

# **Electrochemical Seminar**

**Prague – Dresden**

**Book of Abstracts**



**23. – 25. November 2009**

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Prague – Dresden Electrochemical Seminar

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# Programme

<b>Monday, November 23</b>			
11:00-14:00	Arrival, registration, accommodation		
12:00-13:30	Lunch		
<b>14:00-16:00</b>	<b>Section 1</b>		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
14:00-14:05	<b>L.Kavan</b>	L. Kavan	Opening
14:05-15:00		W. Plieth	Nucleation, nucleus growth, death of the nucleus: The process chain of electrodeposition
15:00-15:20		J. Hnát	Heterogeneous anion exchange membranes for electrolytic splitting of water
15:20-15:40		P. Zálaha	Electrochemical microreactor for oxidation of 4-methylanisole
15:40-16:00		L. Bandžuchová	Voltammetric monitoring of phytochelatin synthesis in plant cells exposed to cadmium using p-AgSAE
16:00-16:20	Coffee break		
<b>16:20-19:20</b>	<b>Section 2</b>		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
16:20-17:20	<b>W. Plieth</b>	J. Procházka	Templated photocatalytic growth of silver on variety of TiO <sub>2</sub> surfaces.
17:20-17:40		M. Zukalová	Nanofibrous TiO <sub>2</sub> : A new material with extraordinary properties
17:40-18:00		J. Polonský	Titanium suboxides as a catalyst support for PEMFC
18:00-18:20		K. Macounová	Elucidation of reaction mechanism of oxygen evolution on RuO <sub>2</sub> and doped RuO <sub>2</sub> electrodes
18:20-18:40		R. Kodým	Mathematical modeling: effective tool for optimization of electrochemical cells with bipolar electrode arrangement
18:40-19:00		V. Hudská	Liquid film embedded electrode for (spectro)electrochemical investigation of redox systems soluble in nonaqueous solvents
19:00-19:20		P. Rapta	Electrochemistry, EPR and UV-Vis spectroscopy of antioxidants in wines
19:30	Dinner		
20:30	Excursion		

<b>Tuesday, November 24</b>			
<b>9:00-12:00</b>	<b>Section 3</b>		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
9:00-10:00	<b>M. Heyrovský</b>	C. Kvarnström	Conducting polymers in room temperature ionic liquids
10:00-10:20		E. Dmitrieva	The influence of the phenazine structure on the polaron formation in polyaniline: An in situ ESR-UV/vis/NIR spectroelectrochemical study
10:20-10:40		K. Haubner	Synthesis and characterization of thiophene oligomers as promising materials for organic electronic devices applications
10:40-11:00	Coffee break		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
11:00-11:20	<b>M. Heyrovský</b>	S. Klod	The mechanism of electrode reactions – – a combined in situ NMR and in situ ESR spectroelectrochemical investigation
11:20-11:40		A. Svitova	The cyclization of the diphenylamine structures in anodic reactions: A cyclovoltammetric study
11:40-12:00		M. Matis (P. Raptá)	In situ ESR-UV/Vis/NIR spectroelectro-chemistry of N,N,N',N'-tetrakis-(4-aminophenyl)benzidine and its N,N,N',N'-tetra-(4-methoxyphenyl)-substituted quarterphenyl homologue
12:00-13:30	Lunch		
14:00-17:00	Excursion		
17:00-17:20	Coffee break		
<b>17:20-19:20</b>	<b>Section 4</b>		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
17:20-18:20	<b>C. Kvarnström</b>	M. Heyrovský	The development of polarography
18:20-18:40		A. Liška	Electrochemical investigation of intramolecular electron interactions in Mono-, Di-, Tri - and Tetranitrocalix-[4]-arenes and their models
18:40-19:00		L. Šimková	Electrochemical study of intramolecular degradation of new explosive 2,2-dinitroethen-1,1-diamine
19:00-19:20		V. Vyskočil	Damaging effects of genotoxic fluorene derivatives on DNA detected voltammetrically using an electrochemical DNA biosensor
19:30	Dinner		

<b>Wednesday, November 25</b>			
<b>9:00-11:50</b>	<b>Section 5</b>		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
9:00-9:20	<b>L. Dunsch</b>	A. Popov	Vis-NIR and ESR spectroelectrochemical study of $\text{Sc}_3\text{N}@C_{80}(\text{CF}_3)_2$
9:20-9:40		J. Bulířková	Redox characterization of fullerene derivatives in water and DMSO
9:40-10:00		Ch. Kästner	Synthesis, separation and characterization of endohedral cerium metallofullerenes
10:00-10:20		L. Zhang	Electrochemistry of mixed metal nitride cluster fullerenes
10:20-10:40	Coffee break		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
10:40-11:00	<b>L. Dunsch</b>	V. Kolivořka	Adsorption of bovine serum albumin on highly oriented pyrolytic graphite
11:00-11:20		Y. Zhang	Single-crystalline $C_{60}$ hollow nanostructures by sonophysical preparation: Tuning the morphology for catalyst supports in fuel cells
11:20-11:40		M. Zalibera	C82 fullerene: Spectroelectrochemistry, DFT and MD calculations
11:40-11:50	Closing Remarks (L.Dunsch)		
12:00- 14:00	Lunch and Departure		

# Voltammetric Monitoring of Phytochelatin Synthesis in Plant Cells Exposed to Cadmium Using p-AgSAE

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Phytochelatin (PCs) are plant peptides, which are synthesized from glutathione in presence of various heavy metals. This reaction is catalyzed by enzyme PC-synthasa. Phytochelatin play very important role in detoxification processes of plants from heavy metals. They form complexes heavy metal-PC, where heavy metals lose their toxicity. Concentration of PCs corresponds to the concentration of heavy metal in medium. Therefore, PCs can be considered biomarkers of environmental pollution by heavy metals. General structure of these peptides is  $(\gamma\text{-Glu-Cys})_n\text{-Gly}$ , where Glu is glutamic acid, Cys is cysteine, Gly is glycine and  $n$  lies between 2–11 (ref. [1–3]). Cysteine is amino acid containing one thiol group. In presence of this kind of compounds so called “Brdička reaction” can be recorded. This type of reaction was discovered by R. Brdička in 1933 and it was first time described in literature [4]. This reaction is characterized by catalytic evolution of hydrogen on mercury in alkaline solutions. The mostly used catalyst is Co(II), but sometimes Ni(II) is used too. This reaction was found as a suitable method for voltammetric determination of cysteine and cysteine containing peptides, because hydrogen evolution provides characteristic peaks (one peak in case of cysteine and more peaks in case of glutathione and PCs) at mercury electrodes [5, 6].

Polished silver solid amalgam electrode (p-AgSAE) is one modification of silver solid amalgam electrodes, which were described by Yosypchuk and Novotný in [7] and independently by Mikkelsen and Schroder [8]. These electrodes are used in different modifications: p-AgSAE, m-AgSAE (AgSAE covered by mercury meniscus) or MF-AgSAE (AgSAE covered by thin mercury film) [7]. Silver solid amalgam electrodes represent very suitable alternative to HMDE due to their high hydrogen overvoltage, good mechanic stability, very simple preparation for measurements, absence of liquid mercury (especially p-AgSAE) and high sensitivity [7, 9].

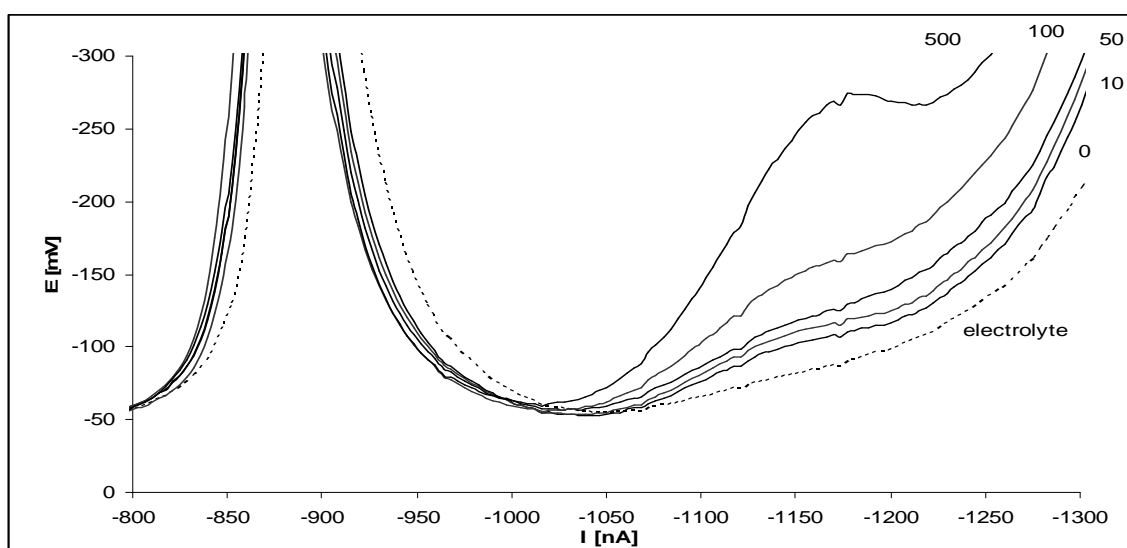
All measurements were performed by DPV in three electrode setup (using p-AgSAE or HMDE as a working electrode, saturated argenticchloride electrode as a reference and Pt wire as auxiliary electrode). 0.1M ammonium buffer with 0.001M Co(II) was used as a base electrolyte. At the first were carried out the analyses of PCs` components: cysteine and glutathione. We found that p-AgSAE is more suitable for these substances determination than HMDE, in particular due to the high sensitivity and better possibility of peak evaluation. Then we used again both electrodes for analyses of synthetic PCs (PC2 and PC3). We determined LODs and some other statistic parameters using ADSTAT [10]. We found that p-AgSAE is more sensitive in determination of mentioned peptides than HMDE. LODs of both PCs on p-AgSAE were 10 times lower than LODs at HMDE (e.g., LOD (PC2) at p-AgSAE was  $3.3 \times 10^{-8}$  M). Further, it was found that PC2 and PC3 provide the same response. Therefore, we could use both peptides as standards for determination of PCs in natural samples.

Voltammetric analyses of natural samples were realized at p-AgSAE only. We got two sample sets of plant cells extract (*Nicotiana tabacum*), which were prepared in Institute of Experimental Biology of Masaryk University in Brno. All samples were characterized by their absorbance at 280 nm and they were diluted to the same absorbance (to the same peptides concentration) before each measurement. First set of cell extracts was exposed to  $50 \mu\text{mol l}^{-1}$  CdSO<sub>4</sub> for 3 (Cd3D) or 5 (Cd5D)



days. The samples, which were not exposed to cadmium (K3D and K5D), provided no any signal in the region of expected “Brdička reaction”. On the contrary, Cd3D and especially Cd5D provided well developed peak about potential  $-1200$  mV. Concentrations of PCs in Cd3D and Cd5D were determined using the standard addition method. The highest level of PCs was confirmed in Cd5D. The other set of samples was exposed to different levels of cadmium ( $c(\text{CdSO}_4) = 0, 10, 50, 100$  and  $500 \mu\text{mol l}^{-1}$ ) for the same time. In the Figure 1 it is possible to see that the highest current response was recorded in case of sample denoted as “500”, which was exposed to the highest level of cadmium ( $500 \mu\text{mol l}^{-1}$ ) and the lowest current in case of sample denoted “0”, which was not exposed to cadmium at all.

Finally, we can conclude that used amalgam electrode is a suitable tool for voltammetric monitoring of phytochelatin synthesis in plant cells.



**Fig. 1.** Comparison of voltammetric signals provided by samples of plant cells extract (*Nicotiana tabacum*), which were exposed to different level of cadmium.

#### Acknowledgement

Financial support of this work was provided by the Ministry of Education, Youth and Sports of the Czech Republic by the project MSM 0021627502.

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# Redox Characterization of Fullerene Derivatives in Water and DMSO

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Fullerene (C<sub>60</sub>) is a highly hydrophobic compound and it is considered to be insoluble in water. Different approaches for preparing aqueous solutions of C<sub>60</sub> have been reported. An ultrasonic treatment of a two-phase mixture of water and toluene containing C<sub>60</sub> results in a brownish-yellow aqueous emulsion containing C<sub>60</sub>. Other method is based on the creation of an inclusion complex of the C<sub>60</sub> inside a cavity of gamma-cyclodextrin.

Mainly the host-guest complexation with cyclodextrins was suggested for creation of water-soluble forms of fullerene. New methanofullerene conjugates with cyclodextrins were recently synthesized. A covalent attachment of cyclodextrins to fullerene could promote the formation of an intra-molecular complex. We expect that the change of the reversible redox potentials of fullerene derivatives complexed with a covalently bound cyclodextrin could confirm the internal complexation and eventually yield an estimate of the stability constants. The most suitable techniques for electrochemical characterization of fullerene derivatives proved to be the low-frequency phase-sensitive AC polarography and the steady-state voltammetry.

Redox potential is an important parameter in electrochemical characterization of new compounds. The determination of the formal redox potential of fullerene in aqueous solution has never been done before. We were interested in determination of the formal redox potentials of fullerene, methanofullerene, fullerene-cyclodextrin complex and methanofullerene conjugates with cyclodextrins in aqueous and dimethylsulfoxide solutions. We identified the formal redox potentials either as the half-wave potential of a reversible steady-state current-voltage wave or as the peak potential of the faradaic real and/or imaginary admittance component. The difference of the formal redox potential of the first electron transfer step of complexed and free form of fullerene was used for the estimation of the binding enhancement caused by the change of the redox state of C<sub>60</sub>. The binding enhancement defines the ratio of stability constants of the reduced and oxidized forms. The determination of formal redox potentials in water yields only the first two electron transfer step.

## Acknowledgements

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# The Influence of the Phenazine Structure on the Polaron Formation in Polyaniline: An *in situ* ESR-UV/vis/NIR Spectroelectrochemical Study

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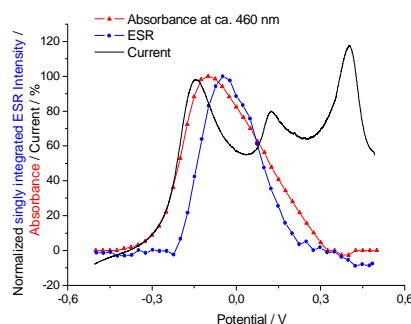
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It is well accepted in the scientific community, that polyaniline consists of a linear arrangement of the monomers. Since the early work of Willstätter the phenazine rings have been considered as a part of the polymer chains [1]. While most studies on the electronic structure of polyaniline and the changes upon doping use the linear structure model the influence of phenazine structures on the formation of charged states in polyaniline is not yet studied and understood in detail. Here we present *in situ* ESR-UV/vis/NIR spectroelectrochemistry of the copolymer of aniline und a phenazine derivative (3, 7-diamino-5-phenylphenazinium chloride, phenosafranine) upon charging. While the structure of the copolymer has been confirmed by mass spectrometry and IR spectroscopy spectroelectrochemistry was done at polymer films prepared by electropolymerization.

It has been shown that *in situ* ESR-UV/vis/NIR spectroelectrochemistry is a perfect tool to follow the formation of polarons in conducting polymers and copolymers. Here we follow the role of the phenazine structure in the stabilization of charged states in polyaniline. By *in situ* ESR-UV/vis/NIR spectroelectrochemistry it was clearly demonstrated that the polaron formation in polyaniline and its phenazine copolymers is not the first step in charge injection but occurs at higher electrode potentials than the first charge transfer into the polymer film. At the early stage of the charge injection into the polymer a *polaron pair* is formed as concluded from the absorption pattern and the absence of an ESR signal. A reaction mechanism of the formation of charged species in polyaniline is proposed demonstrating the very special role of polyaniline in the stabilization of charges.

Furthermore, the influence of phenazine rings on the middle peak in the cyclovoltammograms of polyaniline was studied proving that the middle peak is not associated with the presence of phenazine rings in the polymer.



**Figure 1.:** The potential dependence of current, singly integrated ESR intensity and absorption peak at ca. 460 nm of polyaniline normalized to the maximum of ESR intensity.

## Reference

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# Synthesis and Characterization of Thiophene Oligomers as Promising Materials for Organic Electronic Devices Applications

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Novel oligomers based on  $\beta$ -substituted thiophene derivatives were synthesized with the aim to build-up a small molecule organic field-effect transistor (OFET).  $\alpha,\omega$ -dicyano substituted  $\beta,\beta'$ -dibutylquaterthiophene molecules (DCNDBQT) and 5-cyano-2(butyl-4-phosphonic acid)-3-butylthiophene (CNBTPA) as template layer were synthesized and characterized by spectroelectrochemistry, differential scanning calorimetry and thermal gravimetric analysis. The developed materials exhibit excellent thermal and optical properties.

We investigated the properties of the applied films of DCNDBQT by different cast methods: spin-coating and vacuum sublimation. Excellent structural properties were found for up to 9 DCNDBQT molecule thick films prepared through vacuum sublimation as investigated with UHV non-contact AFM and XRD. X-ray and AFM data indicate that the DCNDBQT molecules form a well-ordered terraced structure exhibiting step heights of 1.5 to 1.8 nm. Hence, the DCNDBQT molecules are linked to the functional SAM interface layer by H-bond interactions standing practically perpendicular to the TiO<sub>2</sub> template, and thus providing optimal orbital overlap between neighbouring thiophene rings that can be used to construct and operate a OFET-structure.

For the first time the newly synthesized DCNDBQT was studied by voltammetry as well as by *in situ* ESR/Vis-NIR-spectroelectrochemistry. Structure displays one reversible reduction and two oxidation steps (with the reversible first one). The electrochemical band gap was found to be 2.25 eV, which is in good agreement with optically one and falls within the range of semiconductor materials. ESR and Vis-NIR spectra recorded during the first anodic and cathodic steps show the presence of radical cation and radical anion respectively.

The reaction mechanism of the charge transfer reaction is discussed.

# The Development of Polarography

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According to IUPAC nomenclature polarography is voltammetry with dropping mercury electrode (DME). It started in 1922 when the first current - voltage curves were measured of electrolytic reduction of oxygen in aqueous solutions of dilute electrolytes with the indicator dropping mercury electrode, originally used for studying surface tension of polarized mercury. The current was measured point-by-point with damped mirror galvanometer, presence of electroactive substance in the solution was indicated at a particular potential by a step-shaped increase of the mean current, called henceforth the "wave". It was soon empirically established that the exactly reproducible waves contained information about both quality and quantity of the dissolved substance. The name "polarography" was introduced in 1924, after an instrument called "polarograph" was built for automatic photographic recording of current - voltage curves in order to speed up the measurements. Polarography soon turned out to be a rapid and sensitive method for organic and inorganic analysis.

After about a decade of collecting experience with polarographic behaviour of various species sufficient material was gathered to enable building up theoretical principles of polarography. That consisted in quantitative formulations of different kinds of currents encountered with the DME and in their experimental verifications. - First it had to be found out what effect on polarographic currents has electric conductivity of the electrolysed solution. In solutions of low conductivity the electrostatic field between the electrodes increases the transport of positively charged species and decreases the transport of the negatively charged species to the cathode. Currents affected in that way by the low solution conductivity are the **migration currents**. In order to avoid such effect in polarography sufficiently conducting supporting solution of some strong electrolyte has been used, usually of 0.1 M concentration. - Most common in polarography have been the currents occurring in conducting supporting electrolytes when the dissolved electroactive substance approaches the electrode by diffusion; they are the so-called **diffusion currents**, quantitatively expressed by the Ilkovič formula. By combining this with the Nernst formula the equation of **reversible polarographic wave** and the expression for the polarographic **half-wave potential** have been obtained. - For charging the electric double layer of each drop of the DME to the applied potential a small non-faradayic **charging current** is necessary which becomes important when the concentration of the electroactive species and its corresponding faradayic current is small. - In case of a reversible electrode reaction when the electroactive substance or its reaction product is strongly adsorbed at the electrode surface, a separate wave appears on the polarographic curve. In case of adsorption of the reaction product it appears before the main wave and in case of adsorption of the substance it appears after the main wave. When the electrode surface is fully covered by adsorption, the equation for mean **adsorption current** of constant wave height is valid. - In case the electroactive species is formed by a chemical reaction in the vicinity of the electrode the polarograph records **kinetic current**, and when the active species is produced near the electrode surface by a catalytic process, the polarographic response is **catalytic current**. - Specific currents which produce polarographic curves of characteristic shapes are the **polarographic maxima**. Maxima **of the first kind** are caused by stirred solution around the drop produced by change of adsorption of electroactive species in course of its electrode reaction, and the maxima **of the second kind** occur in concentrated supporting electrolytes when the rate

of flow of mercury through the capillary exceeds a certain limit. - All the above listed currents have been quantitatively characterised by equations and can be experimentally distinguished and identified. Their thorough study has been completed by the end of nineteen-fourties and they represent the basis of the so-called "**classical polarography**", product of the "Prague polarographic school".

Further development of polarography was based mainly on utilization of the progress in instrumental technology, and that occurred mainly beyond the Prague school. - From the beginning of nineteen-fourties papers on **a.c.polarography** were appearing. In that on the d.c.voltage applied to the polarographic cell with DME a small a.c.voltage was superimposed and the resulting a.c.signal was measured. If the recorded signal was **in-phase** with the applied a.c.voltage, the recorded curve had the shape of derivative of the polarographic wave, if the measured signal was **out-of-phase**, the curve indicated capacity of the electrode double layer. A.c.polarography applied to study of adsorption at DME has been called **tensammetry**, a special modification of the original method was **second harmonic a.c.polarography**. - Another variation of a.c.polarography was **square wave polarography**, in which the square-wave shaped alternating voltage of small amplitude superimposed on the linearly changing voltage was applied to the electrode and the corresponding current was measured only in the last phase of each square signal in order to suppress charging current from the curve. In that way the sensitivity of polarographic measurements was increased. - The idea to measure current only in the last phase of the mercury drop when the charging current is negligible and thus to increase the sensitivity was realised in **tast polarography**. - On a similar principle the sensitivity of measurements was increased in the **pulse polarography**, both in **normal** and in **differential** variation. In the normal method the potential was applied to the electrode in linearly increasing right-angle voltage pulses, one to each drop at the end of its growth, in the differential version the voltage pulses were of constant amplitude, superimposed on linearly increasing voltage.

The above methods of advanced polarography can be applied to hanging mercury drop electrode (HMDE) - in that way the corresponding methods are called **voltammetric**. Although in those methods one mercury drop remains hanging during the whole polarization scan, the curves repeated with fresh drops are well reproducible. In voltammetry the sensitivity can be further increased by accumulating the substance at constant potential prior to application of the polarizing signal. The following electrochemical dissolution of the accumulated species is called the **stripping** - either **anodic, cathodic** or **adsorptive**.

Apart from the above listed frequently used methods of advanced polarography there are specific modifications of polarography described in literature, which were developed for special purposes. These are, e.g., **radio frequency** -, **rapid** -, **square wave intermodulation** -, **high level faradayic rectification** -, **demodulation** -, **charge step** -, **white noise a.c.** -, **resonance attenuation** -, etc. - When normal polarographic method was used for some particular purpose, the results have been often published under titles like **chromatopolarography**, **photopolarography**, **radiopolarography**, **radiation polarography**, **magnetopolarography**, **sonopolarography** and others.

In recent years, based on experience with polarography, the current-controlled electrolysis with HMDE has been successfully applied in research - the methods used in that case belong systematically to **chronopotentiometry**.

# Heterogeneous Anion Exchange Membranes for Electrolytic Splitting of Water

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Hydrogen has a potential to play in the future a role of the reliable, secure and clean energy vector. Nowadays hydrogen is produced predominantly from the fossil fuels. This is predetermined by the economical aspects of the existing competitive processes. Nevertheless, this approach is not sustainable from the point of view of the long term development. It is not compatible with the philosophy of the hydrogen economy and gradual increase of the part of the human society energy demands covered by the renewable sources. This philosophy is connected with the splitting of water as a main hydrogen source on the earth. Hydrogen production from the water can be attained either by the thermal or electrochemical splitting.

The most important barrier to the broader hydrogen economy implementation in the daily life is the challenge of getting hydrogen economically to the point of use. This includes technological issues of hydrogen production, storage and transportation. Currently used centralized large capacity hydrogen production units are in the future visions into the certain degree replaced by the decentralized production. For this purpose electrolytic water splitting represents the most favorable technology. This is due mainly by the high complexity and material demands of the thermal process.

Typical future utilization of this type of the process is related to the increased production capacity of the renewable power sources. These are often characterized by low predictability and controllability (*e.g.* in the case of wind and solar energy). Water electrolysis represents in combination with these sources a practical way of converting the surplus electrical energy into chemical one, which can be reused during the period of the excessive energy demand. Since this approach is related to the multi-steps technology (water electrolysis, hydrogen compression and hydrogen burning for the energy production, *e.g.* by the fuel cell), all the processes have to be highly efficient in order to maintain sufficient efficiency of the entire technology. This is a prerequisite of the economically competitive process.

At present days water electrolysis represents a well-established technology using 25-30 wt. % KOH solution as an electrolyte. Drawback of this technology represents utilization of the concentrated KOH solution as an electrolyte. This increases complexity of the technology and reduces efficiency of the process (pumping energy, interelectrode distance, inserted inert separator of significant thickness). In contrast to this arrangement, polymer electrolyte membrane (PEM) cell can provide minimization of the mentioned negative aspects. This concerns especially reduction of the interelectrode distance and avoiding presence of an inert separator in the interelectrode space. An additional effect represents likely reduction of the KOH concentration in the solution flowing through the electrode compartments, in an ideal case down to zero. PEM type electrolyzers can be divided into two main groups: acidic and alkaline ones. The main advantages of the individual types of technologies can be summarized as follows. Acidic process is characterized by the fast electrode reaction kinetics and high power density. Alkaline process on the other hand doesn't require platinum metal based catalysts. Acidic technology is a subject of an intensive research already for at least last

decade. This is (beside high energy density as its main advantage) related also to the availability of the sufficiently conductive and stable polymer electrolyte membrane on the base of the perfluorinated sulphonated polymers. Main drawback of the alkaline technology represents from this point of view absence of the anion selective polymer material showing sufficient stability in the alkaline environment. With an increased attention being recently paid to the reduction of the platinum metals demand of the water electrolysis technology the alkaline technology starts to be studied intensively during the last years again.

Within the framework of this study stability of three different ion exchange groups in the alkaline environment at the conditions relevant to the water electrolysis was determined. Subsequently influence of the polymer binder on the resulting membrane properties, *i.e.* mechanical properties, morphology, ion exchange capacity and ionic conductivity were followed. For this purpose a series of heterogeneous anion exchange polymer membranes was produced at the Institute of Macromolecular Chemistry AS CR. Finally, selected membranes were tested in laboratory alkaline PEM electrolyzer utilizing 10 wt. % KOH solution and nickel foam electrodes under ambient pressure and laboratory temperature.

#### **Acknowledgement**

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# Liquid Film Embedded Electrode for (Spectro)electrochemical Investigation of Redox Systems Soluble in Nonaqueous Solvents

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To investigate (spectro)electrochemical properties of new redox systems synthesised usually in mg quantities we need a special equipment suitable for such task. Presented arrangement was developed to perform electrochemistry of new synthesized phthalocyanines, available usually in mg-amounts, as well as a “bulk” (spectro)electrochemistry and coulometry in relatively short time scale. Preferably it is designed to perform electrochemistry of water insoluble phthalocyanines.

The principle of the operation is in utilization of a thin layer of nonaqueous phase immiscible with water where the studied compound is dissolved. The film of nonaqueous phase embedded to the solid supporting electrode is overlaid by aqueous electrolyte solution where the reference and counter microelectrodes are immersed. The volume of nonaqueous phase where electrochemical reaction takes place can be typically less than  $10^2 \mu\text{l}$ . Low amounts of studied compounds allow performing also stability measurement and intermediate products detection respectively, which task is usually not feasible in a traditional (bulky) arrangement of the cell.

In our work we have employed newly synthesized phthalocyanine derivative with fullerene and have compared its electrochemical behavior with cobalt tetraneopentoxy-phthalocyanine under different conditions, in various compositions of aqueous solution and in presence of different quaternary ammonium salts in nonaqueous phase. The charge transfer redox activity of phthalocyanine-fullerene derivatives showed four reversible redox peaks characteristic for fullerene and phthalocyanine respectively.

## Acknowledgements

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# Synthesis, Separation and Characterization of Endohedral Cerium Metallofullerenes

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The special role of cerium in the family of metallofullerenes in their cage size and the stability of the endohedral structure is to be understood.

Therefore endohedral cerium metallofullerenes were produced by arc vaporization using the method of Krätschmer and Huffman. Core drilled graphite rods were filled with a mixture of cerium metal or cerium oxide, respectively, and graphite powder. The fullerenes were extracted from the crude soot and the targeted endohedral cerium metallofullerenes were separated and purified by several HPLC (High Performance Liquid Chromatography) steps.

Isomeric pure cerium metallo fullerenes were investigated by NMR, ESR and vibrational spectroscopy methods to obtain information about cage symmetry and influence of the endohedral cerium on the fullerene cage.

The special electrochemical properties of the endohedral cerium metallofullerenes were studied by cyclic voltammetry. It was figured out that the  $\text{Ce@C}_{82}$  has three reversible reductions and one reversible oxidation step while the  $\text{Ce}_2\text{@C}_{80}$  shows two reversible reductions and one reversible oxidation.

# The Mechanism of Electrode Reactions – – a Combined *in situ* NMR and *in situ* ESR Spectroelectrochemical Investigation

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Due to the increasing number of (especially organic) electrode reactions and the development of spectroscopic techniques the modern field of spectroelectrochemistry facilitates *in situ* observations of processes at electrodes by spectroscopic methods. Having these methods at hand an experimental insight into the complex mechanisms of electrode reactions is accessible.

The development of NMR spectroelectrochemistry provides a powerful method for the study of structural or electronic changes of diamagnetic molecules in any electrochemical reaction mechanism. For the investigation of paramagnetic structures ESR spectroelectrochemistry is the method of choice to detect such species and to characterise their electronic state via the g-value and hyperfine splitting with additional calculations of the spectra.

Here a combined *in situ* NMR and *in situ* ESR spectroelectrochemical study of a reaction mechanism is presented detecting and describing the whole number of paramagnetic and diamagnetic intermediates and final products in an electrode reaction. The reduction of p-benzoquinone to hydroquinone is followed by both these spectroelectrochemical methods to demonstrate the power of their combination. The results of both *in situ* spectroelectrochemical methods at the same redox system are used to get the complete electrochemical mechanism of p-benzoquinone in aqueous solutions at selected pH values thus demonstrating the influence of the proton on the reaction mechanism.

# Mathematical Modeling: Effective Tool for Optimization of Electrochemical Cells with Bipolar Electrode Arrangement

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Electrochemical cells with bipolar electrodes are widely used in chemical industry. For example, significant part of the chlor-alkali electrolysis technology representing nowadays one of the most important electrochemical industries is build-up on the bipolar electrode arrangement. The high capacity bipolar electrolyzers are constructed also for hydrogen production by the alkaline water electrolysis. The most advantageous property of the bipolar electrodes in comparison to the monopolar one consists in the simpler electric circuitry. Only terminal electrodes are connected to the external power source. This is particularly interesting in the processes operating at elevated pressure and/or temperature. The simpler electric circuitry of bipolar electrolyzers is also preferred in the case of microstructured devices. In addition, the bipolar electrodes arrangement enables to operate cell at higher cell voltage and lower current load than the monopolar one. It reduces the ohmic losses in the electric circuitry and minimizes energy losses related to the AC current rectification.

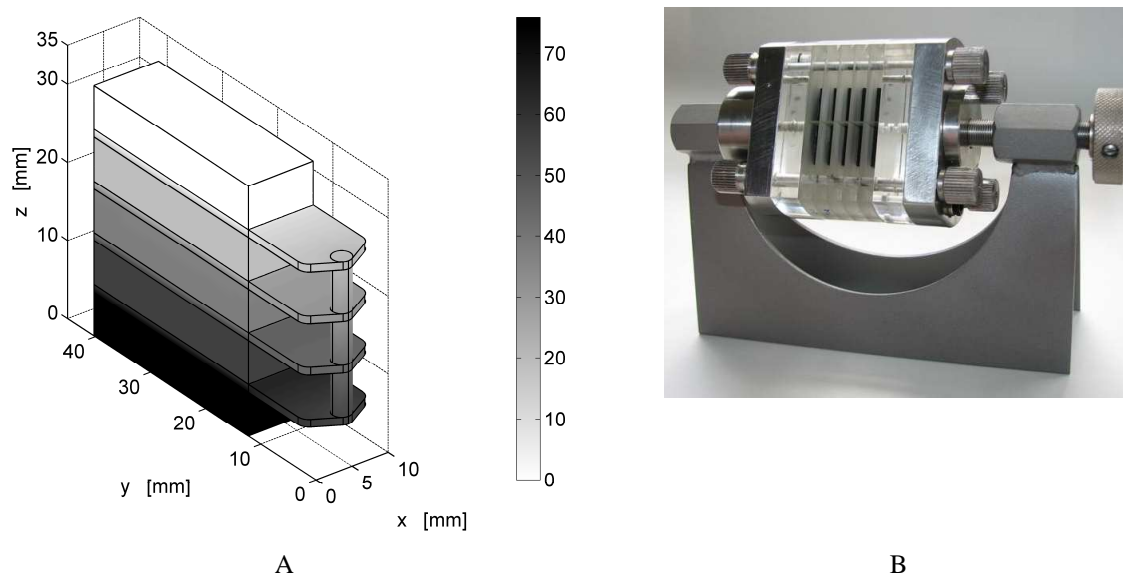
However, the design of such industrial units has to take into the consideration danger of significant efficiency losses caused by the so called parasitic (or by-pass) current. It is related to the cell geometry, mainly of electrolyte solution supply, circulation and removal circuitry. It is because it provides pathway for the conduction of certain portion of electric current aside the bipolar electrode body. This reduces process efficiency. Large size and high capacity industrial scale devices development and optimization leads to extremely high costs. Therefore, theoretical description of these systems, *e.g.* via mathematical modeling, represents a powerful tool in terms of the solution of this problem.

From the mathematical point of view two basic types of models of the bipolar electrode systems can be distinguished. The first one is characterized by the separation of the individual electrochemical cells of the electrolyser by an insulating barrier. The second type than consists of the bipolar electrodes placed in the electrolyte allowing parasitic current flow directly along the electrodes sides. The solution of the first model is currently well established. On the other hand, the modeling of the second type of the model was firstly proposed and validated [1] by the authors of this contribution. Within this work the effort made in this field is presented. Firstly, the experimental determination of the local Galvani potential and current density distribution in a model electrochemical cell in a bipolar arrangement is presented. The artificial extension of the bipolar electrode thickness has allowed experimental determination of the local electrode potential and current density distribution along the bipolar electrode body. The corresponding mathematical model based on finite volume method was developed and validated by means of obtained experimental data.

In the next part of this work the practical importance of both types of models is documented using examples of the design and optimization of the industrially relevant applications. Here *a)* design of the cell for Direct Drinking Water Disinfection (DDWD) and *b)* design of the Bipolar Microstructured Electrochemical Reactor (BMER) for electroorganic synthesis will be discussed.

DDWD represents method of the water disinfection based on the formation of disinfecting agents directly by the electrolysis of the treated potable water. In the course of the process the chloride ions naturally present in the source water are oxidized at the anode to chlorine. The produced chlorine then represents main disinfecting specie.

The design of the BMER is demonstrated using model reaction represented by anodic 4-methylanisole methoxylation. This reaction was chosen because of its practical importance. The hydrogen formation is considered as the counter electrode depolarization reaction. The interelectrodes distance of  $100\ \mu\text{m}$  is used to reduce the ohmic losses in the low conductive organic electrolyte. The gas phase formation, however, represents main challenge with respect to successful utilization of this cell geometry. Due to low interelectrode distance the gas bubbles formed occupy significant part of the electrode surface. It finally results in drop in the process efficiency. It was thus necessary to propose an electrolysis cell of suitable construction to minimize impact of this phenomenon. The electrochemical reactor with bipolar electrode arrangement represented an optimal solution. The proposed BMER allows operating the cell at elevated pressure to minimize volume of the gas phase. Furthermore, it enables the continuous removal of the gas from reaction mixture. Figure 1 (A) shows results of the calculation of the Galvani potential field in the BMER using the proposed mathematical model. Figure 1 (B) presents the photography of the constructed BMER.



**Figure 1:** A – Galvani potential field in the BMER calculated by mathematical model;  
B – photography of the BMER designed on the base of the mathematical model results.

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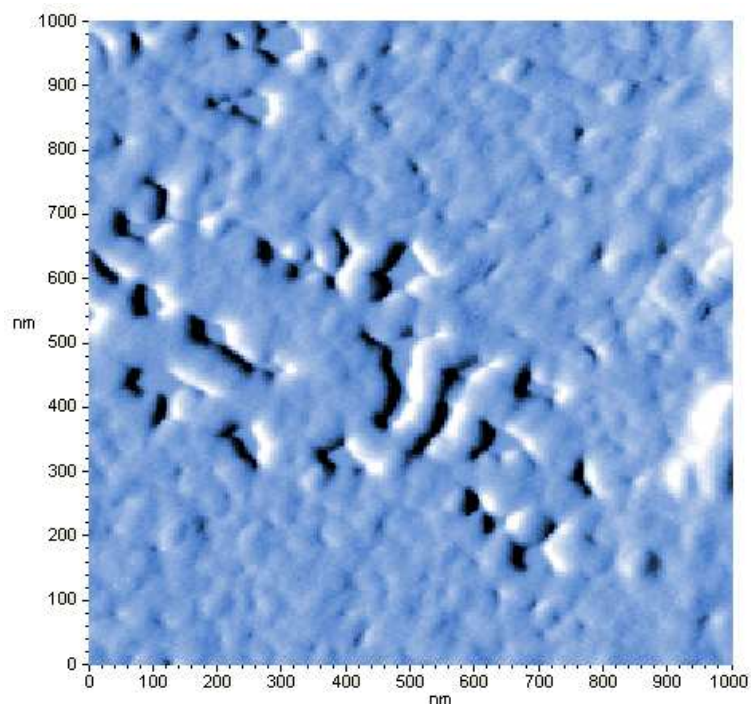
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# Adsorption of Bovine Serum Albumin on Highly Oriented Pyrolytic Graphite

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In the present work, we investigate the adsorption of bovine serum albumin (BSA) on highly oriented pyrolytic graphite (HOPG). We employ acoustic alternating contact mode of Atomic Force Microscopy (AAC AFM). In this method, the AFM cantilever oscillation is driven by the piezo actuator. The sample surface is investigated by measuring the cantilever oscillation amplitude. The feedback circuitry maintains the amplitude constant and thus, measures the surface topography and gains the phase-sensitive information about the surface. We analyze the adsorption of BSA on HOPG at various bulk concentrations in water solutions.



We find that BSA is prone to adsorption even at very low concentrations (0.010  $\mu\text{g/mL}$  and 0.10  $\mu\text{g/mL}$ ). At these bulk concentrations, adsorbed BSA molecules tend to form isolated clusters that sparsely cover the HOPG substrate. We show that the molecules change their position in time. However, when higher bulk concentrations (1.0  $\mu\text{g/mL}$ ) are used, BSA molecules form stable interconnected associates that retain their position in time. The surface coverage is roughly  $\frac{1}{2}$ . The adsorption from very concentrated solutions (500  $\mu\text{g/mL}$ ) results in stable protein structures with surface coverage approaching unity (see the figure).

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# Conducting Polymers in Room Temperature Ionic Liquids

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The reason for the great interest in RTILs is their good properties such as: high ionic conductivity, high viscosity, low melting point (below 100 °C), sufficient thermal stability and a wide electrochemical window. An important discipline of science that benefits from the use of RTILs is electrochemistry. From an electrochemical point of view, RTILs open a field of new solvents with high conductance (additives not needed) and an extended electrochemical window combined with high stability.

Ionic liquids have been shown to act as good electropolymerization media for conducting polymers. The remarkable influence of polymerization conditions on the resulting polymer material is well known from experiments in organic solvents.

In situ spectroscopic studies of conducting polymers gives insight in the different processes taking place during electrochemical doping. Due to the high absorbance properties of conducting polymers the Attenuated Total Reflection (ATR) technique combined with FTIR spectroscopy is a useful method for analysis of their structures.

Generally, during charging of the polymer film, new bands in the spectral region of ca. 1600 to 600  $\text{cm}^{-1}$  (low energy) are rising due to a strong electron-phonon coupling. Additionally, electronic transitions of formed charge carriers in the band gap enforce formation of broad absorption bands in the range from ca. 7000 to 1600  $\text{cm}^{-1}$  (high energy).

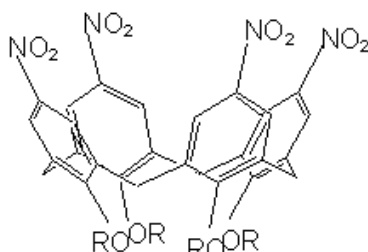
In this study we focus on the ionic liquids induced changes in the properties of different conducting polymers.

# Electrochemical Investigation of Intramolecular Electron Interactions in Mono-, Di-, Tri- and Tetranitrocalix-[4]-arenes and Their Models

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Calixarenes are promising anion receptors as well as ligands for cations due to their capability of the host-guest interaction. These molecules are important for the application in medicine as contrast species for Magnetic Resonance, in analytical or environmental chemistry etc. For these purposes a suitable substitution is necessary, namely on the upper rim. The nitro group can be easily attached to the calixarene molecule and its reduction enables introduction of other functional groups and prolongation of the pendant carbon chains. The electrochemical approach is advantageous not only as an efficient tool for preparative electrosynthesis, but namely from the mechanistic point of view.



Four reducible nitro groups in one molecule provoke many principal questions: What is the intramolecular electronic interaction between them? Are they reduced simultaneously or stepwisely? What is the influence of the lower rim substitution on the reduction of the nitro groups? What is the influence of the conformation of the calixarene (CONE, PACO, 1,2-ALT, 1,3-ALT) on its reducibility? What is the influence of the reduction on the molecular geometry? What are the reduction intermediates and mechanisms?

Before investigation of the authentic calix arenes, the electroreduction of a series of 14 monomeric model compounds - *para*-substituted nitrobenzenes - were studied. Surprisingly, besides the classical mechanism of a 1-electron reversible process followed by an irreversible 3-electron one, several anomalous mechanisms (dianion formation, 6-electron reduction, autoprotonation mechanism, strong hydrogen bonding) were observed and described.

The electroreduction of the tetranitrocalix-[4]-arenes starts with two 2-electron reversible waves corresponding to the presence of two different couples of nitro groups without mutual electronic communication. This result reflects well the finding of the x-ray structural analysis, that the "calix" is in fact not circular, but pinched with a strong " $\pi$ -stacking" of the opposite benzene rings. The first two waves are followed by a single 12-electron wave, indicating that the generated tetrakis-radical anion intermediate involves four equivalent nitro radical anions. Their repulsion is most probably the reason of a strong change in geometry of the calixarene to a circular one.

The reduction of mono-, di- and trinitrocalix-[4]-arenes with different lower-ring substitution were also performed, compared and the differences were discussed and interpreted in terms of molecular geometry and intramolecular electronic communication between the redox centers.

## Acknowledgement

The support from the project KONTAKT, No. ME09002 (MŠMT) is gratefully acknowledged.



# Elucidation of Reaction Mechanism of Oxygen Evolution on RuO<sub>2</sub> and Doped RuO<sub>2</sub> Electrodes

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The oxygen evolution reaction is one of the challenges of the contemporary electrocatalysis. In the literature, two reaction mechanisms are proposed to describe the oxygen evolution reaction on the oxide electrode surface in acid conditions [1, 2]. The first one considers recombination of two S-O groups to form O<sub>2</sub>; the second one operates with formation of surface peroxide intermediates. Both mechanisms assume the electrolyte solution to be a source of oxygen. This assumption can be verified by isotope labeling technique [3].

Potential dependence of the oxygen evolution reaction on RuO<sub>2</sub> and Ni doped RuO<sub>2</sub> electrodes were studied in HClO<sub>4</sub>/ H<sub>2</sub><sup>18</sup>O by combination of potential step experiment and differential electrochemical mass spectroscopy. The results confirm the presence of oxygen exchange mechanisms which depends on applied potentials. At potentials negative to 1.12V vs. SCE, the oxygen evolution reaction in acidic conditions proceeds without active involvement of the electrode surface. At the potentials above 1.12V vs. SCE, the oxygen exchange mechanisms applies and oxygen originally present in the electrode surface released. The extent of oxygen exchange is a function of the electrode composition.

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# **In situ ESR-UV/Vis/NIR Spectroelectrochemistry of *N,N,N',N'*-tetrakis(4-aminophenyl)benzidine and its *N,N,N',N'*-tetra-(4-methoxyphenyl)-substituted Quarterphenyl Homologue**

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In the last time, aromatic or hetero-aromatic compounds being able to donate or to accept electrons easily in reversible processes received a lot of interest. They can be used as electronic materials for manufacturing opto-electronic devices, such as organic photocopyers, OLEDs, OSOLs, and some others, because the reversibility of the appropriate electron transfer processes are important requirements, besides of some others, for the generation and the transport of charged species in such materials. In combination with ESR and UV/VIS/NIR spectroscopy the cyclovoltammetry (CV) is an important analytic method for estimating the ability of organic compounds to lost or to accept electrons and to elucidate the chemical structure and the electronic nature of the reduced or oxidised species generated in course of the corresponding electron transfer processes. New designed in situ thin layer ESR-UV/Vis/NIR cyclovoltammetric experiments were used to study the redox behavior of *N,N,N',N'*-tetrakis(4-aminophenyl)benzidine (1) and its *N,N,N',N'*-tetra-(4-methoxyphenyl)-substituted quarterphenyl homologue (2) in detail. Spectroelectrochemical studies of corresponding cation radicals, dications and even tetracations indicate different stability of higher ions of two model *N,N'*-tetraphenyl-substituted benzidines with different bridge length between two triphenylamine moieties as well as different phenyl substitution.

# Nucleation, Nucleus Growth, Death of the Nucleus: The Process Chain of Electrodeposition

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The electrochemical processes on a growing metal layer can be described as a chain of rate of formation of nuclei, growth of nuclei, and death of nuclei [1]. The rate equations for the partial processes have been described in the literature [2].

By setting up the process chain statistical parameters can be defined as mean density, mean size mean growth rate, mean lifetime, mean death rate of nuclei. Stationary growth of the metal film is achieved if the rate of formation of nuclei is equal to the death rate of nuclei.

From the condition of stationary growth an equation for the dependence of the average grain size on the experimental parameters can be derived.

Several situations of metal deposition with different process parameters will be discussed and compared with experimental results.

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# Titanium Suboxides as a Catalyst Support for PEMFC

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Fuel cell technology will play an important role in energy supply system of the future. Proton exchange membrane fuel cell (PEMFC) represents their most suitable type for mobile applications, or applications characterized by an irregular operation. Despite intensive research in the past years, PEMFC application is still limited due to several drawbacks. Beside high costs, insufficient lifetime represents the main problem. Namely, the carbon support used in today's fuel cells has limited lifetime due to oxidative degradation, mainly on the cathode. Therefore, new supports are being researched in order to improve the fuel cell lifetime.

One possible way reported is based on the utilization of the so-called Magneli phases (non-stoichiometric  $Ti_nO_{2n-1}$  where  $n$  ranges from 4 to 10) as a catalyst support in the fuel cell gas diffusion electrode. This material is supposed to overcome lifetime limitations of carbon black due to its superior stability under severe conditions. However, its specific surface area typically doesn't exceed  $2 \text{ m}^2 \text{ g}^{-1}$ . Within this study preparation of Magneli phases was realized by the hydrogen reduction of various types of  $TiO_2$  at high temperature. Powder containing most conductive oxides  $Ti_4O_7$  and  $Ti_5O_9$  was prepared. Subsequently, vibration mill was used to enhance its specific surface. During milling electric conductivity of the powder decreased exponentially with decreasing particle size. Therefore, only small improvement of specific surface is possible without significant conductivity loss. This makes preparation of highly active catalyst with high noble metal loading based on this type of material difficult task.

Subject of this study was preparation of the platinum catalysts supported by the Magneli phases. Chemical reduction of the platinum salt by formaldehyde in water and by ethylene glycol with and without PVP – poly(vinylpyrrolidone) – as an anti-clustering agent was tested. Prepared catalysts were characterized using cyclic voltammetry and linear sweep voltammetry both for hydrogen oxidation and oxygen reduction. SEM was used to characterize samples morphology. Selected catalysts were characterized in the laboratory fuel cell.

Preliminary results showed that very good distribution of catalyst on the support surface can be obtained by impregnation in PVP stabilized dispersion of Pt nanoparticles. However, due to low surface area of the support, the loading attained is extremely small. It reaches just about 3 wt. % of Pt.

Preparation in absence of PVP resulted in obtaining expected Pt loading, *i.e.* 40 wt. %. The drawback is that clusters of larger nanoparticles appear on support surface. Furthermore, results from fuel cell indicate that the overall performance of the catalyst is inferior to Pt/carbon black catalysts. Roughness of the relatively hard titanium oxide particles results in membrane perforation. Thus production of a good MEA was in this case impossible.

These results show that in the system under study either small nanoparticles with good distribution but small loading or large loading with larger clusters of nanoparticles can be obtained at the present state of knowledge. To obtain good distribution, high loading and small nanoparticles, support specific surface area higher than  $100 \text{ m}^2 \text{ g}^{-1}$  represents a necessary precondition. It can be therefore concluded, that the Magneli phases will not represent suitable replacement for carbon black in fuel cell applications until they can be prepared with high specific surface and at the same time sufficient conductivity.

**Acknowledgement**

Financial support of this research by the European Union within the “Apollon-B” project, Contract No.: NMP3-CT2006-033228 is gratefully acknowledged.

# Vis-NIR and ESR Spectroelectrochemical Study of $\text{Sc}_3\text{N}@C_{80}(\text{CF}_3)_2$

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The current extension of synthetic and separation procedures for endohedral fullerenes, especially those with encapsulated  $\text{M}_3\text{N}$  clusters, has resulted in the availability of these compounds in amounts sufficient for the exploration of their chemical properties and reaction chemistry.<sup>1-3</sup> Recently, a procedure was developed for the trifluoromethylation of  $\text{Sc}_3\text{N}@C_{80}$ ,<sup>4</sup> and several compounds of the formula  $\text{Sc}_3\text{N}@C_{80}(\text{CF}_3)_n$  have been isolated and characterized by mass spectrometry as well as UV-Vis and NMR spectroscopy. In this work, we report in-depth Vis-NIR and spectroelectrochemical study of  $\text{Sc}_3\text{N}@C_{80}(\text{CF}_3)_2$ .

This compound exhibits three reversible reduction and two oxidation steps in *o*-dichlorobenzene at 25°C. The monocation, monoanion, and trianion have been successfully generated and their spectroscopic characterization by ESR and absorption spectroscopy is fulfilled. Spectroscopic properties of the charged states of  $\text{Sc}_3\text{N}@C_{80}(\text{CF}_3)_2$  are compared to those of the parent  $\text{Sc}_3\text{N}@C_{80}$ . DFT calculations are performed to assist in interpretation of the experimental results.

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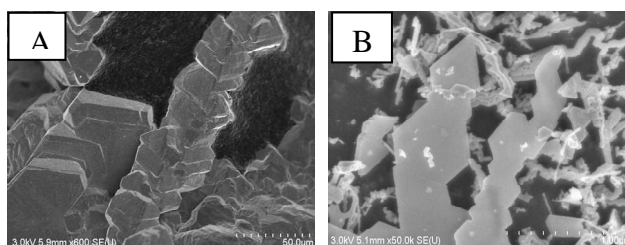
# Templated Photocatalytic Growth of Silver on Variety of TiO<sub>2</sub> Surfaces

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All fundamentals of the development of silver-metal crystals during the oxidative photocatalytic process on TiO<sub>2</sub> surface still have not been completely resolved. To map the photocatalytic growth of silver, organics-free AgNO<sub>3</sub> solution was used in order to avoid the instant reduction of AgNO<sub>3</sub>. Slowing the process down magnifies the differences in the growth mechanism on variety of TiO<sub>2</sub> templates.

Different forms of TiO<sub>2</sub> surface show strong templating character for the growth of silver particles. The selective impact of TiO<sub>2</sub> crystal phase, morphology and doping on the crystal phase, crystal size, shape, orientation, coordination and aspect ratio of the photo-catalytically grown silver is demonstrated.



**Figure 1:** A) Large 3-D silver dendrites developed on pristine TiO<sub>2</sub> nano-anatase film  
B) 1-D and 2-D silver nano-crystals on P-doped TiO<sub>2</sub> structure.

## Acknowledgements

This research was supported by the Academy of Sciences of the Czech Republic (Nos. KAN100500652 and KAN200100801), the Ministry of Education, Youth and Sports of the Czech Republic (COST D35 1P05OC069) and EC No. 229036 NMP3-LA-2009-229036.

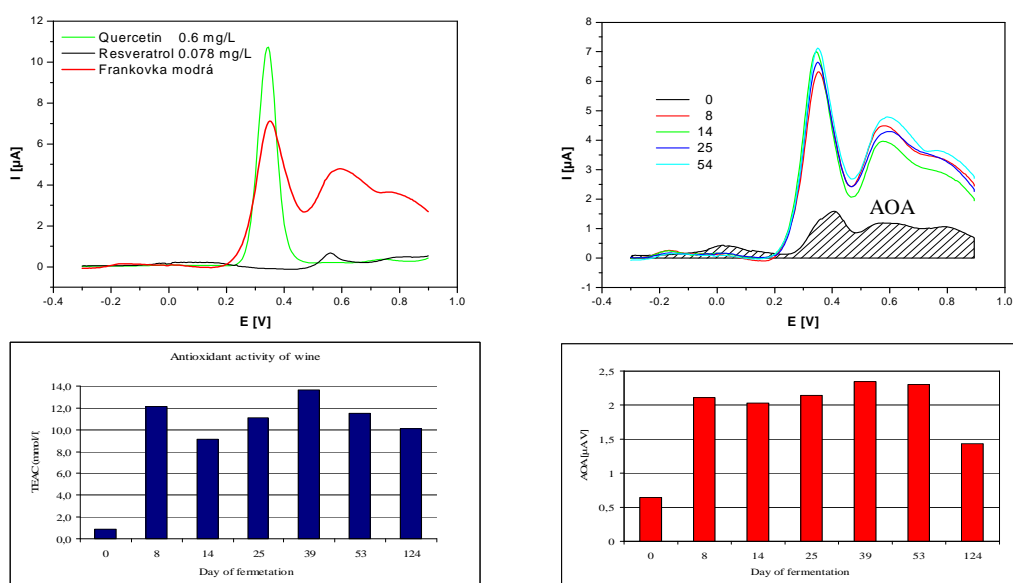
# Electrochemistry, EPR and UV-Vis Spectroscopy of Antioxidants in Wines

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For monitoring of redox processes in wines voltammetric methods are of high interest due to relative low costs and variety of analytical information in voltammetric responses concerning the redox properties of compounds naturally present in wines. A particularly differential pulse voltammetry (DPV) using solid electrode seems to be very promising (see Fig. 1).



**Figure 1:** Comparison of different methods of determination of total antioxidative activity of red wine Frankovka modrá fermented by *S. cerevisiae* FM-VVR using differential pulse voltammetry (AOA - total antioxidative activity in  $\mu\text{A.V}$ ) and UV/Vis spectrophotometry (ABTS test, TEAC – Trolox Equivalent Antioxidant Capacity).

Wine composition depends mainly on vine variety, area of cultivation, climate and wine-making technology and thus UV/Vis spectra of wine samples differ each of other. Therefore a database of UV/Vis spectra of selected wine samples in different state of fermentation depending on wine-making procedure was created. Estimation of radical scavenging capacity (RSC) was performed by monitoring of  $\text{ABTS}^{\bullet+}$  cation radical decrease applying UV/Vis and EPR spectroscopy. UV/Vis studies indicate different antioxidant behavior of selected wine samples from Rača region. A good linear correlation between the antioxidant activities and the intensity of UV/Vis bands at 280 nm and 520 nm as well as DPV response was found confirming the predominant role of phenolic compounds in the antioxidant action of wines.

## Acknowledgements

This work was supported by Research and Development Agency of Slovak Republic under the contracts No. VMSP-P-0052-07, APVV-0488-07 and VEGA project 1/4299/07. We also thank to company Villa Vino Rača, a.s. which enabled practical fermentation experiments.



# The Cyclization of the Diphenylamine Structures in Anodic Reactions: A Cyclovoltammetric Study

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In organic synthesis it is well accepted, that diphenylamine can be transformed into carbazoles under the influence of several metal ions. Some earlier work pointed to this subject of high synthetic interest for the access to new carbazole structures. In general the substituents at the aromatic units of the diphenylamino structure will have a strong influence of the ring closure. Further studies have shown that metal ions like Pd<sup>2+</sup> will have an strong effect on the carbazole formation. While the preparative work in organic synthesis is consuming the expensive Pd salts a matter of choice would be a synthesis at such metal electrodes in preparative organic electrochemistry.

Here we present general studies of the influence of the electrode material on the electrochemical oxidation of substituted secondary diphenylamine derivatives in nonaqueous solutions. Both the influence of the substitution pattern as well as that of the electrode material is presented.

Furthermore, the analysis of the reaction products of a preparative electrolysis is given in detail and the problems of the synthetic route via organic electrochemistry are discussed.

Finally an outlook is given on further voltammetric studies of cyclisation reactions.

# Electrochemical Study of Intramolecular Degradation of New Explosive 2,2-dinitroethen-1,1-diamine

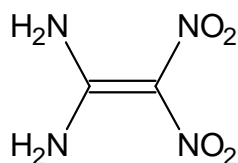
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In our laboratory we study (among others) intramolecular interactions in molecules with multiple redox centres using electrochemical techniques. One of the most interesting recently synthesized molecules in this sense is 2,2-dinitroethen-1,1-diamine (FOX-7) [1, 2]. The structure of this molecule is remarkable due to the combination of two geminal easily reducible nitro-groups in the neighbourhood of two strongly electron donating amino-groups. It is a typical case of the "push-pull" delocalization.

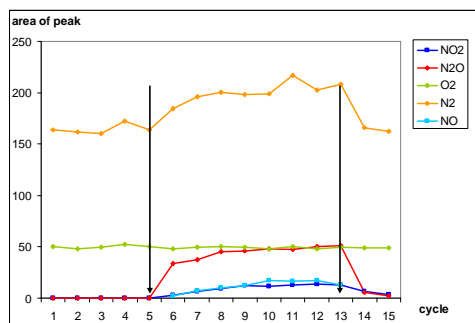


**Figure 1:** 2,2-dinitroethen-1,1-diamine (FOX-7; DADNE; DANE)

Electrochemical reduction or oxidation of this compound has not been studied yet. The attempts for electrochemical oxidation of this compound even in liquid SO<sub>2</sub> gave no response. Polarographic reduction in aqueous buffered solutions shows about 5 consecutive redox processes depending on the pH. The sum of all limiting currents corresponds to 18 electrons, expected consumption for the total reduction of this compound to ethan-1,2-diamine. This product was qualitatively found after chemical reduction of FOX-7 by Zn in HCl, but not after electrolysis.

Reductive electrolysis FOX-7 in acidic and neutral media was surprising: The number of consumed electrons during electrolysis (between 4 – 6 electrons per molecule) is much lower than under polarographic conditions. Moreover, the main products were gaseous, whereas no organic product was identified by extraction from the solution. Therefore we used combination of electrochemistry with GC and with MS analysis. Due to these techniques the following gases were found and identified: NH<sub>3</sub>, N<sub>2</sub>, NO, NO<sub>2</sub>, N<sub>2</sub>O. However, no CO<sub>2</sub> or other carbon containing gaseous product was found. Most probably a part of products remain in the water solution as inorganic ions (cyanamides, nitrites a.o.) and their identification is now under investigation.

The consumption of low number of electrons during the exhaustive electrolytic reduction together with the presence of gaseous products and absence of organic reduction products point to the fact, that during electrolysis an electrochemically initiated degradation of the explosive proceeds, accompanied by multiple intramolecular electron transfer reactions. This process is most probably analogous to the reactions during explosion, but under very low concentration, cooled and slowed down by the solvent and controlled by potential. The aim of this investigation is the understanding of detailed mechanism of intramolecular redox processes during explosion.



**Figure 2:** An on-line electrochemical/MS analysis of gaseous products during electrolysis of FOX-7 in sulphuric acid. Arrows in the graph show the start and the end of the electrolysis, respectively.

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# Damaging Effects of Genotoxic Fluorene Derivatives on DNA Detected Voltammetrically Using an Electrochemical DNA Biosensor

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The emissions of gasoline and diesel engines contribute significantly to ever increasing pollution of living environment. A specific part of exhaust gases is composed of genotoxic derivatives of polycyclic aromatic hydrocarbons. Derivatives of parent hydrocarbon fluorene, mainly its nitro, amino and oxy derivatives, are presently well known hazardous air and water pollutants [1] and great attention is thus paid to their determination in various matrices, especially using modern electrochemical methods [2-4].

In the eighties and the nineties of the last century, L. Möller studied influences of 2-nitrofluorene [5] and 2,7-dinitrofluorene [6] and their *in vivo* metabolites on living organisms and their DNA. In this work *in vitro*, an electrochemical DNA biosensor based on the screen printed carbon paste electrode (SPCPE) has been used for investigation of the interaction between genotoxic nitro derivatives of fluorene (namely 2-nitrofluorene and 2,7-dinitrofluorene) and calf thymus DNA. Two types of DNA damage have been investigated and electrochemically detected at the DNA/SPCPE biosensor: the DNA damage caused by short-living radicals generated by the electrochemical reduction of nitro group, previously described by Abreu [7], and the DNA damage caused by the direct interaction with studied compounds [8].

DNA damage caused by the direct interaction have been also tested by the use of related genotoxic fluorene derivatives (namely of 2-aminofluorene, 2,7-diaminofluorene and 9-fluorenone). The type of direct interaction between 2-nitrofluorene or 2,7-dinitrofluorene and DNA has been characterized using previously tested DNA intercalators [9] (metal complexes of 1,10-phenanthroline –  $[\text{Cu}(\text{phen})_2]^{2+}$  and  $[\text{Co}(\text{phen})_3]^{3+}$ ). Direct damaging effect of 2-nitrofluorene and 2,7-dinitrofluorene to DNA was found to be dominantly intercalative.

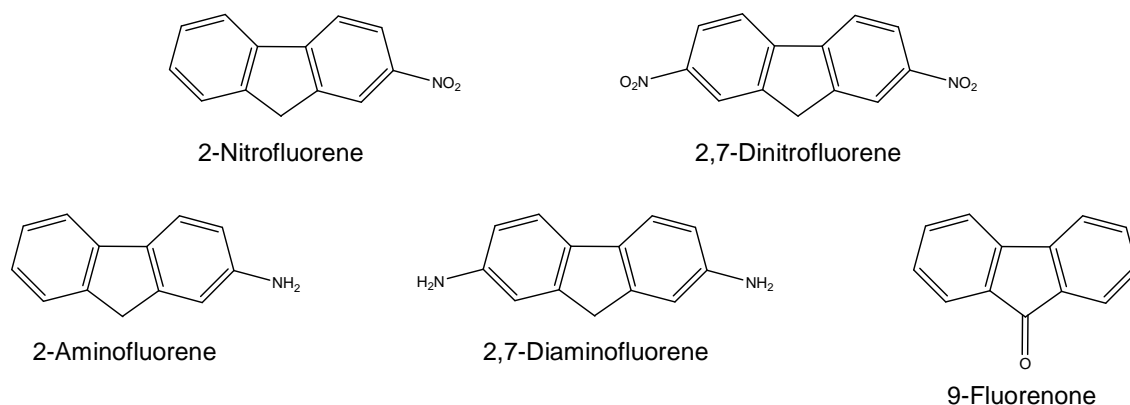


Figure 1: Structural formulas of investigated compounds

### Acknowledgements

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# C<sub>82</sub> Fullerene: Spectroelectrochemistry, DFT and MD Calculations

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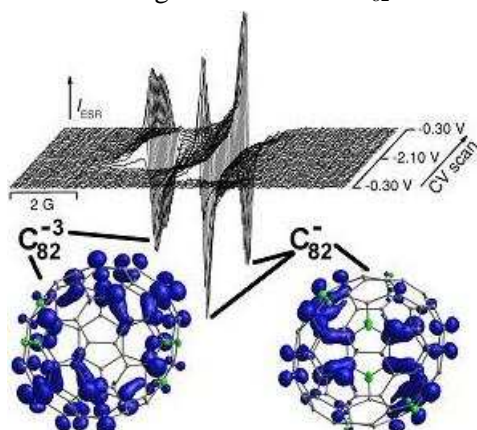
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An extended study of the spectroscopic and redox properties of the C<sub>82</sub> fullerene is presented. Among the nine isolated-pentagon-rule (IPR) isomers of the C<sub>82</sub> fullerene the C<sub>82</sub>(3) isomer with C<sub>2</sub> symmetry is the only stable, empty fullerene structure formed in the arc burning process that can be isolated in an isomerically pure form. The electrochemistry of the C<sub>82</sub>(3) isomer was studied in detail by cyclic voltammetry and spectroelectrochemistry. The ionic species of C<sub>82</sub> with the charge ranging from C<sub>82</sub><sup>+</sup> to C<sub>82</sub><sup>4-</sup> were successively generated in *o*-dichlorobenzene solution at room temperature and characterized by *in situ* ESR and visible/near-infrared (Vis/NIR) spectroscopy.

A systematic and comparative theoretical calculation based on the DFT and semiempirical AM1 and ZINDO methods were performed on the neutral and charged states of C<sub>2</sub>(3)-C<sub>82</sub> fullerene. The relations between the dynamical structure and the total molecular charge were studied using AM1 molecular dynamics (MD). The obtained results show that the shape of the fullerene ball is more-or-less periodically changed around the most probable geometry. On the basis of the evaluated MD geometries and relevant ZINDO transitions, the absorption spectra were simulated. These simulations allowed us to assign individual bands in spectroelectrochemical records where the mixtures of oxidation and reduction products occurred. The presented data give new insights into the charged states of the C<sub>82</sub> fullerene.



**Figure 1.:** ESR spectra of the C<sub>2</sub>(3)-C<sub>82</sub> mono- and tri-anion detected during the *in situ* room temperature reduction of the C<sub>82</sub> fullerene in *o*-dichlorobenzene, together with the spatial distribution of spin density (+ blue, - green) calculated by the TD-DFT.

## Acknowledgements

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# Electrochemical Microreactor for Oxidation of 4-Methylanisole

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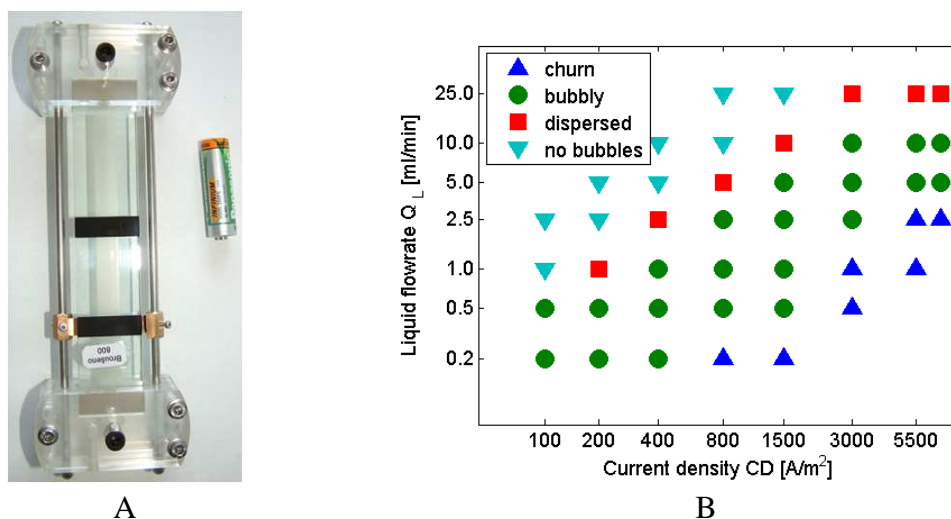
Microstructuring represents a novel approach for design of chemical apparatuses. In some processes, it can solve constantly increasing demands on chemical technologies. Therefore, for last two decades microstructuring has been intensively studied by many engineering laboratories around the world. In electrochemistry, microstructured reactors have also the advantage of smaller ohmic drop, resulting in the lower concentration of supporting electrolytes.

In our work we focus on a study of the electrochemical oxidation of 4-methylanisole, which is currently used in industry [1]. The target is to design a new electrochemical microreactor (EMR) providing the high conversion and selectivity of reaction in only a single pass of reaction mixture through the EMR. In this case, microstructured reactor with a thin electrode gap can significantly decrease operational and investment costs arising from the separation and purification of products.

For successful design of EMR it is necessary to understand the hydrodynamic characteristics of given system. In studied reaction system, it is even more important, because hydrogen bubbles are generated on counter-electrode and with liquid reaction mixture form the two-phase system. Bubbles significantly affect the conversion and selectivity of the reaction by the hindrance of the electrode active surface.

First part of contribution deals with the experimental study of gas-liquid flow in thin-gap EMR. The aim of this part was to experimentally describe the behavior of two-phase flow in the wide range of operating conditions (liquid flow rate and current density). Additionally, effects of increased total pressure in the apparatus, and different electrode roughness were investigated.

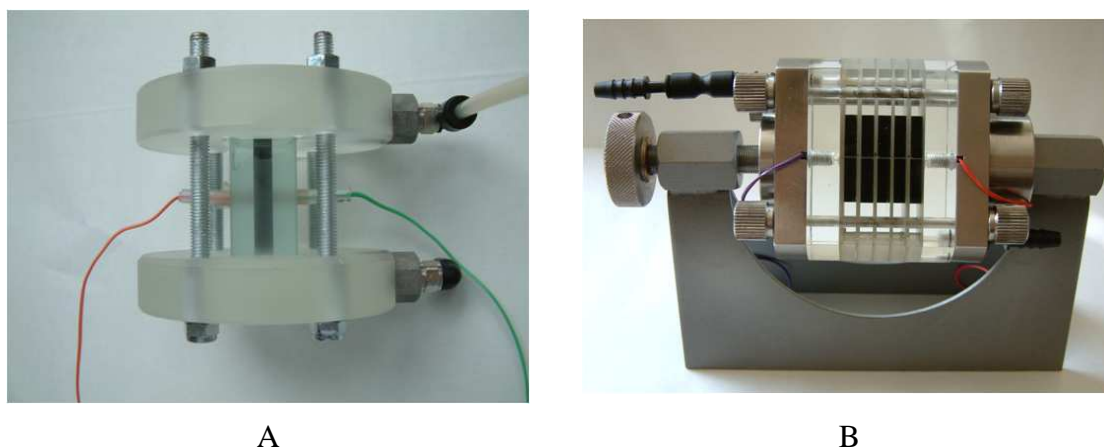
To describe the two-phase flow in an EMR the following characteristics were investigated: flow pattern, bubble size distribution and void fraction. For the determination of these characteristics the flow visualization experiments were carried out using the specially designed visualization cell (Fig 1a). Measured data were evaluated by image processing procedures and yielded information about the hydrodynamic behavior of the EMR.



**Figure 1:** Photo of thin-gap electrochemical flow visualization cell (A); Flow map for electrode roughness 1000 and atmospheric pressure (B)

The results showed that in a thin-gap EMR the four different flow regimes can exist: the flow with no bubbles, dispersed bubbles, bubbly flow and churn flow. From our previous work [2] we know that bubble with smaller diameter than half of interelectrode distance does not significantly affect local current density distribution. Therefore, the dispersed bubbles seems to be the most suitable for electrochemical oxidation of 4-methylanisole. Presented flow map (Fig 1b) indicate the occurrence of different flow regimes for the particular combination of liquid flow rate and current density.

Second part of contribution deals with testing of two newly designed EMRs (Fig 2a – block EMR, Fig 2b – filter press EMR) with bipolar arrangement. Wide comprehensive set of experiments was conducted to study dependencies of conversion and selectivity on reaction mixture flow rate, applied current density and pressure in apparatus. Extensive database of experimental data was acquired. Result showed good agreement with expected results based on first part of contribution and calculations.



**Figure 2:** Developed electrochemical microreactors with bipolar arrangement; 4-gap block EMR (A); 4-gap filter-press EMR (B)

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# Electrochemistry of Mixed Metal Nitride Cluster Fullerenes

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The new class of fullerenes, metal nitride cluster fullerenes (NCFs) with the formula  $M_3N@C_{2n}$  attracted great interest since the first example of NCFs was reported by Dorn *et al* in 1999. The metal nitride cluster fullerenes as a new family of endohedral fullerenes have higher yield than endohedral metallofullerenes, and unusual physical and chemical properties. The high yield of NCFs opens the possibility to investigate these properties and new application of these structures.

Within the NCFs family fullerenes with two or three different metals mixed in the encaged nitride cluster, so called mixed-metal cluster fullerenes, are recognized as the minor members. The stability of the endohedral cluster fullerene is a matter of the size of an endohedral cluster in the  $C_{80}(I_h)$  cage.

Here the non-scandium based mixed metal nitride cluster fullerene (MMNCFs)  $Lu_2CeNC_{80}(I_h)$  has been synthesized and isolated for the first time. The electronic and vibrational properties of  $Lu_2CeNC_{80}(I_h)$  was characterized by UV-VIS, NIR and FTIR spectroscopy. The cage structure of  $Lu_2CeNC_{80}(I_h)$  is determined by  $^{13}C$  NMR spectroscopy with two sharp peaks with the ratio of 1:3 for an icosahedral  $C_{80}(I_h)$  cage. DFT calculations are presented to explain the electronic structure and the spectroscopic properties of this new fullerene structure.

The electrochemical properties of  $Lu_2CeN@C_{80}$  are investigated by cyclic voltammetry and square wave voltammetry. Similar to other trimetallic fullerene clusters, two electrochemically irreversible but chemically reversible reduction steps and one reversible oxidation step was observed.

# Single-Crystalline C<sub>60</sub> Hollow Nanostructures by Sonophysical Preparation: Tuning the Morphology for Catalyst Supports in Fuel Cells

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Fullerene (C<sub>60</sub>) has attracted much attention in materials chemistry owing to its versatile functionalities. The assembly of fullerenes as super-atoms into controlled morphology, size and dimensions allows their physical and chemical properties to be tuned. Low-dimensional C<sub>60</sub> nanostructures, such as nanowires or nanorods, demonstrated fantastic performance in optical devices. However, such complex C<sub>60</sub> nanostructures as hollow bowls/cups have not been realized experimentally up till now. Hollow nanostructure is well-known with widespread applications in, for example, drugs delivery, controlled release of dyes and inks, catalysis or composite materials. As a new form of carbon, C<sub>60</sub> is considered to be an ideal candidate as catalyst supports in fuel cells.

Inspired by the traditional sonochemical preparation of hollow materials in the aqueous solution, we mixed two incompatible organic solvents to produce C<sub>60</sub> hollow nanostructures by a sonophysical method. We demonstrated, for the first time, that single-crystalline C<sub>60</sub> hollow nanostructures, particularly nanobowls, with a large quantity can be prepared in a binary organic solution of m-xylene and acetonitrile simply by ultrasonication. Significantly, by adjusting the concentration of C<sub>60</sub>/m-xylene solution and the volume ratio of m-xylene to acetonitrile, we readily tuned pure and large-scale C<sub>60</sub> nanostructures from one-dimensional (1D) nanorods, nanowires into 2D nanoplates and 3D nanorings and nanobowls. To gain an insight into applications of the C<sub>60</sub> hollow nanostructures, their unique use as a catalyst support for direct methanol fuel cells (DMFC) was further investigated. The C<sub>60</sub> nanobowls, after deposition with Pt nanoparticles, significantly promoted catalytic activity toward methanol oxidation, portending their use in designing fuel cell electrodes. As comparison, the same amount of C<sub>60</sub> and Pt crystallites loading on both electrodes was controlled. The C<sub>60</sub>-hollow-nanobowls/OTE exhibits a much higher methanol oxidation current which is almost 10 times as large as t C<sub>60</sub>-solid-nanoballs/OTE.

In our study we used Field Emission Scanning Electron Microscopy (FESEM), High-resolution Transmission Electron Microscope (HRTEM), Fourier transform infrared (FTIR) spectrum, X-ray Diffraction (XRD) to characterize the C<sub>60</sub> nanostructures, and Cyclic Voltammetry (CV) measurements were applied to evaluate the performance in methanol oxidation.

# Nanofibrous TiO<sub>2</sub>: A New Material with Extraordinary Properties

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Nanofibrous TiO<sub>2</sub> prepared by means of electrospinning represents a novel material with specific properties resulting from its unique morphology. Anatase or rutile nanofibres exhibit “shape memory”. Their shape withstands both high temperature annealing (800°C) and even chemical transformation. Hence, the product of the reaction of nanofibrous anatase with ammonia in gas phase is nanofibrous cubic titanium oxynitride, c-TiO<sub>x</sub>N<sub>y</sub>. In contrary to the preparation of cubic titanium oxynitride from microcrystalline TiO<sub>2</sub>, requiring temperatures above 800°C, the conversion of nanofibrous TiO<sub>2</sub> to TiO<sub>x</sub>N<sub>y</sub> is completed at about 500°C due to its enhanced chemical reactivity. This conversion is fully reversible; the product of the back reaction is again nanofibrous TiO<sub>2</sub>. Fibrous anatase has been recently used as a component improving the performance of dye sensitized solar cells; fibrous TiO<sub>x</sub>N<sub>y</sub> is a material of huge application potential due to its high electric conductivity and hardness.

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