surface and long periods of parameter stability. Additionally, the regeneration / activation / modification procedure applied between recordings should be short and simple. The mechanical and chemical polishing or electrochemical activation are recommended in the literature as renovation methods suitable for solid electrodes. However, these methods are time-consuming and require transfer of the working electrode between systems specified by the different chemical and physical parameters. Therefore the solid electrodes are relatively rarely applied in the routine analytical practice.

An original construction of Au and Ag annular band electrodes and a simple device for fast electrochemical renovation of the electrode surface before each measurement, is presented in the work.

The practical usefulness of the presented electrodes, device and method of the fast electrode surface renovation was confirmed in a large number of experiments. The applied electrodes were renovated short before the measurement and are stored inside the device between recordings. The electrode was reactivated either before the series of measurements or before each one. Long time stability of metrological parameters of the electrode and reliability of the device components were observed. The analytical applicability of the metallic annular band electrodes was confirmed in quantitative determination of Pb(II) and Cd(II) at nanomolar concentrations in the synthetic solutions with and without surfactants and in the certified reference materials. The experiment was performed using underpotential deposition stripping voltammetry (UPD-SV). A very low rate of surfactants adsorption on these electrodes in comparison to HMDE was observed. Also the advantage of the tested electrodes was possibility of working in the presence of oxygen. The advanced signal processing procedures were applied for curves transformation and extraction of the maximum relevant information from the experimental data [3].

Acknowledgements
This work was supported by AGH University of Science and Technology grant (Project No. 11.11.160.799).

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P-080

Application of the amorphous oxides for sample purification for environmental analysis with voltamperometric sensors

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Voltamperometric sensors due to wide range of linear signal response in relation to the analyte concentration, high sensitivity and selectivity, relative inexpensive instrumentation and possibility of miniaturization are favorable in the environmental analysis. In case of portable instruments, the voltammetric sensors may be applied in the field. The main disadventage of such sensors is their sensitivity to non-specific interferences from organic compounds, especially if the contaminants have surface active properties. Besides compounds of antropogenic origin, like surfactants, in the environment there are presented humic and fulvic acids, products of putrefaction processes. In the most common analytical practice to remove them, several methods of sample digestion are applied. The important disadventage of such metods is the difficulty to use them on the spot and complete loss of speciation. The alternatives are more gentle methods consisting in adsorption of the surface active substances on various adsorbers. Most of them may be used in the field. However, not complete removal of the interfering organic compounds, the possibility of adsorption (i.e. loss) of analyte and interaction with the sensor are the weakness of the mentioned procedure.

Several amorphous oxides have been examined as the adsorbers. Among others the most promising are silica dioxide [1] and titanium dioxide. Due to large specific area exceeding 50 m^2/g they adsorb readily surface active substances. Selectivity and efficiency of adsorption depends on type of supporting electrolyte, its concentration and pH. The microstructure of adsorber is very important for efficiency of adsorption as well as for class of surfactants which are effectively removed. Not only the specific area, but also the pores and particle size distribution is important factor in the adsorber choice.

In the present work the different ceramic micro- and nanopowders of titanium dioxide [2] were tested in order to selectively remove surface active substances. The process is enhanced by photocatalitic properties of some types of TiO_2 powders.

Acknowledgements
This work was supported by AGH University of Science and Technology grant (Project No. 11.11.160.799).

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Journal of Nanoscience and Nanotechnology 10(2010)1032-1042

P-081

Electrochemical Identification of Hydrogen Purity For Usage In PEM fuel cells

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Hydrogen, for using in fuel cells is generally produced by variety technologies with different grad of purity. Hydrogen produced from hydrocarbon fuels or other organic compounds generally contents sulphur compounds particularly H_2S and it needs preliminary purification before using in fuel cells applications.

PEM fuel cells are very sensitive to purity of hydrogen than other fuel cells. Last time many attempts for using hydrogen which produced from sodium borohydride (SBH) by hydrolysis method at present of different kind of homogen and heterogen catalysts. Determination of purity of produced hydrogen is very difficult in this case with variety of boran compounds probably are formed in the reactions.

Present research deals with to studying of purity of hydrogen which produced by catalytic hydrolysis of SBH. For this, working condition of anode electrode-catalysts in PEM fuel cell is applied to indicator electrode in simple electrochemical system.

This system alloys to establish H_2 quality.

P-082

Spectroelectrochemical properties of meta substituted monomers with benzene as core center

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Electrochemical sensors and detectors being inherently sensitive and selective towards electroactive species, fast and accurate, compact, portable and inexpensive are very attractive for quick on-site monitoring of various species including dangerous chemicals like carbon oxide, pollutants, environmental monitoring or even clinical analysis. Although many such devices are already used new materials for its production are still widely examined. Among all conductive polymers start to play very important role.

Generally, in conjugated polymers *meta*-substitution is avoided due to the conjugation interruption, and hence worse conductivity than polymers with *para*-substitution. However, in some cases *meta*-linkage could be very useful e.g. when considering receiving of dendrimers or conducting foam-like or crosslinked layers being more sensible for environment and/or resistant for mechanical damage.

A series of various symmetric monomers containing *meta*-linkage were studied. Monomers consist of benzene as core center and attached thienyl, furyl, EDOT and carbazole groups.

All monomers are electroactive and undergo at least two-step oxidation, moreover polymerize in the first oxidation step. Electric and optic properties of polymers depend on aryls linkers and their length.

Attached hydroxyl group to central benzene ring improves electric and optic properties of monomers and polymers. The same effect is not observed for attached methoxyl groups. Polymers with hydroxyl groups have much better conductivity and show better stability in common organic solvents during multiple doping than analogous polymers without hydroxyl groups. Moreover, during oxidation and reduction of *poly(2,4,6-tri(2-thienyl)-1-phenol)* cyclic voltammetry reveals sharp peak which intensity and shape depends on measurement condition, for example proton concentration, film thickness and interruption between scans. That may indicate pure redox reaction. Different behavior of *poly(2,4,6-tri(2-thienyl)-1-phenol)* on conditions indicates that this polymer could be considered as active material in future sensor research.

Two carbazole compounds were compared – where two carbazole groups were N-linked through benzene in relative metha and para position. Only slight difference in oxidation potential were observed. This suggests that other factor than configuration seems to play more important role in the case.

P-083

Adaptation of Pulsation and Organic Additives to Control the Mass Transfer of Copper Electrodeposition

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Various kinds of electromagnetic shielding materials have been available in electronic devices and display panels. Electromagnetic shielding by using metallic sheet is thought the most effective, but it has shortcoming not to emit the accumulated heat within the devices. So, mesh shaped metallic materials with high aperture are applied particularly in the high frequency IT/electronic devices. For this purpose, it is critical to control the mesh shape in the perpendicular direction so as not to reduce optical properties of electromagnetic shielding films.

In this research, the copper plating was deposited by pulse reverse current method with additives. The effect of organic additives, 1-(3-sulfoproyl)-2-vinylpyridineium hydroxide (SVH) and thiourea (TU), on the precision copper electrodeposition was investigated with optical, electrochemical and x-ray diffraction techniques. It was found that SVH played a role as an accelerator and TU as an inhibitor during the electroreduction of cupric ions in acidic Cu electroplating solution. Through electrochemical measurements, TU showed more strong interaction with cupric ions than SVH and dominated overall Cu electroplating process when both additives were present in the solution. In the case of three dimensional Cu electrodeposition on the 20 μm-patterned Ni substrates, SVH controlled the upright growth of Cu electrodeposits and so determined its flatness, while TU prohibited the lateral spreading of Cu in the course of pulse-reverse pulse current adaptation. With microscopic observation, we obtained the optimum organic additives composition, that is, 100 ppm SVH and 200 ppm TU during the current pulsation.

P-084

Gas Sensing Properties of Polyaniline Functionalized Single-Walled Carbon Nanotubes

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Chemical gas sensors have been widely used to detect and monitor various gaseous analytes in many applications including environmental pollution, industrial emission, medical diagnosis, and aerospace. Conventional chemical gas sensors often rely on various bulk-type sensing materials. However, these sensors often have a low sensitivity since they require a large amount of adsorbed gaseous molecules to affect the bulk properties of them. To improve sensing performance, low-dimensional nanostructures, such as carbon nanotubes and metal oxide nanowires/nanodots have been employed to overcome the fundamental limitations of film-based sensors. The ultrahigh surface-to-volume ratio and unique size dependent properties of nanomaterials have resulted in very promising improvements in sensing performance. [1-4]
In this work, the electrical and gas sensing properties of PANI functionalized SWNTs were systematically investigated to develop a better understanding of the sensing mechanism by the measurement of temperature-dependent I-V and FET transfer characteristics. SWNT networks were AC dielectrophoretically assembled prior to the electrochemical functionalization of SWNTs in order to increase the sensing performance of PANI-SWNTs,. The sensitivity and detection limit of PANI-SWNT networks toward NH_3, NO_2, and H_2S were established.

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P-085

The application of hydrodynamic techniques to characterize electrochemical processes in ionic liquids

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The use of forced convection in the characterization of electrochemical systems finds a wide range of applications ranging from electrochemical titration down to nanomolar concentrations, to kinetic studies for fuel cell catalysts. The two major benefits being the ability to readily differentiate heterogeneous and homogeneous processes and to develop theoretical models that exclude transient behaviour. Ionic liquids are a relatively new class of low temperature molten salts with a wide range of potential electrochemical applications, for instance in lithium batteries and electrowinning.

This work demonstrates the use of a RDE (Rotating Disc Electrode) to study the heterogeneous reaction of $[Cu(II)Cl_4]^{2-}$ to $[Cu(I)Cl_3]^{2-}$ in a RTIL (Room Temperature Ionic Liquid) analogue based on choline chloride and ethylene glycol. Particular attention is paid to the dual problems of high viscosity and poor conductivity in ionic liquids, compared to aqueous systems. This work shows that the sensitivity and throughput of hydrodynamic techniques can be extended to treat relatively rapid heterogeneous kinetics by utilizing direct, non-linear fitting of experimental data in preference to classical methods, such as those based on Kountecký-Levich plots.

P-086

Monitoring Hydrophilic –Hydrophobic Character of a Surface Electrode via TiO_2 Nano Particles Addition as Aspect of Interface Phenomena

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The development of nanotechnology is important for many fields able to improve human life and nanosizing effect of materials become a subject of many studies in the last decade.

Taking into account that interactions between cells and biomaterial surfaces are assisted by structures on cell membranes and are responsive to signalling processes that take place at very small dimensions, biocompatibility as an expression of the cell behaviour may be strongly depended on the nanotopography features. In this idea well known biomaterials as Ti and Ti alloys properties is related more recently to the possibility to get a better cellular response due to a nanostructure in the entire bulk or at surface level.

The paper aims on the effect in surface features of TiO_2 nanoparticles addition on the polypyrole coating obtained electrochemically electrode surface via electrochemical polymerization in $LiClO_4$ as electrolyte. The main surface studied property is the hydrophilic character, which is very important in bioapplication, taking into account that the balance hydrophilic – hydrophobic strongly influence cell adherence, spreading and viability. The hydrophilic character was evaluated from contact angle measurements and surface analysis was completed with scanning electronic microscopy and with atomic force microscopy. For all deposited films Mott Schottky determinations were performed and the obtained flatband potential has a variation as a function of TiO2 concentrations due probably to nanoparticles agglomeration.

P-087

System for measuring bidirectional ionic transport

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The system containing two planar mutielectrode galvanic cells designed to monitor ion concentrations at the surface of an ion permeable membrane is described.
The membrane separates two solutions containing ions to be measured.
A distance between the membrane and the multielectrode platforms can be precisely regulated by two independent micro screws without changing orientation of the electrodes. A minimal distance between the membrane and flat multielectode platforms on each side of the membrane is 0.1 mm. It is set by a separator to avoid direct contact. A change of the solutions on either side is via inlet and outlet tubes incorporated in the platforms. The characterization the system performed proved that it can be used for measurements in which instead of the porous membrane a biological cell cultures placed on this membrane are used

Acknowledgment

The Finnish Funding Agency for Technology and Innovation (TEKES SHOK IMO Intelligent Monitoring for Health and Well-being (IMO) program) is acknowledged

P-088

Measurement of Area Specific Resistance of Metallic Interconnects for SOFC

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Metallic interconnects for solid oxide fuel cell (SOFC) have received special attention because of their high electric conductivity, good mechanical property and low cost. However, at present, their commercialization is still very limited due to performance degradation with operation time at high temperature in air. In this work, area specific resistance (ASR) of various metallic interconnect materials was measured with time at 750 ℃ using four points method. The measurement of ASR was performed on half side of the specimen by attaching a Pt mesh with Ag paste only one side and Pt wires are spot-welded directly on the other side of the specimen and on the Pt mesh. The half side ASR measurement showed the same trend with both side ASR measurement method but lower ASR values, sometimes negative values of ASR. The negative ASR value seemed to result from the thermoelectric voltages generated between different metals contacting each other. The real ASR values were obtained by measuring and compensating the thermoelectric voltages. In addition, the ASR values were measured during heating and cooling of various metallic substrates and coatings deposited cathodically and anodically in aqueous solutions. The changes of ASR values are discussed in terms of the formation and growth of oxide films and their electric conductivities.

P-089

Electrochemical sensing of heavy metal ions at carbon paste electrodes modified with new dioxime derivatives

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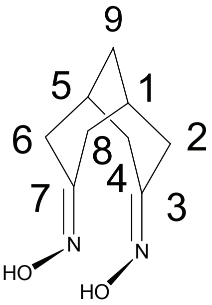
The bioactivity of various oximes and their metal complexes induced steadily growing interest in oxime co-ordination compounds [1]. Chelating ability of oximes is utilized in trace metal analysis and for isolation, separation, and extraction of various metal ions [2]. On the other hand, biological functions of oximes and their *in vivo* metabolism are evidently dependent on their chelation with metal ions [3].
In this context, the chelation ability of two newly synthesized dioxime derivatives, *Syn*-bicyclo[3.3.1]nonane-3,7-dione-3,7-dioxime (*syn*) and *Anti*-bicyclo[3.3.1]nonane-3,7-dione-3,7-dioxime (*anti*), were used to prepare modified carbon paste electrodes for heavy metal ions detection. Their electrochemical behavior was investigated by cyclic voltammetry and the optimum conditions concerning the electrode preparation in order to obtain the maximum sensitivity and the best selectivity for the detection of heavy metal ions have been investigated.



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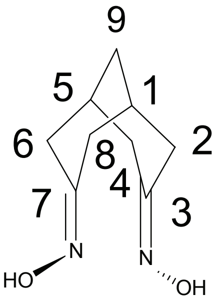

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P-090

Carbon paste electrode for the study of patina originating from the surface of bronze artefacts

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Recently, in an attempt to characterize the effect of inhibitors on the electrochemical behaviour of patina isolated from the bronze substrate, the use of a cavity microelectrode was reported [1]. In order to avoid the influence of bronze substrate on the electrochemical response of the patina, the present work proposes the using of carbon paste electrodes for its investigation. Thus, a carbon paste electrode incorporating patina originating from the surface of different bronze artefacts was prepared and used to study the efficiency of some non-toxic compounds (2-mercapto-5-acetylamino-1,3,4-thiadiazole, **MAcT**, 2-mercapto-5-amino-1,3,4–thiadiazole, **MAT**, cysteine and alanine) as corrosion inhibitors in aqueous electrolytes containing sodium sulphate and sodium hydrogen carbonate.

The obtained results show the beneficial influence of the tested inhibitors on the electrochemical behaviour of patina, the strongest effect being noticed in the case of 2-amino-5-mercapto-1,3,4-thiadiazole.

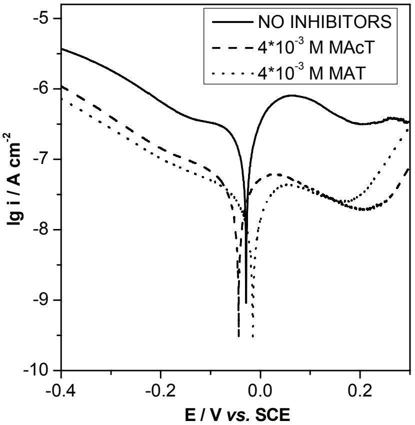

Figure. Influence of thiadiazole derivatives on the anodic and cathodic polarization curves of carbon paste electrode incorporating patina Experimental conditions: 0.2g/l Na_2SO_4 + 0.2g/l $NaHCO_3$ (pH=3); scan rate, 10 mV/min.

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P-091

PdBi Catalysts for Hydrogen Reactions

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Recent advances in electrocatalysis have shown that the choice of materials is a key factor affecting the activity of the catalyst. Currently Pt is commonly used as it exhibits high activity towards hydrogen oxidation (HOR) and evolution (HER) reactions[1-2]. It would be beneficial to identify a more abundant and cost-effective catalyst that exhibits comparable activity to that of Pt towards HOR and HER. Density functional theory (DFT) calculations have shown that nanostructuring Pt with Bi can enhance the electrocatalytic activity towards HER[3]. Considering the nature of HER and HOR, one can assume that Pt-Bi surface alloys should also exhibit increased activity towards HOR. Based on the promotion effect of bismuth the focus of this work was to investigate the Pd-Bi system. Pd-Bi catalysts supported on high surface area Sibunit were prepared and characterized for their activity towards HER and HOR using half-cell configurations. The catalysts showed superior specific activity, reaching values similar to those of pure Pt.

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P-092

Different Strategies for the Development of Electrochemical Sensors Using Novel Nanotechnologies

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Electrochemical (bio)sensors are still very attractive due to their fast response and simple sample pre-treatment. With the miniaturisation of the sensors and development of nanotechnologies, electrochemical sensors are also having novel techniques applied to their development.

Carbon nanotubes (CNTs) have attracted enormous interest from electrochemists in recent years. Their application to sensors and biosensors continues to be very promising. The major problem in developing electrochemical CNT-based (bio)sensors is their insolubility in all solvents. Various strategies have been used to minimize this problem either through covalent or non-covalent functionalisation; functionalised CNTs are easier to disperse in different solvents and polymers [1].

Functionalised multiwalled carbon nanotubes have been used to develop a new type of biosensor, casting them either by cross-linking into a chitosan film using different cross-linkers on graphite-epoxy composite electrodes [2,3], entrapping in a Nafion film [4], or by forming a gel with room temperature ionic liquid [5]. The electrochemical behaviour of the electrodes was evaluated by cyclic voltammetry and electrochemical impedance spectroscopy.

The bioanalytical properties, sensitivity, selectivity, and continuous-measurement lifetime of the biosensor were evaluated at different potentials and will be presented. Perspectives and future work about alternative nanostructure formation for sensor and biosensor preparation will be discussed.

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P-093

Potentiometry Revisited: some Practical Considerations

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Potentiometry is one of the most popular, if not the most popular, electrochemical technique. It is used daily by millions of people around the world and constitutes for many of them the only known electrochemical technique. Because of its extreme versatility and ease of implementation, potentiometry is used worldwide by a broad range of scientists and engineers, from chemists to biologists to geologists with extremely different objectives. As long as the potentiometric measurements are used qualitatively for analytical purposes: titrations or the monitoring of processes, if the measurements are reproducible, the exact meaning of the potentials measured has no great importance. On the other side, if the measurements are used for the determination of thermodynamic data or for prediction calculations, severe experimental precautions must be taken.
In the environmental chemistry area, the precise determination of redox potentials (E_h) of soils is of crucial importance in the context of the underground storage of the nuclear spent fuel. Indeed, E_h is required for the reliable prediction of the future fate of radionuclides emanating from a nuclear waste repository after the corrosion of the containers.
In 1984, Lindberg and Runnells[1] pointed out high discrepancies between E_h values directly measured in the field and those computed on the basis of individual species concentrations that have been determined by applying standard analytical methods. In 1999, the editors of 'Redox: Fundamentals, Processes and Applications'[2], were writing 'this book should help to find the real value of measured E_h of sediments and natural waters'. However, this book, which is the sum of 15 individual, sometimes excellent, contributions, presents problems rather than gives solutions. Recently, in the framework of a collaborative project[3] funded by the Euratom Community, we participated in a four-day intercomparison exercise where researchers from 15 different organizations measured E_h for six series of samples comprising artificial, natural or microbial solutions and suspensions. There are also discrepancies not only between calculated and measured values but even worse between values measured by the different investigators for the same sample.
In this paper, considering: i) the composition and a possible evolution of the different samples with time as well as catalytic processes which can take place at the electrodes surfaces, ii) the shape of the voltammetric curves that we recorded during this exercise, ii) the nature of the electrodes and the hydrodynamic conditions used, iii) the pretreatment of the electrodes, iv) the characteristics of the electronic devices used for the measurement of E_h, we try to explain the discrepancies that were observed between the E_h values measured during this exercise. Moreover, we propose practical rules for the determination of E_h as a function of the nature of under measurement samples.

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P-094

Square Wave Voltammetric detection of furan on platinum and platinum-based screen printed electrodes

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Furan, a volatile oxygen heterocyclic compound, is classified as a possible human carcinogen by International Agency for Research on Cancer (IARC, 1995). Together with its derivatives (furaldehyde, furfuryl alcohol), furan, which is responsible of the flavour of many foods, is formed by commercial or domestic heat treatment in canned, jarred and roasted foods [1], when thermal degradation of carbohydrates, such as glucose, lactose and fructose takes place. Coffee, canned meat and toasted bread appear to be the major dietary furan source for human beings [1]. Particularly worrying is the content of furan in jarred baby foods, which may constitute the sole diet of many infants [1].

Very recently, the European Food and Safety Authority (EFSA), the US Food and Drug Administration (US FDA) and the Swiss Federal Office of Public Health, published several reports [1-3] on the occurrence of furan in food and on the available analytical methodologies. In these reports, the scarce available data indicate that this is an emerging issue in food safety and that there is a relative small difference between possible human exposures and the doses in experimental animals that produce carcinogenic effects. However, a reliable risk assessment would need further data and also new improved analytical methodologies.

Electroanalytical techniques and particularly those based on pulsed voltammetry, which are particularly suitable for trace analysis, constitute an interesting alternative to the present available analytical methodologies in terms of very high sensitivity, low response time, small dimensions and low costs, in the challenge of the identification and quantification of this compounds in food and beverages. Moreover, these techniques can be conveniently used *on-line* and *on-site*, without sample pre-treatments, and may constitute an interesting, reliable and low-cost choice to be used as electrochemical detectors for chromatography.

In this presentation, a Square Wave Voltammetric determination of furan in acetonitrile, using a platinum disk electrode or Pt-based Screen Printed Electrodes (Pt-SPE) is proposed. Linearity range, accuracy, precision, selectivity and specificity, quantification and detection limits of the new methodology have been duly evaluated.

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P-095

Electrochemical SPR Technique for in-situ Characterization of Atifouling Hybrid PPy-NaPSS Coating

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In this paper the efficiency of using conducting polymers as electrode coating material in order to prevent electrode fouling caused by electrochemical oxidation of phenol is investigated. In particular, the use of polypyrrole has been tested. Electrode passivation is dramatically reduced while incorporating anionic surfactants such as poly(sodium 4-styrenesulfonate) into the polymeric structure.

The electrochemical surface plasmon resonance (SPR) technique was used for in-situ characterization of atifouling properties of hybrid PPy-NaPSS coatings

The electrochemical antifouling stability of the polypyrrole based composite coatings was also evaluated by cyclic voltammetry (CV) and contact angle analysis.

The embedding of NaPSS in the structure of polypyrrole film leads to improving of hydrophilic character of the surface accompanied by the growing antifouling ability of the coating.

The surface analysis and roughness evaluation of polypyrrole/poly(styrene sulphonate) composite surface were completed with atomic force microscopy (AFM).

The work shows the effect of the surfactant presence in the polypyrrole film and the concentration influence as well.

A correlation between wettability data, surface topography, roughness and antifouling effect of the hybrid PPy-NaPSS surface was also evaluated.

Acknowledgements
"Authors recognize financial support from the European Social Fund through POSDRU/89/1.5/S/54785 project: "Postdoctoral Program for Advanced Research in the field of nanomaterials".

P-096

SERS sensors based on the bifunctional ligands: the importance of potential-dependent orientation control of adsorbed molecules

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During the last 10 years there were realized numerous analytical techniques based on the Surface Enhanced Raman Scattering (SERS) phenomenon. These applications include trace level ion sensing, e.g. polyatomic anions were determined in aqueous solution at 10^{-9} M [1]. In this work, we discuss the development of SERS method for detection and recognition of ions which lack their own vibrational spectrum.

For this purpose, we propose to use bifunctional ligands (BFL). A BFL molecule have to combine an ion-selective fragment for complexation with the analyte ion, a fragment for sorption at the metal substrate surface, and electron conjugation between both fragments to ensure the sensitivity of SERS spectrum to the analyte. Apparently, crown-O-4 ether derivatives of 1,10-phenanthroline and 2,2'-bipyridile meet these conditions and may be tested as SERS-active sensor substances for Li^+ determination. Recently such substances were synthesized in our group [2, 3].

To guarantee the steric accessibility of the crown fragment for complexation with the analyte ion, the azaheterocyclic part of the BFL molecule should be oriented perpendicular to the metal surface. This favorable orientation may be imposed by applying a certain electric potential to the metal [4]. Thus, SERS experiment combined with electrochemical technique may be a promising way for the development of a new method of cation determination.

With the simplest azaheterocycle: the pyridine molecule as an example, we study here the importance of the proper choice of the applied potential, the pH and the background electrolyte for the SERS experiments with electrochemical treatment. It is shown in particular that if pyridine – Ag^+ complexation takes place (due to anode etching of the electrode) or if the pyridine molecule is protonated, so that the lone electron pair in the nitrogen atom in pyridine is not vacant anymore, the resulting $PyAg^+$ or PyH^+ species are adsorbed only in parallel to the metal surface.

Acknowlegment: This work supported by Federal Targeted Programme "Scientific and Scientific-Pedagogical Personnel of the Innovative Russia in 2009-2013"

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P-097

Synthesis and characterization of conducting copolymer of 1-(4-methyl-3'-thienyl)-2-(ferrocenyl)ethene with EDOT

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The design and synthesis of compounds for any type of applications in material science for use in sensor chemistry and/or electrochemistry are important . The synthesis of such structures directly depends on the availability of target molecules, having useful physical or chemical properties. Sensitivity to light or heat, redox or pH activity, binding selectivity, color reversibility with electrical charge are but some of these [1,2]. Polymers have been considered as organic materials which have characteristic properties such as hydrophobic surfaces, low thermal and electrical conductivities, chemical inertness and low mechanical durability. However, a fundamental progress in the polymer science has changed this prospect. Synthesis of new types of polymeric materials with a remarkable electrical conductivity directly connected the polymer synthesis, applications and electrochemistry science [2,3].
This study deals with electrochemical properies of metal containing conducting polimer namely poly(1-(4-methyl-3'-thienyl)-2-(ferrocenyl) ethene-co-3,4-ethylenedioxy thiophene). 1-(4-methyl-3'-thienyl)-2-(ferrocenyl) ethene was synthesed with 2-(ferrocenyl)ethene, and 3-methyl-4-bromothiophene**.** The structure of monomer was determined via FTIR, ^{1}H-NMR and ^{13}C-NMR techniques. The copolymer was synthesized utilizing this monomer and 3,4-ethylenedioxy thiophene. Structure of obtained copolymer was charecterized by CV, FTIR, SEM, AFM, and UV-Vis spectroscopy. Its band gap (Eg) and λ_{max} were determined. Conductivity study was measured via four probe technique.

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P-098

Construction of a PMMA Microarray Device for Metal Analysis at Very Low Concentrations

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Microelectrodes are very versatile devices for electrochemical and analytical studies owing to high mass transport rates and little interference from interfacial capacitance or solution resistance problems. Moreover, they can be fabricated at very small physical overall dimensions, which allows them to be used in vivo or with very low sample volumes. Some additional advantages are obtained if microelectrodes are connected to each other. Microarray electrodes, which are fabricated by arranging a number of microelectrodes, can increase the absolute current comparable to that of the usual electrode, while maintaining the advantageous properties of the single microelectrode. This increase in the sensitivity associated with the possibility of working with very small sample volumes (a few microliters) can be very useful for analyzing metals at very low concentrations, such as in body fluids.

A new approach to construct a microarray system is reported. Two slices of poly(methilmethacrilate) (PMMA) were cut using a laser cutter (gravograph – LS100). In one of the slides, both a copper wire contact and the gold microfiber (r = 5 µm) were positioned as shown in Figure 1. The contact between the copper wire and the gold microfiber was made by using silver epoxy (Joint Metal LTDA, São Paulo, Brazil). The two slides of PMMA were then sealed using chloroform, in order to sandwich the fibers between both slides. An opening was made with the laser cutter to create the cell (ca. 150 µL) where the sample solution, reference electrode (Ag/AgCl) and counter electrode (Pt) could be inserted. Figure 2 shows stripping voltammograms recorded in a quiescent solution containing 30 nmol L^{-1} Pb(II). Experiments were performed with only one gold microelectrode and with all four microelectrodes interconnected. The benefit of using the microelectrode array is remarkable, so that routine electroanalytical measurements can be performed without using proper instrumentation to amplify current signals and to minimize electronic noise. Future work with the developed device involves measurements of Pb(II) concentration in tear samples.

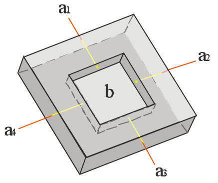

Figure 1: Representative scheme of the microarray device. (a_n) gold microfibers and copper contacts (b) reservoir.

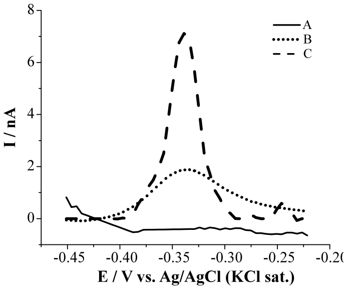

Figure 2: Stripping voltammograms obtained in a solution containing 50 mmol L^{-1} KCl and nitric acid (A), A + 30 nmol L^{-1} Pb(II) with one microelectrode (B) and with the microarray (C).

Financial support: FAPESP, CAPES and CNPq

P-099

H_2O_2 generation dependence on Nafion layer coated on Pt electrode during oxygen reduction

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Polymer electrolyte fuel cells (PEFCs) have attracted much attention as a highly efficient power generation system. It is important to investigate the oxygen reduction reaction (ORR) at the Pt cathode of PEFCs, because the reaction rate of cathode is slow and the mechanism is much complicated than that of anode. The cathode generates H_2O_2 during the ORR. Polymer electrolyte and Pt electrode are degraded by the H_2O_2 that possesses corrosive nature. For Pt/C-ionomer composite cathode, it has been reported that the generation of H_2O_2 is accelerated by the ionomer. In contrast, it has been reported that the H_2O_2 generation is suppressed by Nafion used with Pt/C. In this study, we have focused our attention on Pt disk electrode, and have carefully investigated a generating amount of H_2O_2 as a function of Nafion ionomer thickness overcoated on the Pt electrode.

The electrochemical measurement was performed to estimate the amount of H_2O_2 using a scanning electrochemical microscopy (SECM) system equipped with Pt generator electrode (ϕ 50 μm), Pt detector electrode (ϕ 3 μm), Ag/Ag_2SO_4 as a reference electrode (RE), and Pt wire as a counter electrode (CE). The Pt generator electrode was coated by Nafion ionomer (thickness: ca. 0, 0.09, 0.16, 0.20 and 0.82 μm) using a Nafion solution. The ORR was evaluated by a current-potential curve in O_2-saturated 0.5 mol dm^{-3} H_2SO_4. The generating amount of H_2O_2 was measured by the Pt detector electrode. Generator and detector electrode potentials were settled at -0.4 and 0.6 V vs. Ag/Ag_2SO_4, respectively. The position of detector electrode was scanned for X and Y axis to determine the maximum oxidation current of hydrogen peroxide. The distance between the generator and detector electrodes was fixed to be 10 μm.

Figure 1 shows a relationship between the H_2O_2 detection current and the Nafion layer thickness. The detection current increases with increasing Nafion layer thickness up to 0.16 μm. However, the current turns into decrease in the thicker region. It is demonstrated that there is maximum H_2O_2 detection current at around 0.16 μm Nafion layer.

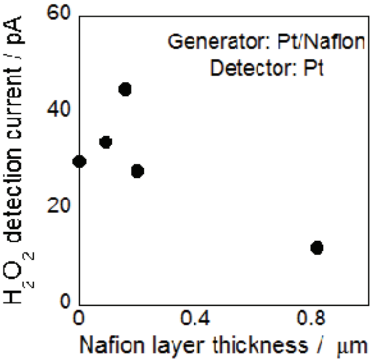

Fig. 1 Relationship between the H_2O_2 detection current and the Nafion layer thickness on the Pt generator.

P-100

Electrochemical behavior of glassy carbon electrode chemically modified with cadmium pentacyanonitrosylferrate in presence of tetrahydrothiophene.

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Tetrahydrothiophene (THT) is a heterocyclic organic compound and THT is used as an odorant in natural gas, a solvent and an insecticide. The pentacyanonitrosylferrate (PCNF) is a member of the polycyanide metal complexing reagents, and reacts with sulfur compounds to form metal nitrosothiolato intermediates[1]. The scope of this work was to develop a modified electrode of cadmium PCNF onto glassy carbon electrode (CdPCNF/GC) and study the electrochemical behavior against the THT.

GC was immersed in a solution containing $1x10^{-3}$ mol L^{-1} de $CdCl_2$, $1x10^{-2}$ mol L^{-1} de PCNF e 0.5 mol L^{-1} de KNO_3 with a pH adjusted in the range 2 – 3. The modification of electrode surface was performed by 150 successive scans of potential swept between -0.2 to 1.0 V with a scan rate of 100 mV s^{-1}. For electrochemical measurements used a potentiostat AUTOLAB - PGSTAT30 with a conventional electrochemical cell with three electrodes: Ag/AgCl as reference electrode, Pt as auxiliary electrode and GC as working electrode.

The CdPCNF/GC was characterized by cyclic voltammetry. The CdPCNF/GC formed showed $E^{0'}$ = 593 mV, I_{pa}/I_{pc} = 0.96 and ΔE_p = 34 mV in a solution of 0.5 mol L^{-1} de KNO_3 with a scan rate of 100 mV s^{-1}. Anodic peak currents were found to be linearly proportional to the scan rate between 10-250 mV s^{-1}, indicating an adsorption-controlled process. The CdPCNF/GC was stable after 7 days of preparation, and front of 150 successive scans, with low signal loss of I_{pa} at around 14%. CdPCNF/GC degraded in alkaline solutions (pH > 9) by hydrolysis. The CdPCNF/GC presented stability and behavior electrochemical similar with the other found in the literature [2].

The CdPCNF/GC in presence of THT (0 to 1,0 V; in buffer BR solution, pH 6,0) and 0.50 mol L^{-1} KNO_3 observed a decay in peak current proportional to the concentration of THT in the range of $6,67x10^{-6}$ mol L^{-1} a $4,00x10^{-5}$ mol L^{-1} with correlation coefficient of -0.994 (n=6) and amperometric sensitivity of 5,01 x 10^5 μA L mol^{-1}. The reduction of peak current indicates that the species was adsorbed probably by nucleophilic coordination of S with NO group[1] of NiPCNF (Eq. 1). In presence of 1.06 x 10^{-4} mol L^{-1} THT anodic peak currents were found to be linearly proportional to the scan rate between 25-300 mV s^{-1}, indicating an adsorption-controlled process.

$$[Fe^{III}(CN)_5NO]^{2-} + RS^- \rightarrow [Fe^{III}(CN)_5N(O)SR]^{3-} \qquad \text{(Eq. 1)}$$

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P-101

Electrochemical Noise Monitoring of SS 304L in Nuclear Reprocessing and Waste Storage Medium

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Electrochemical noise technique is currently in limelight for online corrosion monitoring in process streams [1,2]. The paper highlights the use of electrochemical noise for monitoring and determining the corrosion resistance of SS 304L in nuclear reprocessing and waste storage medium. Electrochemical potential and current noise was acquired simultaneously, as a function of time from SS 304L under solution annealed and sensitized microstructure, in 3M, 4M, 8M, 12M nitric acid and in simulated nuclear high level waste (HLW) at 298 K and 323 K [3,4]. The acquired data was statistically evaluated to derive electrochemical noise- resistance which is inversely related to corrosion rate [3]. Visual examination of the noise-time records for 304L SS in nitric acid showed passivation process [4], a typical noise-time record in 4N nitric acid is shown in fig.1. A decrease in noise resistance occurred with increase in concentration implying higher corrosion rate at higher concentration. In simulated HLW at 298K, electrochemical noise signals depicted destabilization of the passive film by the ions present in the simulated HLW, as shown in fig.2 accompanied by a decrease in noise resistance (Fig.3). The results of the investigation are detailed in the paper.

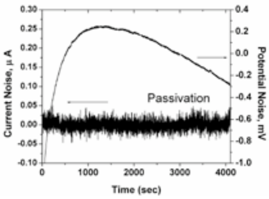

Fig.1 Electrochemical noise for SS 304L

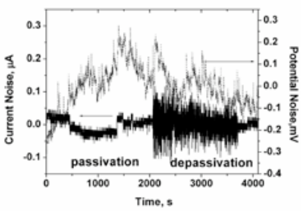

Fig.2 Electrochemical noise for SS 304L

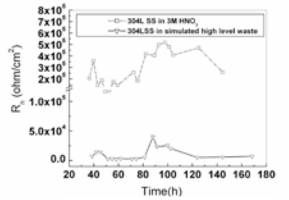

Fig.3 Noise

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P-102

Dispersed Carbon Electrode in Aqueous Electrolyte Solution: a System Sensitive to the Amount of Oxygen Bonded to a Carbon Surface and the Concentration of Oxygen or Added Organics in Solution

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Different carbon materials (activated carbon, AC, carbon black, CB, multiwalled carbon nanotubes, MWCNTs) were used for preparing the electrodes. Their stationary potentials [1] were measured in aqueous electrolyte solutions with respect to SCE. Measurements for carbon electrodes of different oxygen amounts chemically bonded with carbon surface were performed in 0.5 M H_3PO_4 for AC (obtained from plum stones) oxidized with concentrated HNO_3, then heat treated in vacuum at 180, 500 and 900°C [2]. The amounts of oxygen bonded to the carbon surface were measured using XPS method. Results are collected in Table 1(1). In the case of solutions (0.5 M KCl) saturated with nitrogen-oxygen mixtures the electrodes were prepared from CB Vulcan 3 (Cabot) [3] (for results – see Table 1(2)). For electrolyte solutions (0.1 M Na_2SO_4) with different 4-chlorophenol concentrations carbon electrodes were prepared from Short Hydroxyl MWCNTs (Chengdu Organic Chemicals Co. Ltd.)(for results – see Table 1(3)). These relations are just a few examples of the dependence of the carbon electrode potential on the oxygen or organics content in solution or on a carbon surface.

Table 1. Stationary potentials of powder carbon electrodes for various amounts of oxygen bonded to a carbon surface and for various concentrations of oxygen or organics in solution

Parameters			Values		
1	Oxygen surface conc., XPS	(at.%)	2.73	7.09	11.25
	E vs. SCE	(mV)	+196	+342	+447
2	Oxygen conc. in O_2/N_2 mix	(vol.%)	0 (N2)	15.9	20.95 (air)
	E vs. SCE	(mV)	-22	+72	+123
3	4CP conc. in 0.1M Na_2SO_4	(mol/l)	0	0.01	0.05
	E vs. SCE	(mV)	+283	+270	+247

This work was supported by Ministry of Science and Higher Education (project: N N209 099037).

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P-103

Integration of Electrochemical Microsensors on Flexible Film

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In many ways of application (health, environment, …), electrochemical sensors have demonstrated their capability to detect a wide range of (bio)chemical species. In parallel, "Silicon & Polymers" microtechnologies have provided the development of generic electrochemical microcells with many advantages: short analysis duration, low analysis volume, mass fabrication and low cost [1]. Nevertheless, the electrochemical measurement still requires technological developments to be compatible with some specific applications such as skin analysis, smart patchs, smart clothes,….

In order to do so, an electrochemical microsensor was fully integrated on a polyethylene-terephthalate (PET) flexible film (figure 1). The microsensor design involves a gold working microelectrode, a platinum counter electrode and a silver electrode that is oxidized later to form an Ag/AgCl reference electrode. The fabrication process is based on the "lift-off" technique but main technological developments were focused to the deposition of the gold, platinum and silver films on the PET substrate using specific adhesion sub-layers. Finally, the definition of the microelectrodes active areas as well as their electrical insulation were performed by wafer level packaging thanks to a biocompatible, non electro-active SU-8 photoresist layer.

The electrochemical properties and surface states of the different microelectrodes were tested by cyclic voltammetry and compared to massive materials in order to validate their electrochemical behaviour (figures 2 and 3). Since the flexible (Au – Pt – Ag/AgCl) electrochemical microsensors showed reproducible detection properties in liquid phase, first experiments were performed for the skin analysis, evidencing promising results for the oxidative stress measurement.

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Fig 1: *(Au –Pt – Ag/AgCl) electrochemical microcell on PET flexible film*

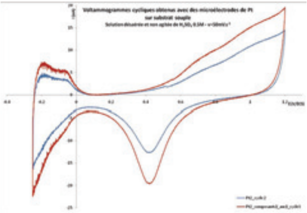

Fig 2: *Cyclic voltammograms of the platinum microelectrode*

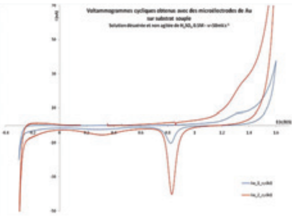

Fig 2: *Cyclic voltammogramf of the gold microelectrode*

P-104

Chemical analysis and sensing using CMOS microcalorimetric sensors and actuators

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We present a low cost, low power, small sample volume (3µl) thermal sensor and actuator for rapid detection and analysis of hydrocarbons in air. The analysis is realized via the measurement of the total reaction heat effect in response to gas pulsing and thermal actuation. The developed chip combines advantages of three fields: (i) CMOS technology with elements of micromachining used for fabrication, (ii) heterogeneous catalysts applied for selective detection of target compounds and (iii) system integration into a microfluidic channel for controlled flow and reaction conditions.

The prototype sensor consists of Poly-Si heaters and Poly-Si, as well as Poly-Si/$TiSi_2$ temperature sensors integrated on a freely-suspended low-stress thermal insulating SiRN membrane. The thin catalyst film is immobilized on top of the membrane. Accurate detection of reaction heats and electrical and mechanical stability up to 700°C are key factors for successful transducer operation. Thus, emphasize was put on the development of a CMOS compatible resistive material exhibiting a linear temperature dependence of resistance up to 800°C, a high TCR (3100ppm/C for Poly-Si/$TiSi_2$) and validated electrical stability at 500°C. The developed transducer system is chemically inert to hydrocarbons. The specificity of the sensor is achieved by immobilization of a selective catalyst. Compatibility of catalyst deposition techniques (sputtering, soft lithography) with the sensor process, its activity and stability has been evaluated.

The presented results demonstrate applicability of the sensor system as a gas detector, screening platform for the catalysts development, as well as an active part of microreactor systems where precise temperature control and actuation are essential.

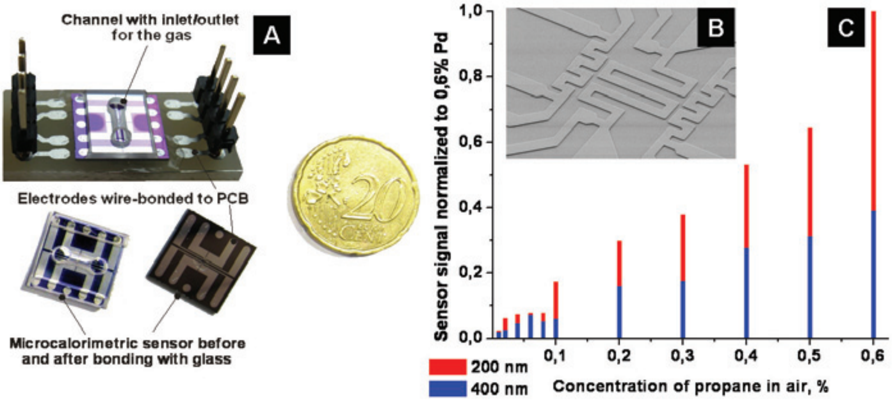

Figure 1.Sensor device (A), top view on heaters/sensors (B), Poly-Si sensor response to propane oxidation in air for devices with membrane thickness of 200, 400 nm (C).

P-105

Application of Ionic Liquids for Preparation of Membrane Phase of Ion-Selective Electrodes Sensitive to Heavy Metal Ions

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Ionic liquids (ILs) are molten salts with the melting point close to or below room temperature. They are composed purely of ions and posses unique properties, including low volatility, tunable viscosity, high conductivity, large electrochemical window and low toxicity. These properties make ILs suitable for many applications in chemical analysis. Among ILs applications, the use of IL/water two-phase system is one of the most promising for electroanalytical chemistry and extraction. The mechanism of the potential formation of ion selective electrodes (ISEs) with a liquid or pseudoliquid (polymeric) membrane depends strongly on extraction and ion-exchange processes between the aqueous and organic phases. It is known that the nature and amount of the lipophilic additive strongly influence the response of the membrane ion-selective sensors, such as reducing the membrane resistance, improving the response behavior and selectivity and in some cases, where the extraction capability is poor, increase the sensitivity of the membrane sensors. Considering all the aspects stated above, we have decided to use ILs as components of the polymeric membrane of ISE selective to cadmium and lead ions, and it was with great joy that we obtained an electrode better characterizing the analytical parameters.

ILs used in this work were: 1-ethyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride, 1-hexyl-3-methylimidazolium chloride, 1-decyl-3-methylimidazolium chloride (DMImCl), 1-Benzyl-3-methylimidazolium chloride (NMImCl). These ionic liquid are known to be immiscible in water but soluble in majority plasticizers. Ionic liquid are used instead of commonly used lipophilic ionic additives (phenyl borates) in the membrane phase, which are introduced to the membrane to reduce the anion interference and to lower the membrane resistance. Additionally ILs keep constant concentration of chloride ions in the membrane phase what guarantee potential stability of internal Ag/AgCl electrode.

In order to evaluate the effect of the addition of ILs to the electrode membrane phase, basic analytical parameters of electrodes containing them in the membrane phase were determined and compared with the parameters of electrodes without ILs in the membrane phase. In order to study the potential creating properties of ionic liquids the electrodes containing IL in the membrane but without ionophore were also constructed and measured.

The research has found that the properties of ion-selective electrode sensitive to cadmium and lead ions such as : detection limit, selectivity and response time can be significantly improved by the addition of ILs to the membrane phase. The best parameters exhibit electrodes having membrane dopped with 1-ethyl-3-methylimidazolium chloride (EMImCl) and 1-butyl-3-methylimidazolium chloride (BMImCl).

P-106

Ionic Liquids Improve Analytical Parameters of Zinc Ion-Selective Electrodes with Solid Contact

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Zinc is widely used in electroplating, pharmaceutical, cosmetics and paint industries. Human body contains about 2g zinc but its large doses can cause fever, chills, gastroenteritis and pulmonary manifestation. Besides zinc can cause anemia, nausea, vomiting, renal failure and internal organs. Therefore rapid and selective methods of its determination are needed. Potentiometric ion selective electrodes (ISEs) are known to offer an excellent low cost tool for the selective, sensitive and rapid determination of a vast variety of analytes in different fields of application. The efforts made so far to develop a good ion-selective electrode sensitive to zinc ions have not been very successful. Most of the sensor reported for zinc ions have poor selectivity and sensitivity. A few years ago we devised zinc-selective electrode based on chelating agent: 2-(2-Hydroxy-1-naphthylazo)-1,3,4 –thiadiazole which selectivity is not satisfactory [1]. Recently it was found out that ionic liquids(ILs) can replace commonly used lipophilic ionic additives (phenyl borates) in the membrane phase. They lower the membrane resistance and reduce anion interference, altogether improving the analytical parameters of the electrode such as detection limit, measuring range ,working pH range and selectivity. Therefore we have decided to use ILs as components of the polymeric membrane of ISE selective to zinc ions.

In this work we studied solid contact electrodes with polymeric membrane based on 2-(2-Hydroxy-1-naphthylazo)-1,3,4 –thiadiazole doped with alkylmethylimidazolium chlorides. In order to evaluate the effect of the addition of ILs to the electrode membrane phase, basic analytical parameters of electrodes containing them in the membrane phase were determined and compared with the parameters of electrodes without ILs in the membrane phase.

As follows from the studies the addition of ILs to the membrane phase improved the analytical parameters of the studied zinc-selective electrodes, especially the improvement in selectivity was notable.

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P-107

Layered Titanate Based Electrode for Determination of Lead: a Promising Class of Materials Toward Heavy Metal

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The class of layered oxides containing quadricvalent metals is often employed in the removal/separation of several radio/bio-toxic metal ions from aqueous solutions. In this work, layered cesium titanate (LCT) is modified on the nickel foam to construct a new electrode for lead (Pb^{2+}) determination. The analysis of Pb^{2+} using stripping voltammetry includes two steps. Pb^{2+} ions are firstly reduced and deposited in a Pb^{2+} solution (40mL) during a preconcentration step biased at -1.0 V (vs. Ag/AgCl), followed by a measurement step by differential pulse voltammetry (DPV) within the potential range of -0.8 ~ -0.2 V (scan rate: 50 mV/s, amplitude: 0.05 V, pulse width: 0.01 s, sampling width: 0.005 s, pulse period: 0.2 s, quiet time: 15 s). Liner calibration curve was found to be from 30 ppb to 10 ppm for Pb^{2+} with a sensitivity of 21.16 µA/µM after a 10-min of preconcentration. The detection limit was estimated to be 11.17 µg/L at the signal/noise ratio of 3. Reproducibility (RSD %) was found to be 5.3 % for a single sensor with six measurements and 6.7 % for six sensors prepared with identical procedures.

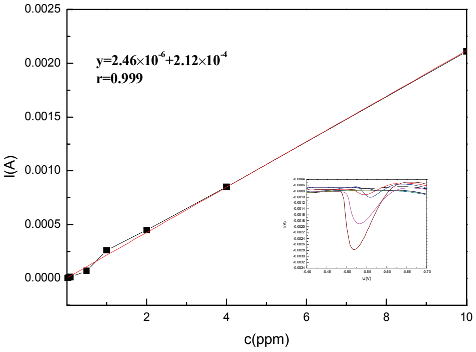

Fig. 1. Calibration plots of Pb^{2+} stripping peak current with Pb^{2+} solution concentration. Inset shows anodic stripping differential pulse voltammograms obtained at LCT electrode in acetate buffer solution (pH 4.5) containing 0.03, 0.05, 0.1, 0.5, 1, 2, 4, 10 ppm Pb^{2+} (from button to top).

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P-108

Redox Properties of Novel Metal Substitued Polyoxometallates

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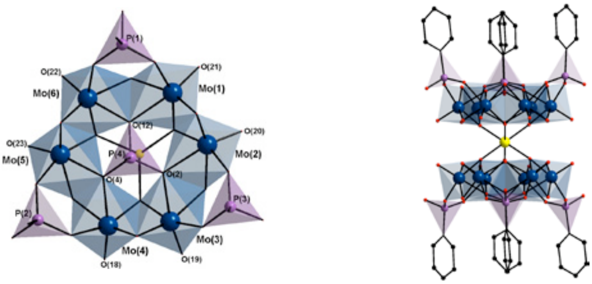
Polyoxometalates (POMs) are molecular structures consisting of inorganic metal-oxygen cluster anions that are unique in their topological and electronic versatility. These clusters (so-called isopoly- and heteropolyanions) contain highly symmetrical core assemblies of MOx units (M= metal atom mostly V, Mo, W). The diversity in their form, composition and possibility of functionalisation of these compounds with various ligands gives them varied properties and applications, such as, photochromic devices, single-molecule magnetism, photochemical catalysis, anti-retroviral activity, hosts for guest-host chemistry, potential molecular electronic devices, building blocks for larger structures and starting points for covalent modification. Recently, a wide spread interest in the POM chemistry is focused on the synthesis and characterization of POM supported transition or rare earth metal compounds to extend their structural multiplicity and versatility. In this work a series of novel metal substituted POMs, shown in Figure 1, of the general formula $(NH_4)_4H_4\{X[Mo_6O_{12}(OH)_3(O_3PC_6H_5)_4]_2\}.8H_2O$, where X is either Co(II), Mn(II), Fe(III), Mg(II) or Ni(II), were investigated for their redox properties. All POMs exhibited a large irreversible redox process at +0.85V (vs Ag/AgCl) believed to be associated with the oxidation of the Mo(V) centres. Upon scan reversal to further negative potentials redox processes associated with the reduction of the Mo(VI) centres is observed. Attempts to surface immobilise these POMs was also attempted through the LBL technique and the employment of conducting polymer matrices.

Fig: 1



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P-109

Electrochemical DO Sensor Using Nanostructured ZnO-doped RuO_2 Sensing Electrode

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Thick-film ZnO-RuO_2 sensing electrodes (SEs) with different mol % of ZnO were prepared on the alumina sensor substrates using a screen-printing method and their structural and electrochemical properties were closely studied by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS) and energy-dispersive spectroscopy (EDS) techniques. Selectivity testing exhibited that the presence of Cl^-, Li^+, SO_4^{2-}, NO^{3-}, Ca^{2+}, PO_4^{3-}, Mg^{2+}, Na^+ and K^+ with a concentration range of 10^{-7} to 10^{-1} mol/L in the solution had practically no effect on the sensor's *emf* response, whereas Br^- had some effects at concentration more than 10^{-3} mol/L. ZnO-RuO_2-SEs were also investigated for potentiometric detection of dissolved oxygen (DO) at a temperature range of 11-30°C. The relationship between DO and the sensor's *emf* was found to be relatively linear with the maximum sensitivity of -50.6 mV/decade was achieved at 20 mol % ZnO at 7.35 pH. Experimental evaluation the pH dependence of ZnO-RuO_2-SEs was quantified and verified to further expand the capacity of these SEs. The response and recovery time to the pH changes for the planar device based on 20 mol % ZnO-RuO_2-SE was found to be ~10 and ~25 s, respectively, at a temperature of 25°C. It has been demonstrated that sintering the appropriate amounts of mixed ZnO and RuO_2 nanostructures not only improves the structure of developed SE but also enhances the device's sensing performance.

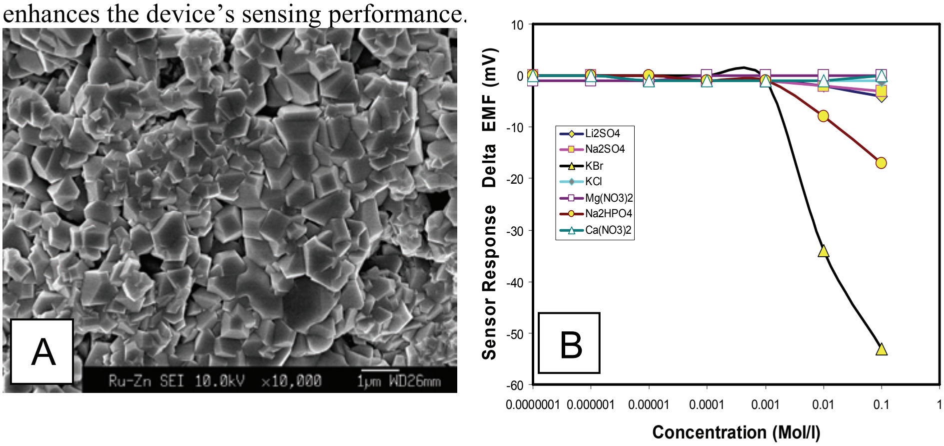

Fig. 1 SEM image of 20 mol % ZnO-RuO_2-SE indicating its surface morphology (A); selectivity of the DO sensor based on 20 mol % ZnO-RuO_2-SE at a working temperature range of 11-30°C (B).

P-110

Application of Electrochemical and Semiconductor Sensors in Automated Equipment for the Detection of Chemical Contaminants

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In the modern world the threat of chemical contamination is very considerable. It may be due to natural causes (earthquakes, floods, volcanic eruptions) or to human agencies, such as fires, explosions and all manner of other industrial accidents, and also acts of war or terrorism. Therefore, chemical contamination needs to be monitored in military and civilian facilities, both mobile and stationary, and also in public places and industrial premises. Automated devices are used for this kind of monitoring. Based mostly on ion mobility spectrometers (IMS) [1,2], they are capable of detecting chemical warfare agents (CWAs) and toxic industrial chemicals (TICs). While IMS detectors are highly sensitive to CWAs – organophosphorus compounds (sarin, soman, tabun, V-agents) at levels of ca 10^{-5} mg/m^3 and blister agents (mustard gas, lewisite) at ca 10^{-4} mg/m^3 – they are not sensitive enough to TICs: detected levels are above maximum admissible concentrations (MACs) (Table 1). This is why work is in hand to adapt and then apply electrochemical and semiconductor sensors to the detection of TICs at the required levels of sensitivity.

Table 1. Detection of CWAs and TICs up to 30 s, at temperatures from -15 to +30°C

Agents	Required (mg/m^3)	Performance (mg/m^3)
Sarin, Soman, Tabun, VX	0.02	0.02
Sulfur mustard	0.2	0.2
Lewisite	0.2	0.2
Phosgene	0.5	10
Cyanogen chloride	0.1	10
Chlorine	1.5	30
Ammonia	20	30

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Optical properties of well ordered silver nanostructures by electrochemical deposition using templates

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Nanostructures metals have attracted much attention in the last few years due to their numerous potential applications in various areas such as materials and biomedical sciences, electronics, optics, magnetism, energy storage, biosensors and electrochemistry[1]. We present here silver nanostructures prepared by an electrochemical deposition method using templates on an indium tin oxide (ITO) substrate and Au coated glass substrate. The fabrication process of the silver nanostructures can be divided in three main steps: polystyrene latex template fabrication, silver deposition on polystyrene template and removing the polystyrene template. The deposition was carried out potentiostatically with a three electrode system [1,2]. The polystyrene sphere template on the substrates and the nanostructured silver film were characterized by scanning electron microscopy (SEM). Micrographs of these can be seen in Figures 1a and 1b. Well ordered nanostructured films of silver with regular arrays of spherical spheres with diameters from 0.40µm to 1µm were prepared. In additional the ITO substrate can be functionalized with aminosilanes layer to improve the attachment between substrate and the silver film. The thickness of the film was optimized by changing deposition potentials. The optical properties of the film will be measured.

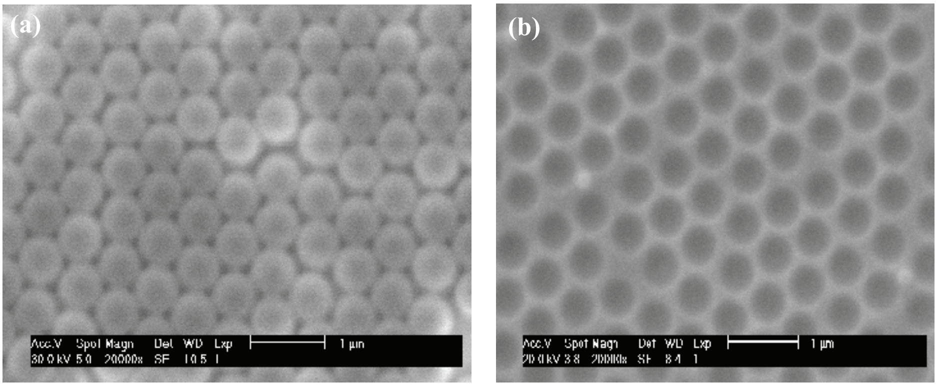

Figure 1. a) SEM image of polystyrene spheres templates (600 nm) on Au coated glass and b) SEM image of silver nanostructures after removing polystyrene sphere template.

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Electrochemical Sensors Based on Nanoparticles of Metalls/Metall Oxides for Clinical Diagnostics

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In the last decade the interest of researchers to development of methods and sensors, which include nanomaterial as the auxiliary or detected component, grew sharply. The combination of simplicity and response rate of electrochemical methods with the unique specificity of immunoreaction, and also the application of nanomaterial lead to the creation of new generation of electrochemical biomimetic- and immunosensors. Results are important for diagnostics to be used on-site and on-line, in particular.

Two approaches are proposed in this work:: the first one is developing of) electrochemical biomimetic sensors for determination of urea and creatinine and the second one consists in development of electrochemical method for pathogen microorganisms determining.

The biomimetic sensors are based on NiO nanoparticles localized on screen-printed carbon electrode as catalysts for urea or creatinine electrochemical oxidation. Solid phase extraction columns, filled with ion-exchange polymer or creatinine molecular imprinted polymer in case of urea or creatinine correspondently were used to provide selectivity of determinations.

Novel diagnostic method for the detection of high pathogenic *Salmonella typhimurium* using Fe_3O_4 nanoparticles and screen-printed carbon electrode is proposed as well. The analysis algorithm includes magnetic nanoparticles interaction with the cells to be determined, magnetic separation of unbound nanoparticles, concentrating of marked cells on the solid substrate (screen-printed carbon electrode) covered with antibodies to the bacteria/antigen. *Salmonella typhimurium* concentration was determined by means of stripping voltammetric registration of Fe^{3+} in the solution generated in acidic destruction of the immunocomplex of *Salmonella typhimurium*/antigen, formed on the substrate surface at the concentrating stage.

In order to avoid the acidic destruction of the immunocomplex, the core-shell Fe_3O_4 nanoparticles, covered by polypyrrole or polyvinilbenzilchloride which are functionalized with a covalently linked quinolinium salt was synthesized.

Immuno-magnetic core-shell nanoparticle assay demonstrates promising probabilities for realization of on-site and in-situ analysis.

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Novel Impedimetric Nanobiosensor Based on Biocatalysis of Catalase at CdTe Quantum Dots/Nafion Modified Glassy Carbon Electrode for Subnanomolar Detection of Hydrogen Peroxide

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Semiconductor quantum dots such as CdTe have been extensively studied in the past two decades due to unique optical and electronic properties which are not available in either discrete or in bulk solids [1,2]. These nanoparticles exhibit quantum size effects including a blue shift of absorption onset, a change in electrochemical potential of band edge, and an enhancement of photocatalytic activities with decreasing crystallite size. Intense interests in QDs focus on their biological applications, which could allow an integration of nanotechnology and biology [3,4].

In this work, a robust and effective nano-composite film based on CdTe quantum dots/nafion modified glassy carbon electrode was prepared by droplet casting. The fabricated nano-composite was used to construct a novel catalase biosensor for the determination of hydrogen peroxide. Direct electron transfer and electrocatalysis of catalase were fully investigated. The results suggested that catalase could be firmly adsorbed at the modified electrode. A pair of quasi-reversible redox peaks of catalase was observed in 0.20 M deaerated phosphate buffer solution of pH 7.0. The nano-composite film showed a pronounced promotion of the direct electron transfer between catalase and glassy carbon electrode. The immobilized catalase exhibited an excellent electrocatalytic activity towards the reduction of H_2O_2. Cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy were used to characterize the performance of the prepared nanobiosensor. The results showed that the prepared biosensor could be used as an amperometric biosensor for H_2O_2 detection. The system was also found well suited for the use of impedimetry as an excellent biosensing system for hydrogen peroxide, with the advantage of overcoming the intrinsic problem of the overpotentials associated with the amperometic methods [5]. The electrochemical impedance spectroscopy measurements revealed that the charge transfer resistance decreases significantly after enzymatic reaction with hydrogen peroxide concentration, so that the proposed modified electrode can be applied as an excellent nanobiosensor to the detection of ultra traces of H_2O_2 (2.0×10^{-10} -2.0×10^{-9} M). The observed high sensitivity, long-term stability and much lower limit of detection of the proposed nanobiosensor, relative to the reported amperometric sensors in the literature, clearly revealed that the nano-composite used not only resulted in facilitated communication between catalase and the modified electrode, but also provided a proper microenvironment for enzyme-substrate interaction.

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