Book of Abstracts

June, 2019

52nd Heyrovsky Discussion on Electrochemistry of Organic Compounds and Biopolymers

Liblice, Czech Republic

Book of Abstracts

52nd Heyrovsky Discussion

on

Electrochemistry of Organic Compounds and Biopolymers

On the occasion of the 60th anniversary of awarding
Professor Heyrovsky by Nobel Prize for the invention of polarography
and dedicated to the Memory of Professor Emil Paleček

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MAIN THEME AND PROPOSED DISCUSSION TOPICS

Electrochemical investigation of organic compounds, biopolymers, and studies of mechanisms of related electrode processes are the main topic of the 52th Heyrovsky Discussion with the following subtopics:

Structure-reactivity relationship in redox-active molecular systems

- *redox mechanistic studies of organic and coordination compounds*
- *bond activation by electron transfer*
- *electron transfer in molecules with multiple redox centers*
- *correlation of experimental data with theoretical calculations*

Electrochemistry and electroanalysis of drugs, bioactive compounds, genotoxic and ecotoxic substances

- *novel electrochemical (bio)sensors/(bio)assays and their applications*
- *combination of electrochemistry with other techniques (e.g., spectroscopic methods)*
- *application of traditional vs. novel electrode materials*

Biopolymer electrochemistry

- *electrochemistry of natural, chemically modified and synthetic nucleic acids*
- *protein electrochemistry and electroanalysis: structure and interaction effects*
- *catalytic hydrogen evolution and other catalytic processes employed in biopolymer electrochemistry*
- *electrochemistry of natural and chemically modified carbohydrates*

Biological membranes, their mimics, and transporting processes

- *transporting processes across membranes*
- *transport through nanopores*

Novel materials and nanotechnology for electrochemical sensors

- *electrode materials and surface modifications*
- *nanostructured surfaces for electrochemical (bio)sensing*
- *nanoobjects for biopolymer labeling*

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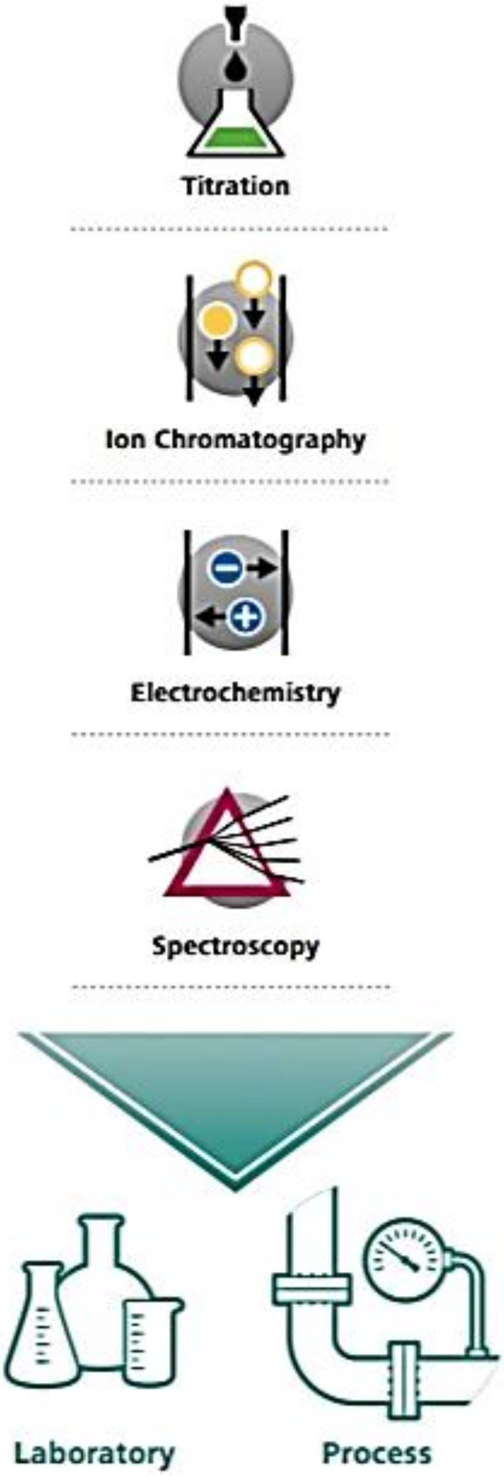

Titration

Ion Chromatography

Electrochemistry

Spectroscopy

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Morphological and Biosensing Properties of Porous Boron Doped Diamond Based Electrodes

Simona Baluchová [1,2], Silvia Sedláková [3], Andrew Taylor [3], Ladislav Klimša [3], Jaromír Kopeček [3], Vincent Mortet [2,3],
and Karolina Schwarzová-Pecková [1,2]

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Boron-doped diamond (BDD) is a well-established electrode material with many unique properties, however, its performance can be significantly improved by enlarging the effective surface area. For that reason, approaches focusing on fabrication of porous BDD-based electrode materials have been emerging and such electrodes have already been successfully applied in electroanalysis of biomolecules.

In this study, complex characterization and analytical performance of various porous BDD-based electrodes used as electrochemical sensors are reported. As-grown porous BDD samples were deposited on different scaffold templates such as carbon nanotubes, SiO_2 nanofibers and their combination with a ratio of 1:1, using a microwave plasma-enhanced chemical vapour deposition (details of similar MW PECVD procedures can be found in ref. [1, 2]). For comparison purposes, the same measurements were performed using conventional planar BDD films and a glassy carbon electrode. The surface morphology of deposited BDD layers on the above-mentioned templates was observed by scanning electron microscopy. To examine their electrochemical behaviour, cyclic voltammetric experiments were performed in order to evaluate the widths of the potential windows and the peak-to-peak separation ΔE_p of various outer- and inner-sphere redox probes. In addition, the values of effective surface areas and double layer capacities were experimentally assessed. Moreover, the effects of the morphology of porous BDD films on their biosensing properties with respect to neurotransmitters and their precursors were thoroughly investigated and the obtained results revealed promising electrochemical features of such materials, implying that the porous and biocompatible BDD surfaces have a potential to lead to the expansion of *in-vitro* and *in-vivo* applications in electroanalysis and neuroscience.

Acknowledgments

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Synthetic TATA Box Recognition by Amino Acids Recognizing the Natural TATA box

Katarzyna Bartold [1], Agnieszka Pietrzyk-Le [1], Wojciech Lisowski [1], Karolina Golebiewska [1], Alexandra Siklitskaya [1], Pawel Borowicz [1], Shuai Shao [2], Francis D’Souza [2],and Wlodzimierz Kutner [1,3]

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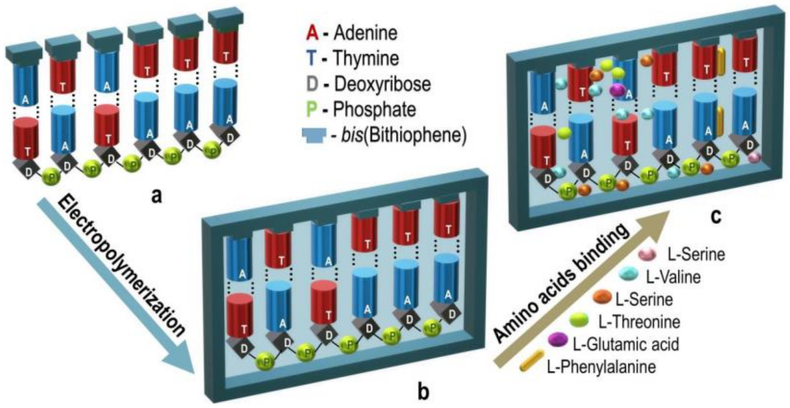
Amino acids present in TATA binding protein (TBP) were demonstrated to recognize a newly prepared synthetic TATA (T - thymine, A - adenine) box [1]. This recognition imitated natural oligodeoxyribonucleotide interactions with amino acids of TBP participating in repairing of damaged dsDNA. By electropolymerization, 5’-TATAAA-3’ was molecularly imprinted using T- and A-derivatized thiophene functional monomers. That way, *hexakis*[*bis*(2,2’-bithien-5-yl)] TTTATA was synthesized in one-step and simultaneously hybridized with the 5’-TATAAA-3’ template. Thus, a stable dsDNA analog of a controlled nucleobases sequence was generated in a molecularly imprinted polymer (MIP) film deposited on the electrode surface. XPS depth profiling revealed that the 5’-TATAAA-3’ was homogeneously distributed in the film. This MIP served as a matrix of a synthetic TATA box with the TATAAA-promoter sequence. This synthetic DNA hybrid was characterized by PM-IRRAS and XPS. Then, TBP amino acids interactions with the synthetic TATA box were examined. Most likely, molecules of L-phenylalanine interacted with nucleobase steps of this synthetic TATA box by π-π stacking while L-glutamic acid molecules easily diffused through outermost layers of the (5’-TATAAA-3’)-templated MIP film. Moreover, L-lysine and L-serine favorably interacted with the phosphate residue of 5’-TATAAA-3’ in the MIP. Real-time QCM piezoelectric microgravimetry and SPR spectroscopy under FIA conditions were used for examining amino acids interactions with the synthetic TATA box.



Scheme 1: A flowchart of a synthetic TATA box preparation and amino acids recognition.

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Morphological, Spectral, and Electrochemical Characterization of Boron-Doped Diamond Electrodes, and their Application in the Sensing of Neurotransmitter Dopamine

Mariola Brycht [1,2], Simona Baluchová [1,3], Karolina Schwarzová-Pecková [1,3], Andrew Taylor [4], Silvia Sedláková [4], Ladislav Klimša [4], Jaromír Kopeček [4], and Vincent Mortet [3,4]

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Boron-doped diamond (BDD) thin films have become a popular electrode material for electrochemical oxidation of neurotransmitters, especially biogenic amines, due to its exceptional properties in comparison with other carbon-based materials [1]. These include low background current, a wide potential window in aqueous solutions in the positive potential region, long term stability, and low proclivity to electrode passivation.

In this work, microwave plasma-enhanced chemical vapour deposition (MW–PECVD) was used to fabricate hydrogen-terminated planar and porous BDD samples with boron to carbon ratio in the gaseous phase of 4000 ppm. Planar and porous BDD films were deposited onto conductive silicon wafers and a 3D template composed of silicon dioxide nanofibers prepared by spin coating, respectively. In addition, as-deposited hydrogen-terminated planar BDD samples were produced using MW–PECVD with linear antenna delivery system (MW–LA–PECVD). A comparison of planar and porous BDD samples prepared by conventional MW–PECVD apparatus with BDD samples grown by MW–LA–PECVD apparatus was performed. The morphological and structural characterization of all samples was carried out by scanning electron microscopy (SEM) and Raman spectroscopy, respectively. Electrochemical characterization of the prepared BDD macroelectrodes was performed by recording cyclic voltammograms of inner-sphere ($[Fe(CN)_6]^{3-/4-}$), and outer-sphere ($[Ru(NH_3)_6]^{3+/2+}$, $[IrCl_6]^{2-/3-}$) redox markers, and peak-to-peak separation (ΔE_p) of these redox markers, along with measurement of the effective surface area (A_{eff}). Moreover, BDD-based electrode materials were tested for applications in sensing of neurotransmitter dopamine in 0.1 mol L^{-1} phosphate buffer solution and 20 mM HEPES buffered saline (both at pH 7.4), which is a biological buffer suitable for all cell culture systems with a high proliferation and cell density.

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A Tale of Two Hemes – Redox Driven Ligand Exchange in Diheme Thiosulfate Dehydrogenase (TsdA) Enzymes

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Diheme cytochromes of the thiosulfate dehydrogenase (TsdA) family catalyse oxidative conjugation of two molecules of thiosulfate ($S_2O_3^{2-}$) releasing two electrons and forming tetrathionate ($S_4O_6^{2-}$) [1]. For *Allochromatium vinosum* TsdA, X-ray diffraction has revealed the active site Heme 1 as having relatively unusual His/Cys$^-$ axial ligation [2, 3]. Heme 2, responsible for interprotein electron exchange, has His/Lys ligation when oxidised but His/Met ligation in the reduced form [3]. This contribution presents protein film cyclic voltammetry, and complementary spectroscopic studies, mapping out the redox properties of *A. vinosum* TsdA.

Redox transformations occur in two potential windows; one between ~200 and 400 mV and another between ~-50 and -300 mV vs SHE. Reversible redox transformation of His/Cys$^-$ Heme 1 is proposed to occur with $E_M \approx -181$ mV. More complex behaviour is attributed to reduction of His/Lys Heme 2, $E_M \approx -129$ mV, that triggers a Lys to Met ligand switch, such that re-oxidation of Heme 2 is resolved with $E_M \approx +266$ mV. The consequences of these observations for catalysis by TsdA enzymes, most of which are predicted from sequence analysis [2-4] to have only His/Met ligation of Heme 2, will be considered.

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Mechanistic, Kinetic and Analytical Studies on the Oxidation and Reduction of Omeprazole at Boron Doped Diamond Electrode

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Unmodified boron doped diamond electrode (BDDE) was used for omeprazole (OMZ) voltammetric behavior investigation as biologically and pharmaceutically important organic molecule. It is possible to oxidize and reduce OMZ in various types of supporting electrolytes while both processes are strongly dependent on pH value of media. As we observed the charge transfer is controlled by diffusion and it is irreversible. This was studied in the pH range from 3 to 10 and characterized by formal potentials (from +1.07 V to +0.89 V for oxidation and from -0.95 V to -1.18 V for the reduction), charge transfer coefficients (0.52 – 0.33 for oxidation and 0.19 – 0.17 for reduction) together with standard heterogeneous rate constants of $10^{-3} – 10^{-4}$ cm s^{-1} order.

Analytical performance was studied with linear sweep voltammetry (LSV) and more sensitive techniques like square-wave voltammetry (SWV) and differential pulse voltammetry (DPV). The lowest detection limits were estimated to 9.1×10^{-8} mol L^{-1} for OMZ oxidation in PBS with pH value of 10 by SWV and 9.1×10^{-7} mol L^{-1} for OMZ reduction in PBS with a pH value of 3 by DPV method.

Based on this methodology, simple, sensitive and cheap analytical technique was developed. It was validated on synthetic, spiked and real samples to demonstrate practical applicability. Pharmaceutical formulations of OMZ and human urine served as real samples. The results are in the statistical agreement with values declared by manufacturer as well as in the case of human urine with the results obtained by HPLC-UV as independent analytical technique widely used for this kind of determination [1].

Acknowledgments

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Nanomaterials Based Electrochemical Nucleic Acid Biosensors

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After the discovery of electroactivity in nucleic acids by Prof. Emil Palecek [1], many electrochemical methods have been developed for the quantification of nucleic acids and its interactions with drugs, proteins etc. [2-6].

Nanotechnology based biosensors have become the one of the crucial topics due to the advantages of various nanomaterials as their unique electronic, optical, and catalytic properties [4-6]. The specific properties of nanomaterials (such as, carbon nanotubes, nanoparticles, dendrimers etc.) offer an excellent prospect for biological recognition surfaces in order to develop highly selective and sensitive electrochemical biosensor platforms detecting a wide range of proteins and nucleic acids.

An overview to electrochemical nucleic acid biosensors based on different nanomaterials has been presented herein with their applications on detection of spesific biomolecular recognitions such as, sequence-selective nucleic acid hybridization and DNA interactions.

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DNA Hybridization and Interaction with Small Molecules Studied by H/D Isotope Effects in Voltammetry and EQCM

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We report on our latest research regarding redox-switching of the viscoelasticity of DNA layers observed on the millisecond time scale [1], as well as very large deuterium isotope effects observed in voltammetric measurements of certain redox-active small molecules that travel through the DNA layer on gold electrodes. To the best of our knowledge, DNA-SAM conjugated with hexammine cobalt(III) (CoHex) shows the largest isotope effect that has been reported so far (kH/kD = 2400) [2]. Hexammine ruthenium(III) (RuHex) does not show this isotope effect, whereas with daunomycin, we have recently observed a significant redox potential shift up to -80 mV. A thin-layer model [3] may explain this voltammetric behavior. RuHex covers the negatively charged DNA strand and provides considerable conductivity, while CoHex (and daunomycin) do not, as illustrated in Fig. 1A&B. Latest results indicate considerable isotope effects also in EQCM depending on the redox molecule interacting with DNA, as well as major differences between ssDNA and dsDNA. These effects will provide new opportunities in drug screening and studies of DNA damage by toxic chemicals.

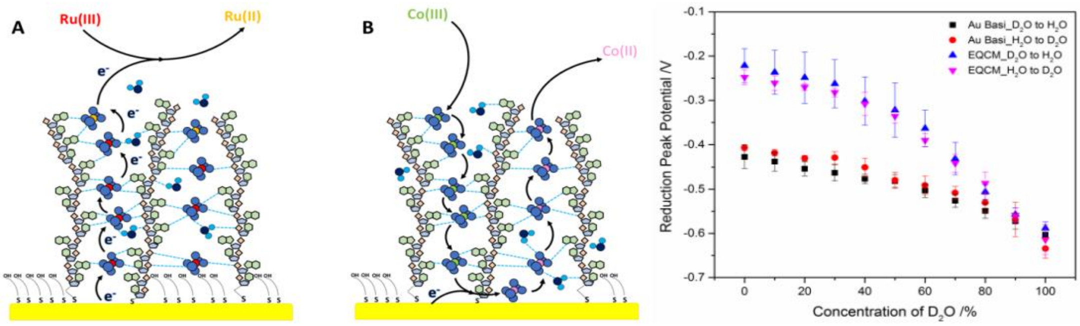

Fig. 1: Left: charge transfer mechanisms in ssDNA-SAMs conjugated with hexammine metal complexes at reductive potentials: A) electron hopping enabled by RuHex and B) diffusion of redox-active CoHex through the SAM. Right: voltammetric isotope effect upon CoHex reduction peak potential.

Acknowledgments
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Electrochemical Study of Sudan I as a Marker Substrate for the Monitoring of Cytochrome P450-Catalyzed Hydroxylation

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Sudan I (1-phenylazo-2-naphthol) is an aromatic azo compound used as an orange colouring agent [1]. In mammalian organisms, Sudan I is metabolized by the microsomal detoxifying system with a central role of the cytochrome P450-family (CYP) hydroxylases [2]. Due to the existing detailed knowledge about Sudan I hydroxylation pathways, in studies involving the CYP enzymes the dye can be applied as a marker substrate. Besides other methods, electrochemistry has been applied to determine Sudan I and related compounds in relevant matrices, with especial attention paid to analysis of food samples [1, 3]. The dye can be detected either via oxidation of its phenolic group, or via reduction of the azo group present in its molecule.

In this study we performed a series of electrochemical measurements to elucidate processes following the primary oxidation or reduction of Sudan I and/or formation of new electrochemically active moieties (such as quinones, aniline or 1-amino 2-naphthol). Comparative measurements were performed with synthetic model compounds to test the possibility of differentiation among various hydroxylation products of the dye. Two types of carbon-based electrodes have been used (pyrolytic graphite and boron doped diamond electrodes) to compare voltammetric responses and/or adsorption properties of the starting compound or product of its electrochemical conversion at different electrode surfaces. Our results suggest the possibility of application of simple electrochemical techniques in the analysis of CYP reaction mixtures using Sudan I as a marker.

Acknowledgments

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Electrochemical Investigation of Substituent Effect on Oxidation Potentials of Novel Antimycobacterial Agents

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Twenty-two derivatives of ring-substituted hydroxynaphthalenecarboxanilides were studied by cyclic voltammetry at a glassy carbon electrode. Based on our previous study of a model compound from this group [1], it was possible to oxidize all the compounds in the studied medium, 10% dimethyl sulfoxide and phosphate buffer pH 7.2. However, their oxidation potential varied in the range from +0.1 V to +0.3 V (vs. $[Fe^{II}(CN)_6]^{4-}$) based on electron-withdrawing or electron-donating properties of various substituents (namely -F, -Cl, -Br, -CH_3, -OCH_3, -CF_3, and -NO_2). Therefore, this relation could be studied using Hammett substituent constants as reviewed by Zuman [2]. Good correlation was found between Hammett's values and potential of oxidation for three series of compounds (*ortho-*, *meta-*, *para-*) based on a position of a given substituent. These compounds were prepared and studied as novel agents that exhibited antimycobacterial activity [3]. *Mycobacteria* are responsible for various illnesses, most notably tuberculosis. Obtained data could be then discussed in relation to antibacterial activities of given derivatives.

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Electrochemical Characterization of Porous Boron-Doped Diamond Deposited on SiO_2 Nanofibres and Carbon Nanotubes Templates

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Porous boron-doped diamond (p-BDD) is a highly attractive material for electrochemical applications. Various methods have been used for preparation of p-BDD. In this work, p-BDD layers were obtained by multi-step chemical vapor deposition (CVD) on a porous template of SiO_2 fibers deposited by spincoating [1]. Here we investigated the effect of addition of carbon nanotubes to the fiber templates on electrochemical properties of p-BDD.

Morphology of porous layers was determined by scanning electron microscopy while concentration of boron was estimated by Raman spectroscopy [2]. Electrical conductivity was measured by Van der Pauw technique. Surface area of samples was investigated by Brunauer–Emmett–Teller (BET) method. Electrochemical characterizations were carried out by Electrochemical Impedance Spectroscopy (EIS) in aqueous solution of potassium chloride (1.0 M).

We found that electrical conductivity has been increased by a factor of two by the addition of carbon nanotubes. Values of electric double layer capacitance (obtained by EIS) were correlated to the surface area. Flat BDD layer (with the same doping level) has been chosen as a reference. The capacitance was proportional to the number of porous layers. At high frequencies (above 1 KHz) the proportionality was almost linear. Interestingly, the capacitance turned out to be dependent on electrochemical history of samples, i.e. whether the samples have been treated at a high positive or a high negative potential. The history typically accounted for the difference in the capacitance of less than 30 %.

Acknowledgments

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Effect of Nanostructured Carbon-Based Materials on Electrochemical Oxidation of Both free and Protein-Bound Tryptophan and Tyrosine

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Recent studies, including results of our laboratory, have shown that electro-oxidation of organic aromatic molecules on nanostructured carbon-based surfaces is influenced by a combination of two factors: (i) the incidence of graphene basal planes as sites of the analyte(s) adsorption due to π-π stacking and hydrophobic interactions and (ii) the occurrence of graphene sheet edges and/or motifs decorated by oxygenous functional groups as entities representing sites/defects conducting electron transfer and thus facilitating electro-oxidation of certain analytes which, moreover, can interact with the nanostructured carbon-based surface by electrostatic forces and hydrogen bonds [1-4].

The aim of this study is to determine how basal- and edge-oriented graphite sheets and graphite oxide surface motifs of graphite-based electrodes affect the electrochemical oxidation of free amino acids tryptophan and tyrosine and tyrosine- and tryptophan-residues bound in some important protein molecules such as albumin or fibrinogen. The effects of some specific nanostructured carbon structures, including single-walled or multi-walled carbon nanotubes and carbon nanofibers, on the electrochemical oxidation of both free and protein-bound tryptophan and tyrosine in microliter volumes have been tested using commercially available screen-printed graphite electrodes modified by these nanostructures.

Acknowledgements

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Silver Amalgam Particles: From Voltammetry to Plasmonics

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Electrochemical co-deposition of silver amalgam particles (AgAP) from the solution of Ag(I) and Hg(II) ions was found to be a convenient procedure for preparation of this electrode material on any conductive material in principle. The AgAP were electrodeposited on the surface of transparent indium tin oxide (ITO) electrodes by double pulse chronoamperometry. The ITO-AgAP was successfully utilized in voltammetric and spectroelectrochemical detection of nitrobenzfurazane, a subunit of perspective DNA redox label. Furthermore, preferential adsorption of fluorescently labelled DNA on AgAP then on ITO was observed by fluorescent microscopy [1]. Bioanalytical application of the AgAP has moreover been proven by analogical adsorption experiments with the DNA and green fluorescent protein (GFP) on basal plane pyrolytic graphite electrodes (bPGE) decorated by AgAP. In addition, intrinsic signals of these biopolymers were successful detected using cyclic voltammetry (peak CA and G) and chronopotentiometric stripping voltametry (peak H), respectively [2]. Vapor-deposited golden film on silicon wafers (AuE) has also been used as a substrate for electrodeposition of AgAP. While electrodeposited mercury destroyed the golden film, the AgAPs could be repetitively re-deposited upon their electrochemical dissolution with sufficient repeatability of redox signal provided by selected model organic nitro-compound, 4-nitrophenol. Voltammetric detection of the DNA labeled by Os(bipy) was also possible at AuE-AgAP [3]. Among the others, our results set up AgAP as a suitable material for introduction of plasmonic functionalities into photochemical and spectroelectrochemical systems [4].

Acknowledgments
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Voltammetric Gas Sensors

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Currently we are facing increasing interest in sensitive and robust gas sensors for volatile organic compounds (VOCs), which can operate autonomously without necessity for maintaining specific operating conditions. VOCs are documented as environmental pollutants with adverse impact upon living organisms and human health, and on the other hand, they are recognized as important biomarkers for several diseases, such as lung cancer and diabetes [1,2]. Electrochemical techniques have been proved as particularly suitable approach for developing a great variety of VOC sensors due to practically unlimited possibilities of using numerous inorganic and/or organic materials as sensing elements, suitability for electrode miniaturization and application of different electrochemical sensing protocols. However, a vast majority of electrochemical VOC sensors are based on chemiresistance in combination with various metal oxides that enable good sensitivity, but limited selectivity. In addition, these sensors exhibit difficulties when operating under humid conditions, in the presence of sulfur compounds and weak acids [3]; usually they need to operate at elevated temperatures in the range of ca. 200 - 500 °C that limits their practical application.

Herein, we will present our resent research in the development of electrochemical gas sensors for detecting low concentration levels of several gaseous analytes belonging to a large family of VOCs. We synthesized and studied several multifunctional materials serving simultaneously as electrolyte, accumulation medium, and derivatization milieu, enabling sensitive voltammetric detection. These materials were examined for their potential use as electrochemical gas sensors for selected aldehydes, ketones and phenols; an example of a successful application in a real environment will be demonstrated.

Further development of the proposed sensing strategy might be beneficially employed in various fields such as clinical diagnostics, environmental and industrial monitoring, food safety, occupational health care, public security, cultural heritage preservation, etc.

Acknowledgments

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Effect of Multiple Anchor Connectivity on the Single Molecule Conductance of Oligophenylene Molecular Wires

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We have studied a series of molecules based on oligophenylene molecular wires containing tripodal anchoring groups which differ in the position of thiols (*meta* versus *para*) on the aromatic rings of the tetraphenylmethane tripod. Their single molecule conductance was obtained by the scanning tunneling microscopy break junction method. Density functional theory combined with the non-equilibrium Green's function formalism was used to understand charge transport properties and provide most probable metal-molecule-metal junction geometries. It was shown that in the molecules studied in this work the most probable molecular junction geometry is the following: three thiolates of the tripod are anchored to one electrode and a single thiolate of the oligophenylene wire to another one. The junction formation probability for *meta* functionalization was 68 % and that for *para* 55 %, respectively. Nevertheless, the conductance-distance histograms for both molecules show two peaks, where a high conductance peak G_H represents the conductance exclusively through the tripodal platform, whereas the low conductance peak G_L represents conductance along the molecule through the tripod–linked molecular wire as described above. Single molecule conductance for *meta*–functionalized wire is $\log(G_L/G_0) = -5.8 \pm 0.5$ and that for *para*–functionalized wire is $\log(G_L/G_0) = -5.6 \pm 0.5$, respectively. These results indicate that *meta* substitution leads to formation of a more stable junction compared to *para*, whereas *para* functionalized tripodal anchoring group has better conducting properties. Experimental and theoretical results will be further discussed in terms of the suitability of these types of molecules as supporting conductors for molecular electronic elements important for the future molecular electronics design [1–4].

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Effect of Surface Modification with Titanium Carbosilicide on the Electrochemical Characteristics of Lithium and Transition Metals Polyanionic Compounds

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The compounds of the so-called MAX phases class (where M is a transition metal, A is an element of the main subgroup of the III-V groups of the periodic system, X is carbon or nitrogen), which were firstly synthesized in the 1970s are widely used as the basis of structural materials due to high mechanical strength, outstanding heat and electroconductive properties, as well as chemical stability [1]. We used one of such compounds – Ti_3SiC_2 (TSC) [2] for the particles surface modification of polyanionic cathode materials for lithium-ion battery e.g. $Li_3V_2(PO_4)_3$/carbon composite (LVP/C). TSC modified LVP/C demonstrates improved electrochemical behavior (Fig. 1) [3].

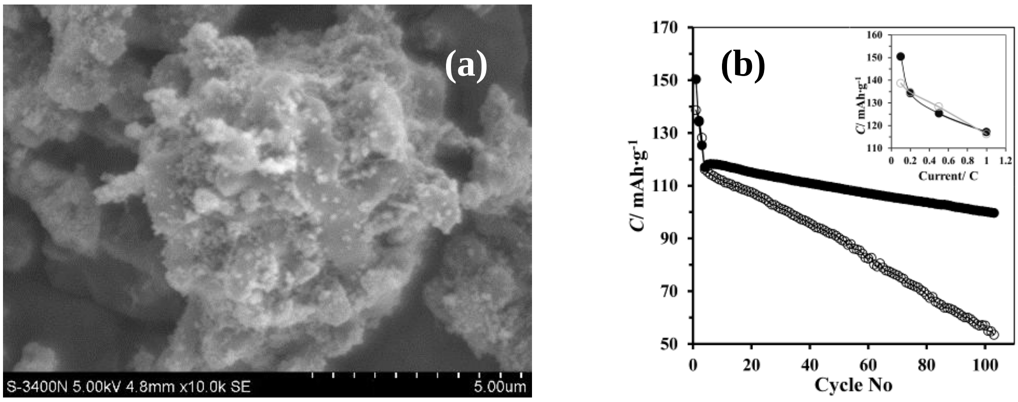

Fig. 1: Scanning electron micrograph (*a*) and galvanostatic charge/discharge capacity behavior (*b*) of the TSC-modified LVP/C-electrode. Empty markers of (b) correspond to the material with bare particles, filled markers – TSC-modified particles.

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Praise of Mercury

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Explosive development of electrochemistry in the middle of the last century can be mostly credited to the pioneering work of Jaroslav Heyrovsky, his students and collaborators. In their groundwork they used mainly, but not exclusively, the dropping mercury electrode [1], which later became the principal tool of electroanalysis. The non-mercury, solid state electrodes came later and extended the domain of applications of electrochemistry to more positive potentials, i.e. to oxidations. But things have changed recently: In the words of late Professor E. Palecek: *"...mercury electrodes have almost completely disappeared from electroanalysis ...."* [2]. Why? The reasons are mostly irrational and political. When politics or religion invades science, bad things happen. Mercury occupies a unique position in the periodic table. Its electronic structure ([Xe] $4f^{14}$ $5d^{10}$ 6s) defines both its physical and chemical properties. The 6s electrons are effectively shielded from the nucleus by the filled 4f shell. That accounts for the relatively low melting point (- 38.8 C) and a high work function (4.5 eV) of Hg. In many respects Hg resembles noble gases in some types of interactions. In this work we report on experiments performed at *sessile mercury drop electrode (SMDE)*. Its principle and function are shown in the self-explanatory Fig. 1. Liquid state at room temperature, high surface tension of the Hg/water interface (415 mN m^{-1}), atomically smooth surface and high hydrogen overvoltage are the most relevant properties from the point of view of the work reported here. Liquid state combined with excellent electronic properties allow us to use it as a miniature Langmuir trough for study of structure and electrochemical properties of adsorbates. Unlike the classical LB trough SMDE allows for both compression and expansion of the surface film [3]. Molecules of interest can be imbedded in the surface film and can be immobilized by the clamping molecules, for e.g. imaging by electron tunneling microscopy [4]. An unexpected but interesting complication is the "Gibbs-Marangoni Effect", which we also studied using SMDE [5, 6].

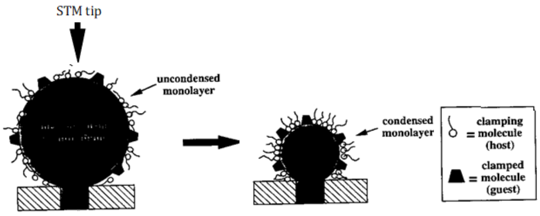

Fig. 1: Sessile mercury drop electrode.

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Voltammetric Approach for a Sensitive Determination of Plant Growth Stimulator 1-Naphthaleneacetic Acid Employing Boron-Doped Diamond as a Sensor

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1-Naphthaleneacetic acid (NAA) or its sodium salt (NAANa) are often applied for plant growth stimulation, mainly for rooting of plants. They are used alone or in mixture with other auxins. Voltammetric approaches aiming to determination of NAA are described mainly on modified carbon electrodes e.g. [1-3]. In the present paper, we focused, for the first time, on monitoring of electrochemical oxidation of NAA in ethanolic acidic media (0.6 M H_2SO_4) employing boron-doped diamond electrode (BDDE) as a stable and sensitive sensor, which does not need any complicated pretreatment or preparation. Moreover, the recorded process undergoes about relatively high positive potentials and two anodic peaks about +1405 mV and 1595 mV, respectively, can be recorded on BDDE due to its wide potential window. Conditions of differential pulse voltammetry (DPV) were optimized and it was reached low limit of quantification (LOQ = 0.445 µg mL^{-1}). The proposed voltammetric approach does not required high cost instrumentation and it was evaluated as time saving, reliable and sensitive. Besides possible voltammetric determination, reaction mechanism of the followed anodic reaction was examined as well and it is displayed in Fig. 1. It was found out that the first oxidation step included creation of relevant alcohol (2) and aldehyde (3) as well and the second oxidation step could be described as oxidation of the aldehyde and creation of insoluble polymeric products of NAA.

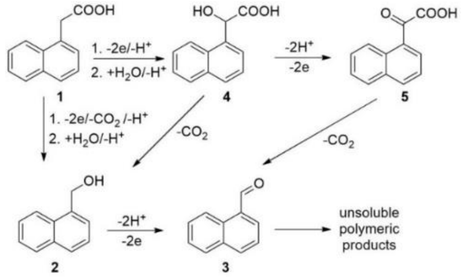

Fig. 1: Mechanism of NAA oxidation in acidic solutions.

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Pyrene Derivatives for Organic Field-Effect Transistors

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Conjugated organic systems are widely used in material science; required properties of these compounds can be easily adjusted by chemical modification. These "green smart molecules" are applied in purely organic electronics based on biodegradable organics. Pyrene derivatives are utilized mainly for components of *OLED* (Organic light-emitting diode), OPV (Organic Photovoltaics) and OFET (Organic field-effect transistor).

Our project is focused on electrochemical investigations of pyrene derivatives and other aromatics interconnected with a cyclobutene bridge representing the "core" – tetra substituted double bond. From the electrochemical point of view, investigation of these molecules extends the knowledge of redox properties and structural transformations of substituted pyrenes in interaction with the "core" double bond.

Electrochemical properties of conjugated systems comprising pyrene, other aromatics (anisyl, tolyl) and cyclobutene were studied at various electrodes in non-aqueous aprotic solutions by the means of polarography, cyclic voltammetry at hanging mercury drop electrode and stationary glassy-carbon electrode, and by voltammetry at rotating disc electrode (glassy carbon).

Pyrene derivatives are good chromophores and redox centers and are suitable for construction of organic semiconductors. In all studied systems, pyrene moiety is reduced to radical anion and subsequently to corresponding dianion. Substituents influence the reduction potential in agreement with induction/mesomeric effect enabling precise tuning of substance properties. The incorporated cyclobutene bridge extends the planar conjugated aromatic system, which has been proved by partial reversibility of its first reduction step. During reduction of cyclobutene, the ring opening and splitting of the CH_2–CH_2 bond by the ECE mechanism occurs [1, 2]. Contrary, direct interconnection of two pyrene molecules by a single bond results in twisted molecule with limited pyrene interaction.

During oxidation, polymerization of pyrene and/or other components was observed. The next step of our investigation is correlation of our experimental results with quantum chemical calculations and analysis of electrolytical products, which enable more precise interpretation of the reaction mechanism as well as further tuning of properties of these molecules for OFETs.

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Electrochemistry and Singlet Fission: Investigation of Fluorinated Derivatives of 1,3-diphenylisobenzofuran

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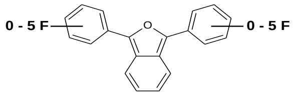
Singlet fission is a photophysical process which can occur if the triplet energy of an organic chromophore is equal or even lower than a half of its singlet excitation energy. In this case the excited singlet state can share its excitation energy with a neighbouring ground-state chromophore and both are converted into two triplet states [1,2]. Singlet fission therefore does not require change of spin of any from the molecules. In this way from one excited molecule two electrons can be separated, hence the effectivity of the transformation of light to electricity can be higher. This is the reason for increasing interest in molecules offering this property.

One of available compounds which are known as promising chromophores for singlet fission is 1,3-diphenylisobenzofuran (DPIBF) [1]. It is evident that redox properties of such molecules for singlet fission are critical for their use in solar cells. Therefore electrochemical investigations of various DPIBF derivatives are very important [3].

Our study is focused on a recently synthesized series of fluorinated derivatives of DPIBF where the influence of number and position of fluorine atoms in the molecule on the first oxidation and first reduction potentials is followed and the respective mechanism suggested. Besides standard steady-state, as well as dynamic electrochemical techniques were used, together with *in situ* UV-vis and EPR spectrometry.



When the derivatives of DPIBF have 1 to 4 fluorine atoms (in one case even 6), their oxidation as well as reduction patterns are in principle analogous to non fluorinated parent DPIBF. From our results it is evident that a) the contribution of fluorine atoms in *p*-position has no big influence on potential values; b) fluorine atom in *m*-position, due to its strong inductive effect, shifts oxidation potential by about 50–60 mV to more positive values; c) two fluorine atoms in *o*-position exhibit steric influence (twisting the phenyl ring out of the plane). Whereas the reduction starts with a one-electron reversible process, oxidation reaction is irreversible, involving two electrons. DPIBFs with 5 and 10 fluorine atoms differ substantially from the rest of the series of fluorinated DPIBFs. Their electrochemical reduction proceeds in two two-electron steps pointing to the change of mechanism. This problem is under study.

Acknowledgments

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Spectroelectrochemical Studies of Perfluoroalkylated Derivatives of PAHs

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The renaissance in the synthesis of small organic molecules with strong electron-accepting properties, that is, organic semiconductors, during the past decade has been spurred by the global economic need for renewable sources of energy and more-efficient and less-expensive electronic devices that preferably include earth-abundant elements. Significant progress in this endeavor requires a deep understanding of the fundamental relationships between molecular structure, solid-state morphology, and electronic and other physicochemical properties of organic semiconductors [1].

Functionalization with electron-withdrawing groups, such as fluorine or perfluoralkyl can have profound tuning effects upon the electronic and optical properties of organic compounds. It is one of the common methods to increase the electron affinity and improve the *n*-type properties of organic semiconductors [2-4]. By functionalization with these electron-withdrawing groups, polycyclic aromatic hydrocarbons (PAHs), such as coranulene [5], sumarene [5], or perylene [2] became interesting as potential organic semiconductors.

Electrochemistry is a common tool to characterize the electron-accepting properties of molecular organic materials. Elucidation of the redox center of electrochemical process including mechanism of complex redox reactions often requires the use of complementary spectroscopic techniques.

In this work, EPR-UV/Vis/NIR spectroelectrochemical studies of perfluoroalkylated derivatives of PAHs will be presented, which are helpful to get insight to the charge-transfer mechanism depending on chemical structure.

Acknowledgments

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Electrochemical Melting of DNA: Optimization and Application

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The electrochemistry of DNA has been an area of active research since the seminal work of Emil Paleček in the 1960s [1]. This research area has since expanded to include both fundamental biophysical studies and applications in biosensing and bioelectronics. While the original studies were performed on mercury electrodes, carbon and gold electrodes have also seen widespread use in the intervening decades. While mercury electrodes have considerable advantages for studying DNA (and other biomolecules), gold's ability to form strong bonds with thiol moieties lends itself to unique experimental possibilities. Self-assembled monolayers consisting of thiol-modified oligonucleotides and mercaptohexanol (or other molecular "fillers") provide reproducible surface coverages and molecular orientations conducive to studying DNA hybridization and melting at charged surfaces [2]. Here we present our studies on the destabilizing effect of applied potentials on short DNA duplexes tethered to gold electrodes via thiol bonds. In particular, we combine successive potential pulses negative of the potential of zero charge with intervening square wave voltammetry to monitor the extent of melting as a function of time, at room temperature [3]. Experimental parameters are varied to examine their effect on the electrochemical melting behaviour including pulse potential, pulse time, NaCl concentration, and DNA surface density. We explore the extent of non-specific DNA absorption and thiol reduction, and present conditions which minimize these processes. Furthermore, we studied the effect of oligonucleotide length, the presence of mismatches, hairpins, and DNA-drug interactions on the melting behaviour.

Our results suggest that information about the DNA stability can be obtained from both the kinetic and equilibrium responses. We propose a model for electrochemical melting in which the extent and rate of melting occurring at a given applied potential depends on the balance between duplex stability and double-layer charge. As the electrode potential becomes more negative the compensating ionic charge necessary in the double-layer increases. This charging of the interface can be achieved via both the migration of counter ions from the bulk of the solution and removal of DNA from the surface by melting. The DNA melts until counterions from solution can provide the necessary charge screening to stabilize the remaining duplexes. This provides a simple electrochemical means of controlling the extent of hybridization and to select for fully hybridized duplexes over partially hybridized, mismatched, or otherwise destabilized duplexes.

Acknowledgments

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Mechanism of Emulsion Formation in an Organic Solvent in the Presence of Hydrated Ions

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A two-electrode cell comprising a liquid/liquid interface has been used to study the water clusters formation in the organic solvent phase following the tetraalkylammonium chloride (TAACl) transport from the aqueous phase. The partition of chloride ions is controlled by the interfacial potential difference induced by the distribution of a common TAA^+ ions in both phases. The transfer of hydrated chloride ions is accompanied by the transfer of TAA^+ ions which concentration at the aqueous side of the interface can be monitored by the open circuit potential (OCP) measurement. The amount of TAACl transported at a given potential to the organic phase exceeds amount of TAACl which could be dissolved. It results in the water clusters formation in the organic solvent phase. The presented mechanism of this process involves an additional water transport to the organic phase completing dissolved water consumed by the water clusters formation. At higher concentration of TAACl in the aqueous phase this process leads to the formation of emulsion in the organic phase.

The analysis of OCP transients lead to the following mechanism of the water clusters formation. In the first step, the TAACl is transported to the organic phase to fulfill the partition of chloride anions. In the next step the chloride ions dissolved in the organic phase form the water clusters utilizing the initial presence of water in the organic phase and water transported by chloride ions. The expended water in the organic phase is replenish by its diffusion from the aqueous phase to fulfill the equilibrium. At any distance from the interface the partition of TAACl between the organic phase and the water clusters must be fulfilled. It can be expected that the partition of TAACl will be influenced by the water cluster size.

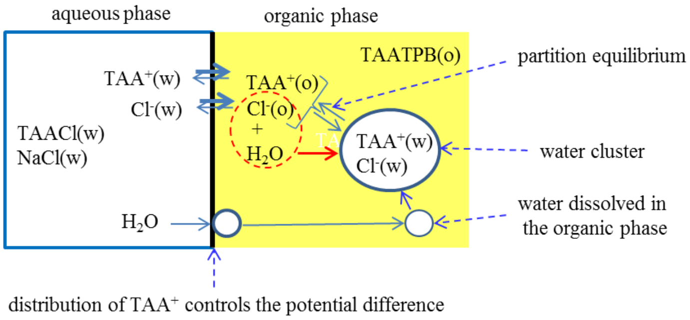

Fig. 1: A cartoon depiction of the mechanism of water clusters formation at a water/organic solvent interface associated with the superfluos extraction of TAACl into the organic phase.

Acknowledgments

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Estimating Reaction Rates Based on the Measurement of Flicker Noise

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Estimation of reaction rates of electrochemical processes in low conductance media is a problem either applying traditional cyclic voltammetry or impedance measurement. Such is the situation in certain organic solvents, ionic liquids or when the electrochemical process takes place under a weakly conducting layer, *e.g.*, in the case of underpaint corrosion.

The measurement of flicker noise offers an alternative solution for those cases. Flicker noise is a typical non-equilibrium phenomena and it is supposed to be generated by the electrochemical processes at the surface thus independent of the high electrical conductance of the electrolyte.

The proposed method is a somewhat contradicting to the normal reasoning about the application of noise measurement. Namely, usually noise measurement is considered to be a non-perturbation method and noise is measured only at the equilibrium or current free potential. Our view on noise measurement is just the opposite: we carry out noise voltage noise measurements at different dc galvanostatic polarizations. We always combine noise measurement with impedance spectra obtained at the same potentials. In contrast to the usual PSD (power spectral density) plots we calculate the so-called relative noise spetra (Srel):

$$S_{\mathrm{rel}}(\omega) = \frac{S_U(\omega)}{4kTZ'(\omega)} \equiv \frac{S_I(\omega)}{4kTY'(\omega)}.$$

We define flicker noise to be a 1/wa feature of the above defined relative noise spectra.

Flicker noise is usually considered to be proportional of the square of the external perturbing dc current. However, the partial currents of the electrochemical processes present et the surface must be also taken into consideration. This way the dependence of the flicker noise on the external polarizing dc current permits the estimation of electrochemical reaction rates. In order to prove the concept examples will be presented both for equilibrium and non-equilibrium processes.

Comparison of Copper Complexes Mimicking Tyrosinase Activity

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Tyrosinase is a biologically important oxidase, which acts as the rate-limiting enzyme for controlling the production of melanin. It belongs to the group of proteins with a bicopper active centre [1]. Due to limited lifetime of this enzyme, e.g., in electrochemical sensors [2], new copper complexes acting as artificial enzymes are designed and studied [3].
The contribution summarizes factors controlling biomimetic (catalytic) activity of selected complexes (e.g. on Fig. 1) towards different substrates (3,5-Di-tert-butylcatechol, dopamine, serotonin, etc.). For this study, electrochemical as well as spectroscopic experiments in aqueous as well as non-aqueous media were performed used. Moreover, another important role plays deposition of artificial enzyme complex on an electrode surface. The obtained results of kinetics of catalytic substrate conversion were compared with those obtained by using enzyme (tyrosinase).

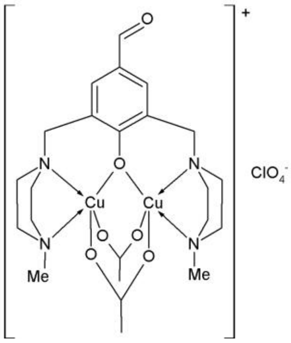

Fig. 1: Structure of studied copper complex.

Acknowledgments

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Amperometric Techniques as Suitable Tools for Determination of Tumor Markers – Vanillylmandelic, Homovanillic, and 5-hydroxyindole-3-acetic Acids

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In a few last years, our attention has been attracted to the possibilities of amperometric determination [1] of three tumor markers vanillylmandelic acid (VMA, Fig. 1A), homovanillic acid (HVA, Fig. 1B), 5-hydroxyindole-3-acetic acid (Fig. 1C, 5-HIAA) at different electrodes (e.g., screen-printed carbon electrodes [2]). They are products of catecholamine and serotonin, respectively, metabolism. Their increased or decreased levels can be used for diagnosis and monitoring of various diseases (neuroendocrine catecholamine-producing tumors (neuroblastoma and pheochromocytoma), post-traumatic disorders, etc.). Voltammetry, HPLC-ED/UV with solid phase extraction and amperometric detection, flow injection analysis with electrochemical detection and some other related techniques have been applied for these purposes.Moreover, a novel method of three phase hollow fiber based liquid/liquid/liquid microextraction coupled with voltammetric determination of HVA and VMA has been developed [3].

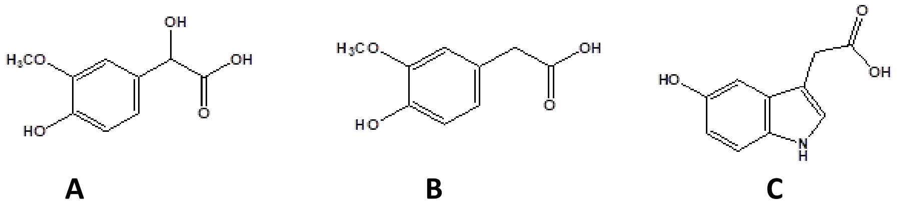

Fig. 1: Structural formula of vanillylmandelic acid (A) and homovanillic acid (B), 5-hydroxyindole-3-acetic acid (C).

Acknowledgements

The research was supported by GA CR (project No. 17-03868S).

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Protein-Protein Interactions at Charged Interfaces. Label-Free Chronopotentiometric Sensing

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Extensive biological and clinical studies led to the identification of protein interaction hubs and nodes that are critical for the acquisition and maintaining characteristics of cancer essential for cell transformation. Methods distinguishing between specific and non-specific interactions are an important component of biochemical pathway studies in cells. In our work, we show that label-free and reagent-free electrochemical methods can be used for this purpose. The combination of constant current chronopotentiometric stripping (CPS) analysis and mercury electrodes enables to investigate the effects of a current impacting on macromolecule layers and their dynamics.

Proteins produce a high electron yield catalytic response, so-called CPS peak H, which is sensitive to structural changes in the proteins [1]. We tested not only free proteins but also those in complexes with other proteins. We found that specific interactions of lectins with glycoproteins [2, 3] as well as antigens with antibodies [4] induced an increase in CPS peak H, while under the same conditions the non-specific binding of arbitrary proteins yielded almost the same CPS peak H as that of the protein adsorbed at electrode. Our results suggest that the proposed CPS method might be an interesting option to complement the already established methods for the analysis of protein-protein interactions.

Acknowledgments

This study was supported by project No. 18-18154S from the Czech Science Foundation.

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Probing dT_n Blocs in Telomeric DNA Repeats and Quadruplex-Duplex Transitions using Electroactive OsO_4, 2,2’-Bipyridine Complex

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Osmium tetroxide reacts with C5=C6 double bonds in pyrimidines to form osmate glycolates, which are stabilized by nitrogenous ligands such as 2,2’-bipyridine (bpy). Reactivity of these moieties towards OsO_4,bpy (Os,bpy) are influenced by the DNA structure. In duplex DNA the bases are protected from the modification (reviewed in [1]). The Os,bpy-DNA adducts are electroactive and yield a specific voltammetric signal, peak α (Fig. 1).

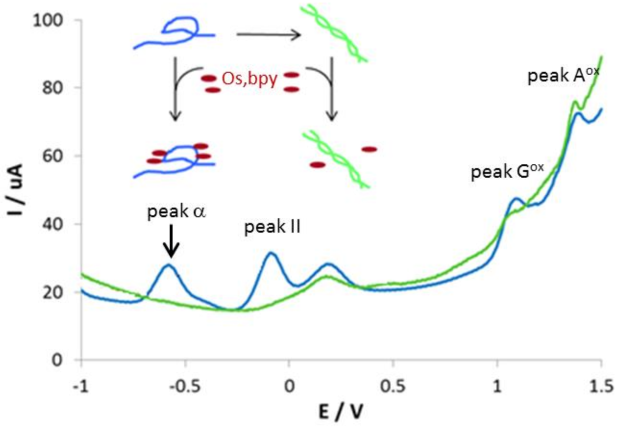

Fig. 1: Scheme of Os,bpy treatment of single-stranded (blue) and duplex (green) DNA with Os,bipy and resulting square-wave voltammograms (corresponding colors).

In this work we used Os,bpy DNA modification for probing thymine residues and their accessibility in synthetic oligonucleotides derived from telomeric repetitive sequences $d(T_nAGGG)_4$. Peak α height was increasing with n when the G-rich strand was modified in the absence of the complementary C-rich one $d(CCCTA_n)_4$. Under such conditions the G-rich strands were either unstructured (particularly in the presence of Li^+ ions) or adopted guanine quadruplex structures (in the presence of K^+) in which the thymine residues were located in single-stranded loops [2] (and thus reacted with Os,bpy). Upon addition of the C-rich strand the DNA double-helix was formed, resulting in diminution of the peak α. This transition was faster in the presence of Li^+ than in the presence of the quadruplex-stabilizing K^+.

Acknowledgments

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Polarized Liquid – Liquid Interface Meets Forensic Challenges

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Electrochemical sensing, although very well recognised in the scientific literature, has only few commercial successes. We strongly belief, that in the era of smart devices and miniaturization, electroanalysis will undergo a renaissance and will constitute a core of modern chemical sensors. As a matter of fact, forensics are concerned with a number of chemical entities that needs to be subjected to continuous monitoring e.g. illicit drugs, explosives or biomarkers. In this respect we continuously develop new electroanalytical methodology based on the interface between two immiscible electrolyte solutions (ITIES).

ITIES is a truly unique platform holding a number of individual properties. It is self-healing; renewable and scratch resistant. Detection at ITIES can arise from the simple interfacial ion transfer reaction whereas selectivity is governed by molecular partition. We have harvested these characteristics and perform model studies where we investigated the interfacial behaviour of cocaine and 15 different cutting agents at the water – 1,2-dichloroethane interface. We found that the detection of cocaine at the pristine ITIES gives desired selectivity as we further verified on real street samples [1]. In another example, we combined the electrochemistry driven adsorption of acid phosphatase (semen biomarker) to the ITIES together with *in situ* interfacial silica deposition. The latter was performed by electrochemically transferred proton from the aqueous phase to the organic phase containing silica precursor species (proton catalysed sol – gel process of tetraethoxysilane). Fortunately, the protein adsorption to the ITIES occur at the potential where interfacial silica deposition was triggered. This method allows the acid phosphatase pre-concentration from diluted solutions and its further removal from the interface thanks to the rigid nature of the silica [2].

Another important aspect of electrochemical sensing is electroactive surface downscaling. Miniaturization down to micro- or nano-scopic dimensionality improves electroanalytical output, reduce volumes of consumed chemicals and the volume of an investigated sample. We continuously develop miniaturization methodology using cheap and readily accessible materials (clean room free methods). The example is a very simple method allowing the ITIES miniaturization with the silica fused micro-capillaries that can be used to support the aqueous or the organic phase [3].

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Low-Cost Pencil Graphite-Based Electrochemical Detector for HPLC: Application for Antipsychotic Drugs Detection

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Pencil graphite electrode (PGE) possess a desirable electrochemical properties, such as good conductivity, wide potential window, low capacitive current, chemical stability and fair mechanical strength [1]. Despite aforementioned benefits, PGEs have not seen widespread use in flow systems, especially in HPLC [2, 3].

Concentric thin layer detection cell of novel design, based on PGE, was constructed and incorporated into a HPLC system. Performance of detection cell was tested on two sets of phenolic acids and tocopherol vitamers, former in high aqueous and latter in high organic mobile phase. Detection system was able to reach near-coulometric efficiency, over 80% at FR 200 µL.min^{-1}, with LODs in subnanomolar range.

Capability of this design was demonstrated on set of seven antipsychotic drugs (Fig. 1) in blood serum sample. LODs of developed method were in order of tens nmol.L^{-1}.

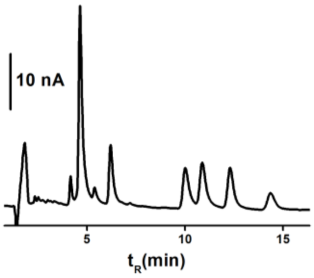

Fig. 1: Chromatogram of 0.5 µmol.L^{-1} chlorpromazine, olanzapine, quetiapine, clozapine, promazine, promethazine and levomepromazine, E_{det} = 1000 mV (vs. Ag/AgCl).

Acknowledgments

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Electrochemistry of Steroids at Carbon-Based Electrodes

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Electrochemical approach has long been considered problematic for detection of steroids a maximum of one double bond within the steroid skeleton, as reviewed in [1]. Direct oxidation of cholesterol, and selected oxysterols and phytosterols has been reported in non-aqueous media of acetonitrile at glassy carbon (GC) and boron-doped diamond (BDD) electrodes [1,2]. Further, electrodes modified with compounds structurally resembling active centers of cholesterol oxidase were employed for determination of cholesterol in food products [3].

In this contribution, a novel approach for oxidation of steroids will be presented, based on their chemical activation by acid-induced dehydration prior the direct electrochemical oxidation of its reaction products [4]. Similar approach is known for cholesterol as Liebermann-Burchard reaction, used for its colorimetric assay [1]. This combination of reaction steps was succesfully applied for oxidation of cholic and chenodeoxycholic acids in mixed media of acetonitrile – perchloric acid at reasonable potentials of around +1.2 V vs. Ag/AgNO3 when using water content under 5% for voltammetry at GC and BDD electrodes. These primary bile acids posses an axial 7α-hydroxyl group favouring the dehydration step due to antiperiplanar position to the hydrogen atom at C(8). The sterols with Δ5 double bond (*e.g.*, cholesterol, stigmasterol) provide the oxidation signal at *ca* +1.5 - +1.7 V and the sterols with Δ5,7 double bonds originally present in their structure (*e.g.*, ergosterol, 7-dehydrocholesterol) are oxidized at lower potentials of *ca* +0.8 -+1.0 V. These structure-dependent potential differerences enable their simultanous determination using voltammetric techniques or multiple-pulse amperometric detection in flow injection analysis with limits of detection in the 10^{-6} mol L^{-1} concentration range. Further, attempts on identification of reaction mechanisms and their products using mass spectrometry and nuclear magnetic resonance will be presented.

Acknowledgments

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Cyclovoltammetric Characterization of Polylactic Acid/Carbon Black Composite Filaments for the Construction of 3D Printed Electrodes

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Fused deposition modeling (FDM) 3D printing has been recently recognized as an inexpensive, fast, reliable, adaptable and environmentally friendly technology to fabricate electrodes and cells for electrochemical applications. It has been demonstrated by cyclic voltammetry that electrodes printed from conductive composites of polylactic acid (PLA) and graphene are capable of sensing electroactive species. [1,2] However, obtained faradaic response is distorted due to substantial kinetic hindrance related to limited exposure of the graphene phase to the electrode/electrolyte interface. In this work, we explore the applicability of a PLA/carbon black composite as an alternative to PLA/graphene composites and present a simple electrochemical pretreatment procedure to activate electrodes. We take cyclic voltammetry employing $Ru(acac)_3^{0/1-}$ as an electroactive probe to demonstrate that the PLA/carbon black composite filaments treated by the optimized procedure show superior performance in comparison to PLA/graphene composites and approach characteristics of metallic electrodes.

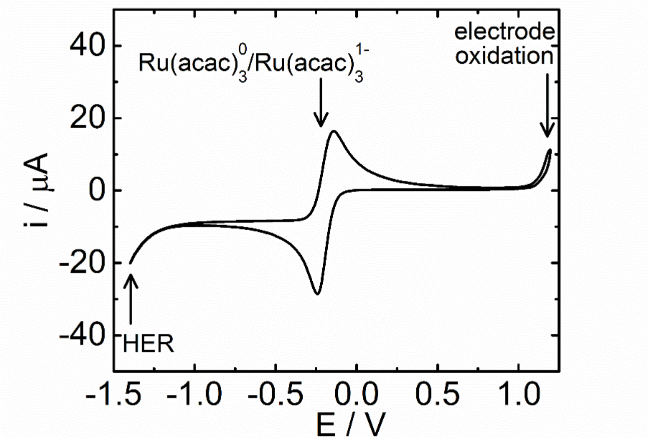

Fig. 1: CV obtained at the interface of PLA/carbon black composite and aqueous 0.3 mol.L^{-1} Na_2SO_4 electrolyte containing 5 x 10^{-4} $Ru(acac)_3$ as the electroactive probe at 25 mV/s.

Acknowledgments

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Voltammetric Determination of Anthraquinone-2-Sulphonate in Physiological Saline Solution on Various Electrode Surfaces

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Anthraquinone-2-sulphonate (AQS) is an easily available substance used as a model compound for the development of novel electrochemical methods for determination of anthraquinone-based anti-cancer drugs (*e.g.*, Doxorubicin, Daunorubicin, and Epirubicin). Effectiveness of these drugs is limited by various factors such as adverse drug effects, drug resistance or fixed doses, which can potentially lead to patient overdose or to insufficient dosage. Development of method for therapeutic monitoring of anti-cancer drugs in blood might help with the cancer treatment by individualized dosages for each patient [1, 2].

Therefore, this contribution is focused on the development of electroanalytical methods for the determination of anti-cancer drugs based on anthraquinone moiety in physiological saline solution (NS – normal saline). Since in the future, connection with liquid-flow system and dialysis catheter possibly inserted into blood circulation of patients is envisaged, there is a necessity of using NS as a carrier solution. For voltammetric determination of AQS in NS, various working electrodes, including glassy carbon electrodes provided by two different commercial suppliers, boron-doped diamond electrode and polished silver solid amalgam electrode (p-AgSAE) were tested. These electrodes were employed in a conventional three-electrode set-up (the reference electrode: Ag|AgCl (3 mol L^{-1} KCl) and the auxiliary electrode: a platinum wire), placed into a voltammetric vessel containing 5 mL of sample consisting of AQS in NS and differential pulse voltammetry was applied for analyte determination. Subsequently, voltammetric responses were evaluated after addition of the standard AQS solution into a cell in order to verify that obtained signals are dependent on AQS concentration. Moreover, repeatability of the proposed methods was assessed, and the best results were obtained on p-AgSAE.

Acknowledgments

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UV-Vis Spectroelectrochemical Investigation of Hydroxy Compounds Complexation with Copper

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The positive effect of polyphenolic compounds against certain diseases consists in the inhibition of certain enzymes, vascular protection, anti-hepatotoxic, anti-allergic, anti-proliferative, anti-osteoporotic and anti-inflammatory properties [1]. Also the antioxidant activity of hydroxy compounds depends on the number and the position of hydroxyl groups in their molecule [2]. Flavonolignans are the important group of polyphenols exhibiting antioxidant and hepatoprotective properties. Among them natural compound silybin produced in the plant *Silybum marianum* (L.) Gaertner attracts the special attention [3]. The reaction of flavonolignans with metallic cations, especially the ability of the copper and iron complexes formation, has a significant importance for bioactivity and pro-oxidation action. In addition, transition metals could be used for selective oxidation and development of synthetic protocols and biosensing methods for flavonolignans and other polyphenols [4]. The electrochemical oxidation of silybin leads to the formation of a hydroxylated product in the presence of water [5]. The chemical reaction of silybin with copper dication was studied by electrochemistry, UV-Vis spectroelectrochemistry and spectrophotometry. Two competitive processes, i.e. silybin oxidation by copper dication and Cu-silybin complexation, participate in reaction.

Acknowledgements

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Detection of 6-Diazo-5-oxo-L-norleucine by Screen Printed Carbon Electrode Covered by Amalgam Particles

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6-Diazo-5-oxo-L-norleucine (DON) is a non-standard amino acid, which was originally isolated from *Streptomyces* in a sample of Peruvian soil [1]. As glutamine antagonist, DON is used as inhibitor of different glutamine utilizing enzymes. Due to its similarity to glutamine it can enter catalytic centres of these enzymes and inhibits them by covalent binding, or more precisely by alkylation [2]. DON is not approved as pharmaceutical agent, but is tested in combination with a recombinant glutaminase in clinical trials for the treatment of different solid tumours [3]. Moreover, novel prodrugs based on DON's structure are currently synthesized and their antitumor activity tested [4,5].

Herein, disposable screen-printed carbon electrode (SPCE) was used as a conductive surface for electrochemical deposition of silver amalgam particles (AgAP). [6] Advantages of this miniaturized 3-electrode system results in significant decrease of the consumption of metal mixture solution for the deposition and required volume to 200 µL for sample analysis. Voltammetric detection of the DON are compared to bare SPCE and HMDE.

The electrochemical deposition of AgAP from Ag^+ and Hg^{2+} solution on the surface of SPCE (in this case) was confirmed to be a suitable procedure for preparation of new electrode material, which evinces close electrochemical properties to HMDE. Its mechanical stability and simply automatable preparation procedure offer broad application possibilities.

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Voltammetric Behavior of Anti-inflammatory Drugs from Oxicam Class

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Oxicam drugs are a group of structurally closely related substances with anti-inflammatory, analgesic and antipyretic activities [1]. In this work, voltammetric behavior of four representatives of this group, namely meloxicam, lornoxicam, piroxicam, and tenoxicam (Figure 1), was studied using boron doped diamond electrode (BDDE). This electrode was applied due to its specific electrochemical properties, especially the wide potential window allowing the observation of signals at about very positive potential values [2-4]. Mechanism of the electrochemical oxidation was investigated with high performance liquid chromatography-mass spectrometry analysis of analytes solutions electrolyzed on carbon fiber brush electrode [5]. Finally, voltammetric methods for all the above-mentioned drugs were developed and applied for real samples analysis.

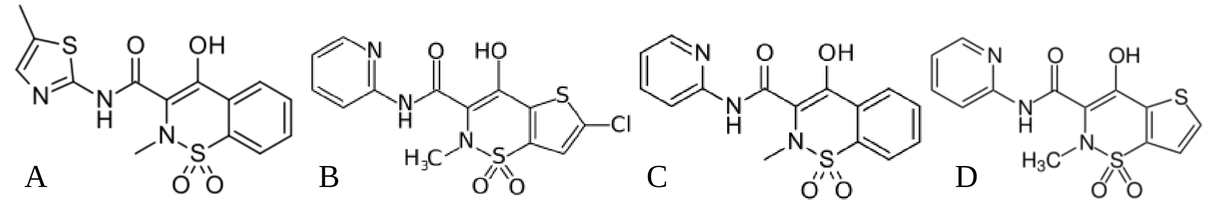

Fig. 1: Structural formula of meloxicam (A), lornoxicam (B), piroxicam (C), tenoxicam (D).

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The Role of Constant Current Potentiometric Stripping Analysis in Studies of Toxic Metal Ions Transport

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Plants are at the beginning of food chain and, metals in form of complexes with different ligands are transported within their cells [1]. In experiments with model phospholipid membrane with incorporated ion channel [2], transport of cadmium or lead ions, free or complexed with citric acid, malic acid or phytochelatin PC_2 was studied [3, 4]. Electrochemical Impedance Spectroscopy was applied for the membrane formation and stability, the amount of ions transported across membrane under selected interval has been determined with anodic stripping voltammetry. The Potentiometric stripping analysis with different values of reducing current (CCPSA) revealed labile behavior of Cd-malate and Pb phytochelatin. For those complexes, higher amount of ions was transported across model membrane, comparing to the transport of free ions. Consequences leading to higher amount of toxic metals in plant tissues [5, 6] can be therefore easily elucidated from CCPSA experiments.

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Oxidation of Purine Nucleobases Can Occur Through Radical Polymerization Sensitive to their Arrangement on the Electrode

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Oxidation peaks provided by purines adenine and guanine are the most frequently utilized signals in the label-free DNA sensors [1], yet to this day the exact mechanism of their oxidation within intact DNA remains speculative. While detailed MS or HPLC analyses of oxidation products of monomeric DNA components (free bases, nucleosides or nucleotides) has been already performed and detailed mechanisms of underlying oxidation processes have been proposed, similar analysis with DNA is, to our best knowledge, missing. When describing oxidation mechanism of the purines within DNA, work describing monomer analysis is usually cited, and analogical oxidation mechanism is expected. But both purines have been shown to be oxidized through radical reaction, which can yield wide spectrum of products including polymers linked through bases. It has been shown that adenine, adenosine, 2’-deoxyadenosine and 2′,3′-dideoxyadenosine (summarized in [2]) yield different oxidation products, despite the fact, that their respective oxidation peaks have very similar position. Similarly, differences in oxidation products have been observed between guanine and guanosine [3]. We suggest that due to involvement of rapid radical reaction during purine nucleobases oxidation, their spatial arrangement on the electrode surface (as monomers or as well as within DNA structure), plays important role on the course of their oxidation.
Use of the broad potential window of the pyrolytic graphite electrode demonstrated in our previous work [4] and switching of the potential sweep to the opposite direction allow detection of the oxidation products directly *in situ* and could help to elucidate the underlying mechanisms.

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Electrochemical Detection of Tetraplex DNA Based on Cyclic Naphthalene Diimide Carrying Ferrocene Unit

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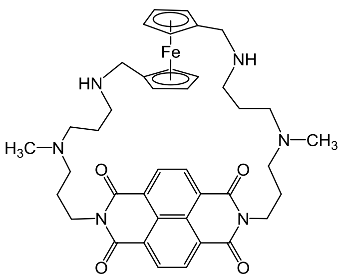
Detection of telomere DNA is important from the viewpoint of cancer diagnosis. This come from the fact that telomerase activity to elongate telomere DNA is strongly correlated with cancer development. Telomere DNA is known to form tetraplex structure and its stabilizer is expected as anti-cancer drug. We have been developing a cancer diagnosis using the electrochemical detection of an elongated telomere DNA tetraplex with naphthalene diimide carrying two ferrocene moieties [1]. This is based on the effective stacking between the electron-deficient naphthalene diimide plane and the G-quartet from electron-rich guanine bases as units of tetraplex DNA. Furthermore, we found out that cyclic naphthalene diimide obtained by the connection between both termini of their substituents from both amide parts bound to tetraplex DNA specifically [2]. Its cyclic structure inhibits to bind to DNA duplex with an intercalating manner, whereas no disturbing with its stacking with G quartet of tetraplex DNA.

Here, we designed and synthesized cyclic ferrocenylnaphthalene diimide, **1**. Ligand **1** is expected to form the charge transfer-type complex between electro-rich ferrocene and electron-deficient naphthalene diimide parts resulting in the diminished oxidation current of ferrocene of **1**. However, it is expected that ferrocene oxidation current should recover after bound to tetraplex DNA, where the naphthalene diimide stacked with G quartet of tetraplex DNA and weakened the charge transferee type interaction. Ligand **1** bound to tetraplex DNA with high preference using isothermal titration calorimetry. Additionally, the oxidation current of 1 was rarely observed in bare electrode and, however, its current was observed in the case of the tetraplex DNA immobilized electrode from cyclic voltammetric experiment.



1

These results show the possibility of electrochemical tetraplex DNA detection using **1** and improved the performance of the electrochemical cancer diagnosis using **1**.

Acknowledgments

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PEO-PVDF Based Polymer Electrolytes for Uniform Lithium Metal Deposition

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Main reason preventing successful deployment of rechargeable Lithium metal batteries is connected with the inhomogeneous and electrochemically unstable Solid electrolyte interphase (SEI) formation on lithium metal surface [1,2]. At present the application of polymer electrolytes (PEs) is one of the promising approaches to SEI stabilization [1, 3, 4].

In this study the possibility of SEI stabilization formed on Li-metal anode in contact with PEs based on poly(ethylene oxide) (PEO) and Polyvinylidene fluoride (PVDF) polymer blends has been investigated. The integrated approach was proposed to study the composition and properties of Li/PE SEI layers including electrochemical tools: chronopotensiometry and impedance spectroscopy and physical methods: *in situ* X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), Differential scanning calorimetry (DSC), *in situ* neutron reflectometry (NR).

As the result, lithium cation transference numbers $\boldsymbol{t}_{(\mathrm{Li}^+)}$, conductivities and electrochemical stability windows of PEO-PVDF PEs were determined using electrochemical methods. Information on the chemical composition, bonding and homogeneity of Li/PE interphase was obtained by means of XPS. Thus, the influence of PE composition on SEI properties and stability was evaluated and the reaction mechanism of Li/PE SEI formation was proposed. In order to monitor PE/Li SEI formation, nucleation and growth of a new phase in PEO-PVDF PEs we suggest using *in situ* NR. NR provides averaged information of surface layers evolution, thus, allows to avoid locality of the obtained information. Preliminary experiments on contrast optimization by using deuterated solvents have being performed in originally designed three electrode electrochemical cell. Next we plan to deposit polymer electrolyte films directly on ultra-flat working electrodes for monitoring of lithium plating in solid polymer electrolytes such as PEO-PVDF.

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Electrochemical Evaluation of Bioactive Electron Donors and Electrophilic Molecules: General Concept

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The regulation of a number of cellular processes is closely related to the effects of electrophilic and nucleophilic substrates and their combination. Finding novel bioactive molecules with high electron acceptor (electrophilic) or donor (antioxidant) capacity is currently an important task of biochemical research. From a methodological point of view, electrochemistry plays an important, if not crucial role in the research of bioactive electrophiles and antioxidants [1]. Structure-redox activity relationship (SAR) studies supported by multispectral methodologies and theoretical approaches [2] are crucial for elucidating the mechanism of electron donor oxidation and reduction of electrophilic species (Fig. 1). The talk will be mainly devoted to poly-hydroxy aromatic antioxidants and fatty acid electrophiles to demonstrate the general concept and limitations in this research area.

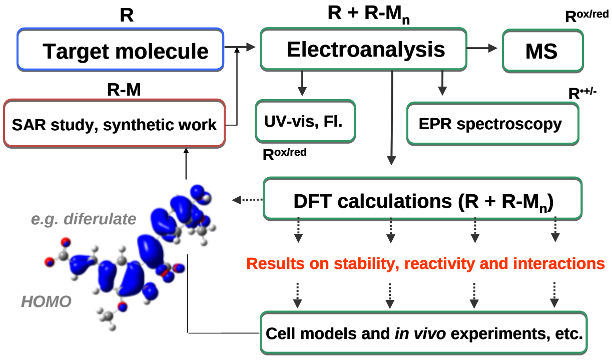

Fig. 1: Experimental design for structure-redox activity relationship (SAR) study. *Abbrev.* R-M: target molecule (R) structurally modified (M) repeatedly (n), $R^{ox/red}$: oxidation or reduction products and, $R^{*+/-}$: radical forms of R, MS: mass spectrometry, EPR: electron paramagnetic resonance, DFT: density functional theory as a computational method, ultraviolet-visible (UV-vis) and fluorescence (fl) spectroscopy.

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Preparation of Patterned Copper Foam Electrodes Employing Masks Manufactured by 3D printing

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Copper foams manufactured by hydrogen evolution reaction assisted electroplating on copper substrates were recently recognized as large-scale electrodes for the electrochemical reduction of carbon dioxide to selectively form C2 products [1]. In this work, we employ fused deposition modeling 3D printing technology to pattern copper substrates with the goal of achieving higher active electrode area in comparison with foams formed on planar copper substrates. Polylactic acid (PLA) based microstructures were printed on the copper substrate to serve as deposition masks for the formation of copper foams. We optimize the printing conditions and demonstrate that PLA masks are stable and lead to the formation of copper foam microarrays of dimensions precisely dictated by the geometry of the 3D printed PLA mask.

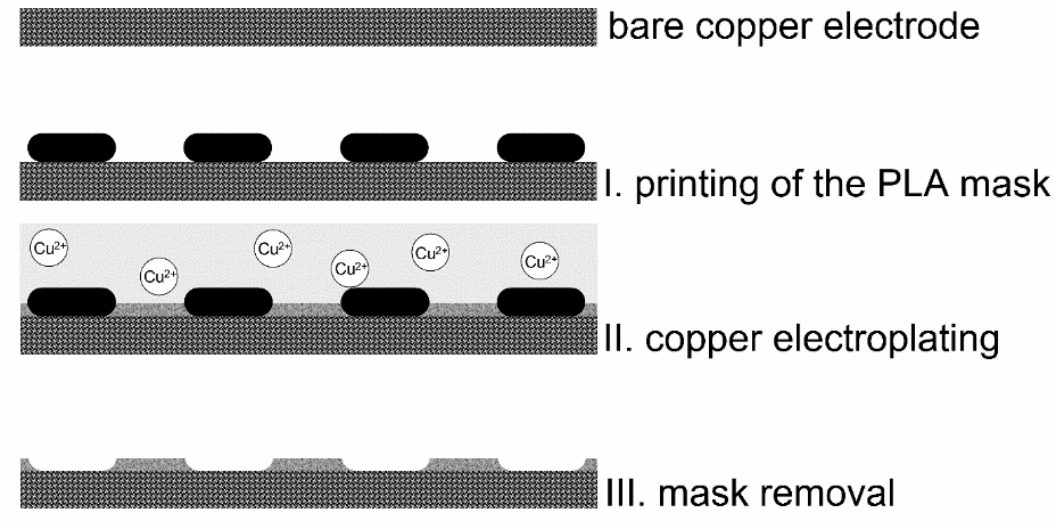

Fig. 1: Schematic depiction of the procedure to manufacture patterned copper foam electrodes used in this work.

Acknowledgments
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Electrodes with Immobilized Free Radicals for the Voltammetric Evaluation of Antioxidant Activity

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Estimation of the antioxidant properties of individual compounds and real samples of complex antioxidant composition is of interest as far as allows screening the samples under investigation and to evaluate their quality. One of the common parameters for the antioxidant properties characterization is the antioxidant activity based on the reactions with stable free radicals. Among them, 2,2-diphenyl-1-picrylhydrazyl ($DPPH^•$) is the most frequently used standard radical. Another free radical of interest is galvinoxyl ($GO^•$) (Fig. 1).

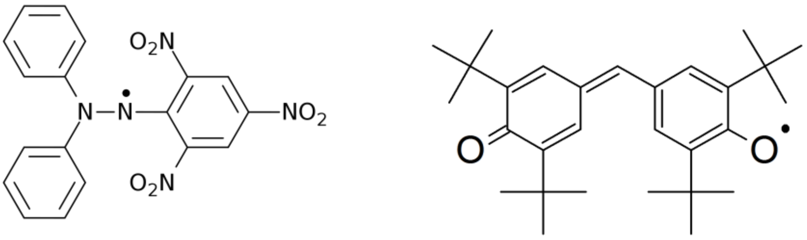

Fig. 1: Structures of 2,2-diphenyl-1-picrylhydrazyl and galvinoxyl radicals.

The antioxidant activity is expressed as a portion of the reduced radicals via the reaction with antioxidants of the sample or equivalents of the individual antioxidants. The reactions of the antioxidants with free radicals are based on the electron transfer that allows use electrochemical methods for the monitoring of this process.

The voltammetric behavior of $DPPH^•$ and $GO^•$ on the glassy carbon electrode (GCE) has been studied. The immobilization of radicals on the electrode surface has been applied for the voltammetric characteristics improvement. Nevertheless, further increase of the system sensitivity was required that has been achieved using GCE modified with dispersions of CeO_2 nanoparticles in cationic surfactant cetylpyridinium bromide medium (CeO_2-CPB/GCE) as a platform for the radical immobilization. The effect of CeO_2 nanoparticles concentration on the $DPPH^•$ and $GO^•$ response has been evaluated. $DPPH^•$- and $GO^•$-modified electrodes have been characterized by scanning electron microscopy and electrochemical impedance spectroscopy.

The electrodes created have been successfully applied for the voltammetric evaluation of natural phenolic compounds antioxidant activity expressed as the EC_{50} parameter and antioxidant activity of medicinal herbs tinctures, infusions and decoctions as relative $DPPH^•$ and $GO^•$ inhibition. The results obtained agree well with data of standard spectrophotometric method. *F*- and *t*-tests confirmed the similar precision of the methods and the absence of systematic errors of the determination.

Convenient and efficient voltammetric methods have been developed for the evaluation of antioxidant activity based on the reaction of antioxidants with $DPPH^•$ or $GO^•$ immobilized on the electrode surface. The approaches are simple, reliable and significantly reduce the reagent consumption as well as exclude the disadvantages of standard spectrophotometric methods like instability of the reagent solution, measurements in the organic medium only and complications of the colored samples analysis.

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