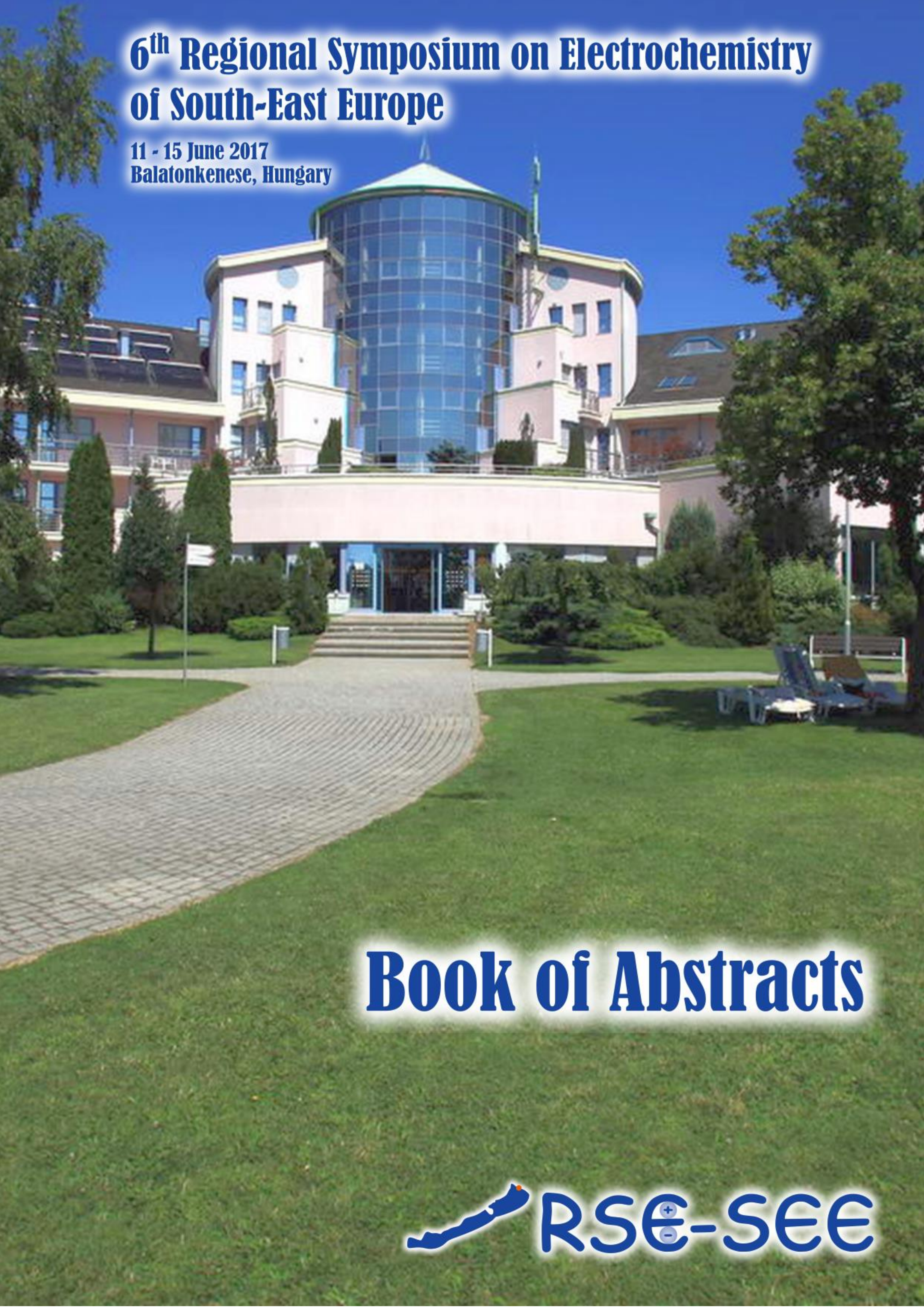

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ABSTRACTS OF THE TALKS

/ordered by the appearance in the scientific program/

PL 216

High-throughput methods with online analytics – from fundamental electrocatalysis to real applications

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Electrochemical energy conversion in continuous reactors like fuel cells and electrolyzers is thought to play an essential role in the future energy landscape, particularly considering the ambitious goals set out by the German "Energiewende". Despite more than a century of intensive research and enormous developments, however, the understanding of the reactions, devices and their long-term behavior is still lacking in several aspects. In this presentation I will try to demonstrate the novel insights that we have obtained over the last years on particular issues related to fundamental electrocatalysis. The focus will be clearly set on high-throughput screening via the scanning flow cell (SFC), which is a big asset in disentangling the enormous parameter space spanned by the different potential materials, electrolytes and operating conditions of electrochemical reactions. Moreover, the benefit of coupling various analytical tools online to the SFC for the determination of interface stability and of reaction selectivity will be shown by some examples. Based on this I will also provide a short personal perspective on future directions in electrochemical energy conversion research, which will be closely linked to the strategy that we follow in the newly founded Helmholtz-Institute Erlangen-Nürnberg for renewable energy.

References:

[1] *Katsounaros, I.; Cherevko, S.; Zeradjanin, A.R.; Mayrhofer, K.J.J.; Oxygen Electrochemistry as a Cornerstone for Sustainable Energy Conversion; Angewandte Chemie – International Edition 2014, 53, 102 – 121.*

[2] *Cherevko, S.; Keeley, G.P.; Geiger, S.; Zeradjanin, A.R.; Hodnik, N.; Kulyk, N.; Mayrhofer, K.J.J.; Dissolution of Platinum in the Operational Range of Fuel Cells; ChemElectroChem, 2015, 2, 10, 1471–1478.*

[3] *Polymeros, G.; Baldizzone, C.; Geiger, S.; Grote, J.P.; Knossalla, J.; Mezzavilla, S.; Keeley, G.P.; Cherevko, S.; Zeradjanin, A.R.; Schüth, F.; Mayrhofer, K.J.J.; Electrochimica Acta, 2016, 211, 744-753.*

KN 177

Advanced testing analysis for SOFC degradation studies

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Some of the most severe hurdles towards deployment of solid oxide fuel cells (SOFC) are lifetime and durability, which still determine large part of the total costs. Since the required life of SOFC stacks for stationary applications is considerably high (with a target to reach 80000 hours in 2020), new and improved tools for quick evaluation of the state of health and lifetime prediction are needed. The current requirements for operational stability of fuel cells define the parameter "degradation rate" (DR). It should be less than 0.1% / 1000h. Long term durability tests are performed usually at constant load and the degradation rate is determined by the voltage decrease as a function of the operation time. Periodically volt/ampere characteristics are taken and impedance measurements at the operation working point are performed. However, their information capability and potential are not exploited enough in respect to quantitative evaluation of some degradation phenomena.

This talk aims at introducing a new testing analysis approach with increased information capability in respect to presentation and evaluation of degradation which applies differential analysis of the volt-ampere (I/V) characteristics, determining the differential resistance (DR). Thus the change in the I/V curves during operation becomes comparable in respect to the extracted Differential Resistance. Since the derivatives are more sensitive to small deviations, the method has very high sensitivity. Its noise immunity is additionally increased by the applied spectral transform. The testing analysis is successfully approbated on SOFC cells (Fig. 1). It can be applied for every system that gives volt-ampere characteristics.

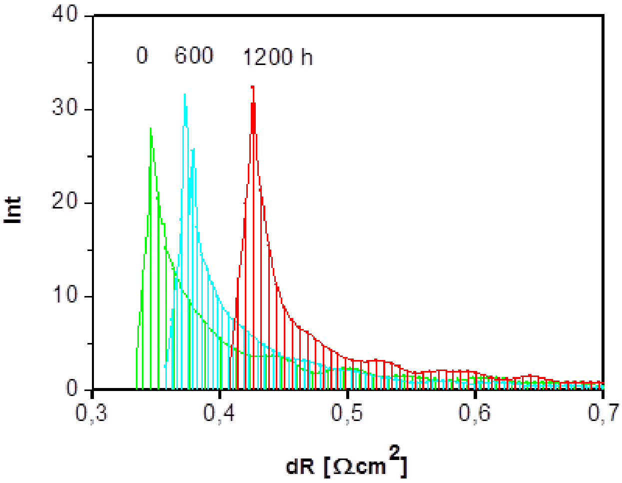

Figure 1: Differential Resistance spectra of SOFC cell during long term operation

Acknowledgments
The research has received funding from FP7/2007-2013 Fuel Cells and Hydrogen Joint Undertaking (FCU-JU-2013-1) under grant agreement No 621207 and the Bulgarian National Science Fund under grant agreement E02/3/12.12.2014.

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In situ characterization of gassing processes in lithium-ion batteries by DEMS-DEIRS

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Gas evolution has a profound effect on the functioning of state of the art lithium-ion batteries. On the one hand, it is the natural concomitant of SEI formation; on the other hand, because of the demand for high terminal voltages, it is the consequence of electrolyte or electrode material oxidation. This happens at the expense of the efficiency. Furthermore, the presence of gases in the cell raises safety concerns.

In general, it is important to understand gas formation processes. First, to be able to develop novel electrolyte mixtures or tailor electrolyte additives that form a stable SEI. Second, to optimize the surface and/or structure of cathode materials to affect both their bulk oxidative properties upon delithiation and electrocatalytic activities. Differential electrochemical mass spectrometry (DEMS) is one of the most appropriate tools to qualitatively elucidate gas evolution reactions in electrochemical systems [1].

Herein, we report on the *in situ* gas analysis by means of differential electrochemical mass spectrometry and infrared spectroscopy (DEMS-DEIRS) [2] of various battery systems. We analyze the SEI formation on graphite, which is the most common anode material and the influence of electrolyte additives on the SEI stability. The impact of temperature and constant voltage/OCV periods on the first charge cycle (so-called formation process) is investigated, too [3]. Their effect on both the gassing and electrolyte salt decomposition is described.

The stability problem of the most common electrolytes at high voltages is discussed through the example of either NMC ($LiNi_xMn_yCo_zO_2$) type materials or with high voltage spinels ($LiNi_{0.5}Mn_{1.5}O_4$) [4]. The electrocatalytic activity of the individual active material particles seems to play a decisive role in the oxidative decomposition processes. Through the application of modified cathode surfaces a relation between surface activity and the amount of produced gases is revealed. Beyond the decomposition of the electrolyte, oxygen evolution is the crucial factor at high cathode potentials. This effect is particularly apparent for overlithiated and high Ni content materials. Monitoring gassing over 20 cycles uncovers interesting changes being only recognizable in "long term" tests. We demonstrate the importance of potentiodynamic cycling in addition to the traditional galvanostatic test with DEMS-DEIRS in the exploration of reaction mechanisms. Pressure measurements complete the analysis in terms of validation of gas amounts.

References:

[1] Berkes, B. B.; Jozwiuk, A.; Vracar, M.; Sommer, H.; Brezesinski, T. & Janek, J. (2015) Anal. Chem. ***87****, 5878*

[2] Berkes, B. B.; Jozwiuk, A.; Sommer, H.; Brezesinski, T. & Janek, J. (2015) Electrochem. Commun. ***60****, 64*

[3] Berkes, B. B.; Schiele, A.; Sommer, H.; Brezesinski, T. & Janek, J. (2016) J. Solid State Electrochem. ***20****, 2961*

[4] Michalak, B.; Berkes, B. B.; Sommer, H.; Bergfeldt, T.; Brezesinski, T. & Janek, J. (2016), Anal. Chem. ***88****, 2877*

OEN 147

Characterisation of thermally induced battery failure on cylindrical 18650 lithium ion cells

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Cylindrical lithium ion cells of the 18650 format (18 mm diameter, 65 mm length) are subjected to an external heat influx. Elevated temperature leads to degradation of the electrolyte, the separator and the electrode material [1]. Exothermic reactions initiate a self-propagating decay of the cell components. During the first venting and the exothermic phase mainly CO_2 is released from the cell. This is related to the degradation of the SEI layer and electrolyte deterioration [2,3]. The exothermic phase culminates in the thermal runaway indicated by a venting incident upon reaching the maximum temperature of more than 700 °C. At this event, large quantities of flammable and toxic gas are released from the cell. Characterisation is performed by monitoring the cell temperature, measuring the amount of gaseous emission and quantifying the components in the off-gas stream.

The cells under test are conditioned according to a CC/CV charging routine to a state of charge of 100% using a BaSyTec battery test system. The cell under test is fastened within a sample holder and three type-K thermocouples are affixed onto the can. The thermal ramp test is conducted within an electrically heated tubular reactor flushed with N_2. Heat is applied as a continuous ramp of 0.5 °C min^{-1} by an electric resistance furnace. The cell temperature is logged continuously over the whole experiment. Gaseous emissions take place once the cell's integrity is compromised by internal pressure build-up from degradation reactions and evaporation. These emissions displace liquid water from a system of communicating vessels, allowing the precise calculation of the gas volume released from the cell. Evaluation of the Joule-Thomson cooling during first venting, the exothermic onset, the self-heating rate and the maximum temperature is performed. Assessment of these characteristics and the behaviour of gas release specifies the points of automated gas sampling for the ex-situ analysis by micro-GC (Figure 1). By determination of the gas composition at characteristic events valuable information on the degradation of Li-ion cells is gained.

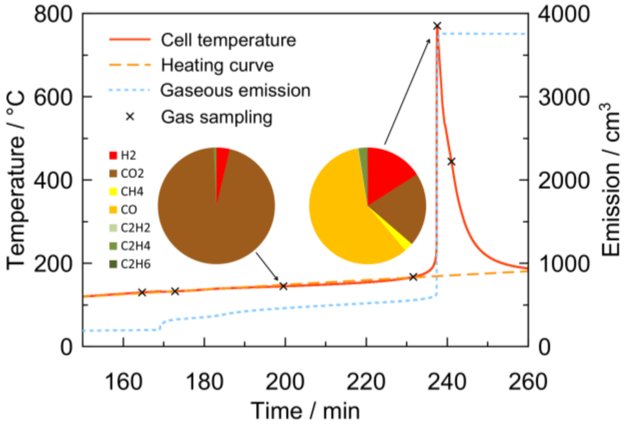

Figure 1: Overview of a thermal ramp test containing the thermal response of the cell and points of gas sampling for GC analysis. The gaseous emissions (blue dotted line) are plotted cumulatively over the total experiment. Gas compositions are given for the exothermic phase and the final venting [4]

References:

[1] *Q. Wang, P. Ping, X. Zhao, G. Chu, J. Sun, C. Chen, J. Power Sources. 208 (2012) 210–224. doi:10.1016/j.jpowsour.2012.02.038.*

[2] *A.W. Golubkov, S. Scheikl, R. Planteu, G. Voitic, H. Wiltsche, C. Stangl, G. Fauler, A. Thaler, V. Hacker, RSC Adv. 5 (2015) 57171–57186. doi:10.1039/C5RA05897J.*

[3] *J.L. Tebbe, T.F. Fuerst, C.B. Musgrave, ACS Appl. Mater. Interfaces. (2016) acsami.6b06157. doi:10.1021/acsami.6b06157.*

[4] *M. Lammer, A. Königseder and V. Hacker*, RSC Adv., *(to be published).*

OEN 132

Electrochemical study of fast Li-ion transport in $Li_3V_2(PO_4)_3$-electrode

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Lithium-vanadium phosphate ($Li_3V_2(PO_4)_3$) based composite electrodes, having NASICON-type structure, have been found as capable to provide extremely fast lithium transport properties. Their structural, morphology and surface characteristics as well as electrochemical properties have been studied by a combination of methods: X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET), laser diffraction particle size distribution (PSD), as well as electrochemical methods: potentiostatic (PITT) and galvanostatic (GITT) intermittent titration techniques, electrochemical impedance spectroscopy (EIS), and constant current chronopotentiometry. There were found significant differences in the rate of lithium diffusion depending on the lithiation stage. According to the PITT, GITT and EIS data, lithium diffusion coefficients drop abruptly by 2–3 orders of magnitude (from 10^{-9} to 10^{-12} $cm^2 \cdot s^{-1}$) in the 4.3–4.4 V potential range vs Li/Li^+. Observed phenomenon was attributed to the $LiV_2(PO_4)_3 \leftrightarrow V_2(PO_4)_3$ phase transition. The electrochemical extraction/insertion of two lithium equivalents can occur at ultra-high rates (up to 320 C) from/into structurally more accessible Li2 and Li3 sites, while the de/intercalation of the third lithium equivalent from/into the Li1 position is supposedly hindered kinetically. For the electrochemical data analysis special theoretical models were developed and applied. These models take into account geometry and phase structure of the diffusion space, as well as the properties of the phase boundary interfaces. Morphology parameters of the material were obtained by SEM, PSD and BET methods, and introduced into the mathematical data processing procedures.

Authors wish to thank Russian Science Foundation (project #15-13-10006) for financial support of the work.

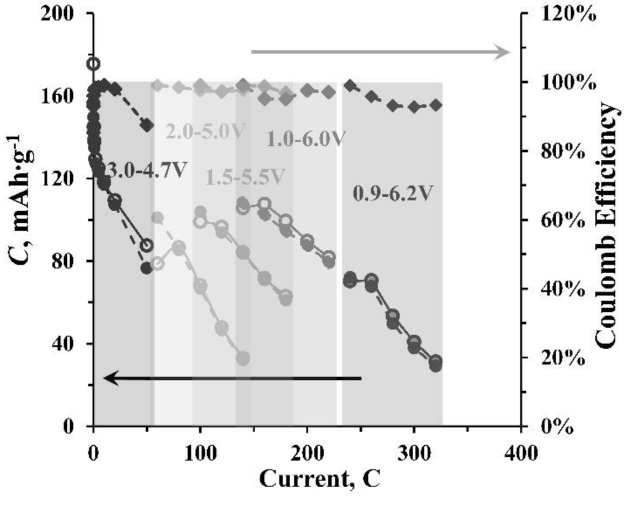

Figure 1: Dependencies of the specific capacity (charge – empty markers, discharge – filled markers) and coulomb efficiency on the C-rate of the $Li_3V_2(PO_4)_3$ based composite electrode (the arrows indicate the graphs belonging to the vertical axis: the points on nearly horizontal curves relate to the right axis (Coulomb efficiency), points on the sloped curves relate to the left axis (specific capacity, C))

OEN 141

The electrochemical behavior of magnesium alloys for secondary magnesium ion batteries

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Magnesium has been suggested to replace lithium in secondary batteries, because of its high energy density (3833 mAh cm^{-3}), natural abundance (5th most in earth crust), and negative standard reduction potential (-2.362 V *vs.* SHE). In addition it can be handled more safely, because metallic magnesium reacts very slowly with water and air at room temperature. A huge advantage in contrast to lithium ion batteries is, that magnesium does not form dendrites during electrodeposition and therefore the volumetric and gravimetric capacity of the anode can be increased by a factor of about 5 compared to graphite Li intercalation materials [1].

Due to its negative electrochemical reduction potential, magnesium reacts readily with oxygen and water. Unlike other passivating metals, the oxide layer does not prevent the bulk material from further corrosion. Therefore, it is essential to alloy magnesium to improve the corrosion stability and the workability for the production of thin foils. Although this could be achieved with zinc or gadolinium [2-4], it is important to ensure that alloying has no effects detrimental to the intended use of the magnesium.

We report on the electrochemical behavior of the alloys Mg-1.5 wt. % Zn, Mg-1.5 wt. % Gd, and Mg-1 wt. % Gd-1 wt. % Zn in the 0.25 M $(PhMgCl)_2$-$AlCl_3$/THF electrolyte. in. The concentration of the alloying elements and the oxygen content were determined by X-ray diffraction and glow-discharge optical emission spectroscopy. Cyclic voltammetry (Figure 1) and galvanostatic cycling was conducted in a three-electrode arrangement with the magnesium alloys as working and auxiliary electrodes and pure magnesium (99.9 %, Goodfellow) as reference electrode.

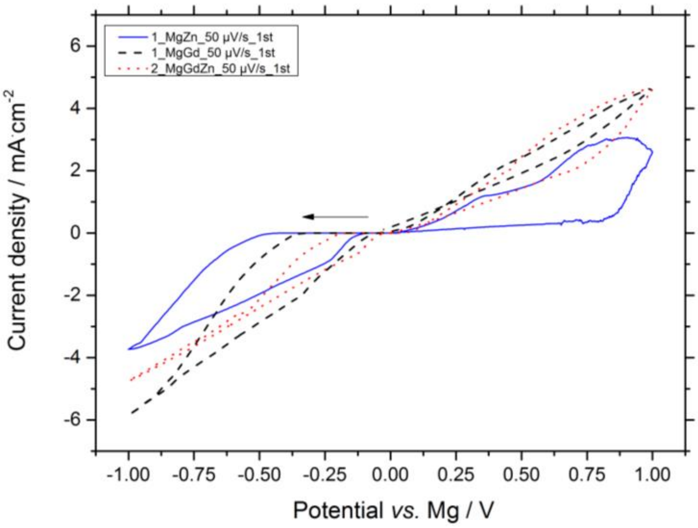

Figure 1: Cyclic voltammograms of three Mg alloys in 0.25 M APC electrolyte, v = 50 µV/s starting from the open circuit potential (~ 0.0 V) in cathodic direction.

References:

[1] H. D. Yoo, I. Shterenberg, Y. Gofer, G. Gershinsky, N. Pour, D. Aurbach, Energy Environ. Sci., **2013,** 6, 2265-2279.

[2] T. Prosek, A. Nazarov, U. Bexell, D. Thierry, J. Serak, Corros. Sci., **2008,** 50, 2216-2231.

[3] H. Yan, R. Chen, E. Han, Mater. Charact., **2011,** 62, 321-326.

[4] N. Stanford, D. Atwell, M. R. Barnett, Acta Mater., **2010,** 58, 6773-6783.

OEN 151

Electrochemistry under off-normal conditions: Assessed from an EU policy-making perspective

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The growing market uptake of electric vehicles around the world has triggered the need for global harmonization of testing of electric vehicles and of their rechargeable electrical energy storage systems. Multiple testing methods to assess battery safety are described in scientific literature and in standards, but these methods cannot always immediately be used for regulatory purposes. The most relevant factors considered for policy making will be discussed using the external short circuit test as an example to facilitate improved understanding of specific policy-making related requirements for battery testing methods.

The External short circuit test simulates a situation when the battery terminals are inadvertently electrically connected. As a result, the stored electric energy rapidly converts to mainly heat, which may trigger safety related events such as gas venting, thermal runaway, fire and even explosion. During external short circuit tests performed the initial short circuit current was found to be 200-300 times higher (Figure 1) than the normal operating current and the outcome (e.g. rupture, venting, melting of the terminals) of the test was very sensitive to the initial and boundary conditions (e.g. manufacturing differences). In this presentation the phenomena occurring at extremely high currents will be identified and different models will be proposed from simple equivalent circuit model to detailed description of the electrochemical double layer. Finally the findings will be analyzed from a policy-making perspective.

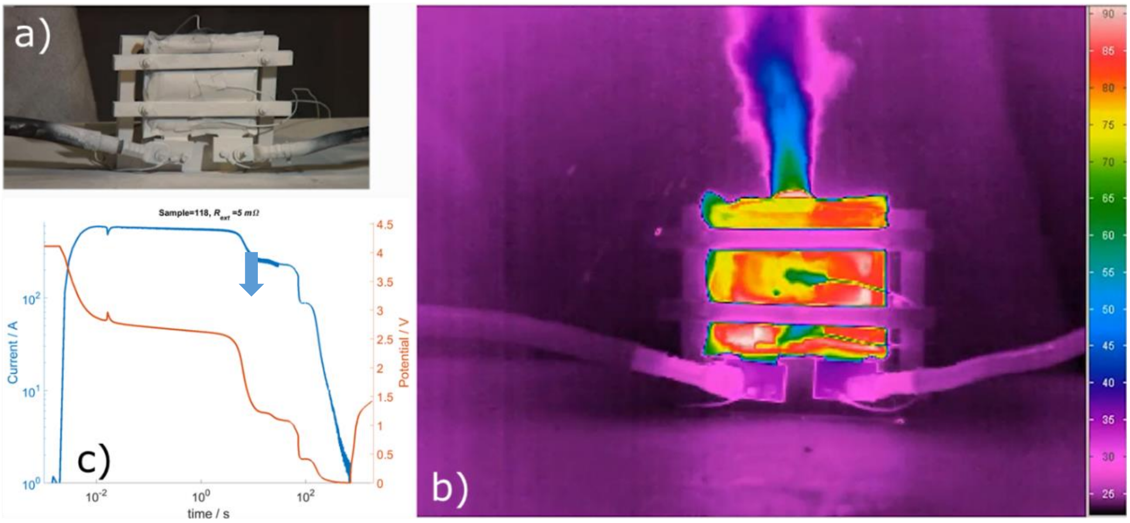

Figure 1: Video image (a) and IR image (b) at the moment of cell rupture (marked by the blue arrow in c) during short circuit test of a 10 Ah NMC(1:1:1)-Graphite cell at 5mΩ. The development of current and potential with time is shown in (c). Max. current 595 A, max. temperature 87 ℃ measured by the thermocouple

OGN 125

Oxidation of bioflavonoids in respect to their chemical structure

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Bioflavonoids are widely distributed in nature, mainly in vegetables and fruits, and in beverages such as wine and tea [1]. They have important antioxidative, antihepatotoxic, anti-carcinogenic, antiviral and anti-inflammatory properties [2].

The significant differences in the oxidation behaviour of flavanols and flavanones will be discussed. Only a small difference in the presence of a double bond causes different oxidation behaviour of these pharmacologically active compounds. The research is based on electrochemical, UV-Vis and IR spectroelectrochemical, molecular orbital calculation and chromatographic studies [3-6].

The oxidation pathways of flavonoids were studied in non-aqueous and aqueous solutions. Oxidation is given by the distribution of various dissociation forms in the solution [3,6]. Their oxidation mechanisms resemble the ‘schema carre’ reported by Jacq [7], which assumes that protonation reactions are much faster than electron transfer processes.

These flavonoids were used as natural colorants in historical tapestries since 15 century. The determination of oxidation pathways and identification of degradation products has importance for the restoration works and saving of the Cultural Heritage.

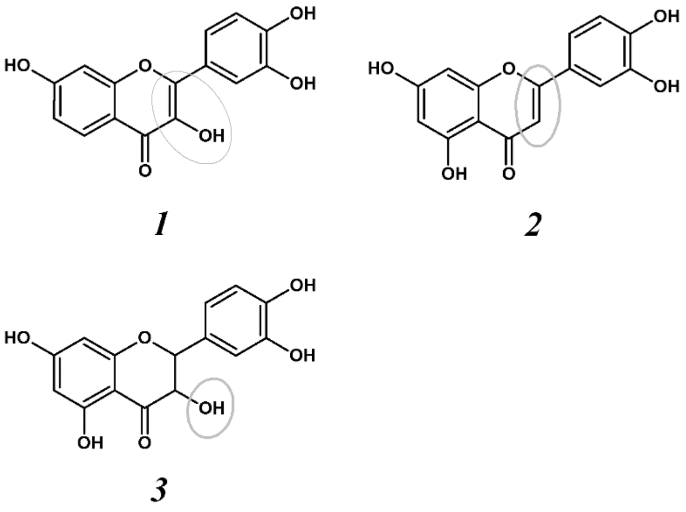

Figure 1: (1) Flavonol, (2) Flavone, (3) Flavanone

Acknowledgement

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References:

[1] *Di Carlo, G., Mascolo, N., Izzo, A. A., Capasso, F.: Life Sci.,* ***65****, 337-353 (1999).*

[2] *Matsuda, H., Morikawa, T., Ando, S., Togucida, I., Yoshikawa, M.: Bioorg. Med. Chem.,* ***11*** *1995–2000 (2003).*

[3] *Ramešová, Š., Sokolová, R., Degano, I.: The study of the oxidation of the natural flavonol fisetin confirmed quercetin oxidation mechanism. Electrochim. Acta* ***182****, 544-549 (2015).*

[4] *Kocábová, J., Fiedler, J., Degano, I., Sokolová, R.: Oxidation mechanism of flavanone taxifolin. Electrochemical and spectroelectrochemical investigation. Electrochim. Acta* ***187****, 358-363 (2016).*

[5] *Sokolová, R., Ramešová, Š., Kocábová, J., Kolivoška, V., Degano, I., Pitzalis, E.: On the difference in decomposition of taxifolin and luteolin vs. fisetin and quercetin in aqueous media. Monatsh. Chem.* ***147****, 1375-1383 (2016).*

[6] *Ramešová, Š., Degano, I., Sokolová, R.: J. Electroanal. Chem.,* ***788****, 125-130 (2017).*

[7] *Jacq, J.: J. Electroanal. Chem. Interfacial Electrochem.,* ***29****, 149 (1971).*

OGN 111

Cathodic breakdown of deep eutectic solvents based on choline chloride and urea

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Ionic liquids analogous, known as deep eutectic solvents (DESs), are considered as an alternative to traditional solvents and ionic liquids. They exhibit some properties similar to ionic liquids, such as a wide electrochemical window, a low vapor pressure, and good solvent properties, which make them good electrolytes in some electrochemical applications, like metal electropolishing or electrodeposition [1].

In order to be successfully applied as a basic electrolyte in metal electrodeposition, one of the features that the solvent should provide, is a wide electrochemical window. If this is not the case, i.e. when cathodic or anodic breakdown of a basic electrolyte occurs in parallel to metal deposition, the current efficiency will be low, and electrolyte and/or metal deposit may be polluted with the breakage products.

This work aims to investigate processes that occur on a working electrode, when a mixture of choline chloride and urea is used as a basic electrolyte in metal electrodeposition. A literature survey evidences that the metal (Zn, Mn, Co, Cu, Cr) electroreduction from this kind of DES, usually proceeds with current efficiency lower than 100%, denoting that some electrolyte breakage occurs. Yet, it seems that there are not many data related to the cathodic breakage of this DES. Some papers conclude that the first cathodic reaction that occurs is decomposition of choline cation [2], while the other sources assume that the hydrogen bond donor, i.e. urea, is reduced firstly [3].

In order to get insight into the cathodic processes in basic choline chloride-urea DES, we used cyclic voltammetry and electrochemical impedance spectroscopy. In the electrochemical setup, working electrodes were Pt rotating disc, and Pt or steel plates. Reference electrode was saturated calomel electrode or Ag wire (at temperatures higher than 100 °C), while Pt wire was used as a counter electrode. The cathodic decomposition products were analyzed by infrared spectroscopy. A particular attention was given to the influence of water addition on the cathodic electrochemical behavior of DES.

On the basis of the results collected until now, we may assume that in basic choline chloride-urea DES, the cathodic reaction which starts at the most positive potential, is the reduction of the urea decomposition products, such as ammonium ion. Water influences the electrochemical behavior of this DES significantly, because it changes the equilibrium in urea spontaneous decomposition process.

Acknowledgement:

The authors would like to acknowledge networking support by the COST Action MP1407

References:

[1] *A. Abbott, K. Ttaib, G. Frisch, K. McKenzie, K. Ryder, Phys. Chem. Phys. 11 (2009) 4269.*

[2] *D. Yue, Y. Jia, Y. Yao, J. Sun, Y. Jing, Electrochim. Acta 65 (2012) 30.*

[3] *E. Gomez, E. Valles, Int. J. Electrochem. Sci. 8 (2013) 1443.*

OGN 166

Electrochemical and morphological investigations of poly(3,4-ethylenedioxythiophene) films in different electrolyte solutions

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PEDOT films of different "nominal" thicknesses (about 0.2 – 3.4 µm) were deposited on gold and glassy carbon substrates and their electrochemical properties were studied in aqueous sulfuric acid, sodium sulphate, perchloric acid and sodium perchlorate solutions. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) were used for the electrochemical and morphological investigations. According to cyclic voltammetric results the redox capacity of the films increased monotonically with the film thickness. In the high frequency regions of the impedance spectra, a small diameter capacitive arc could be observed. Its diameter grew with the thickness of the film. If the films are thick enough the medium frequency range is dominated by a so-called "Warburg-section". The low frequency part indicated capacitive behavior. By comparing the spectra recorded in different electrolytes, the different conductivity of the solutions and the effect of the different counter-ions were clearly observable. According to SEM images, thicker films on gold show random-like, but quite well-ordered arrays of islands and trench-like structures. "Cauliflower" like structures typical for PEDOT films electrodeposited from aqueous solutions [1] could be observed both on gold and glassy carbon.

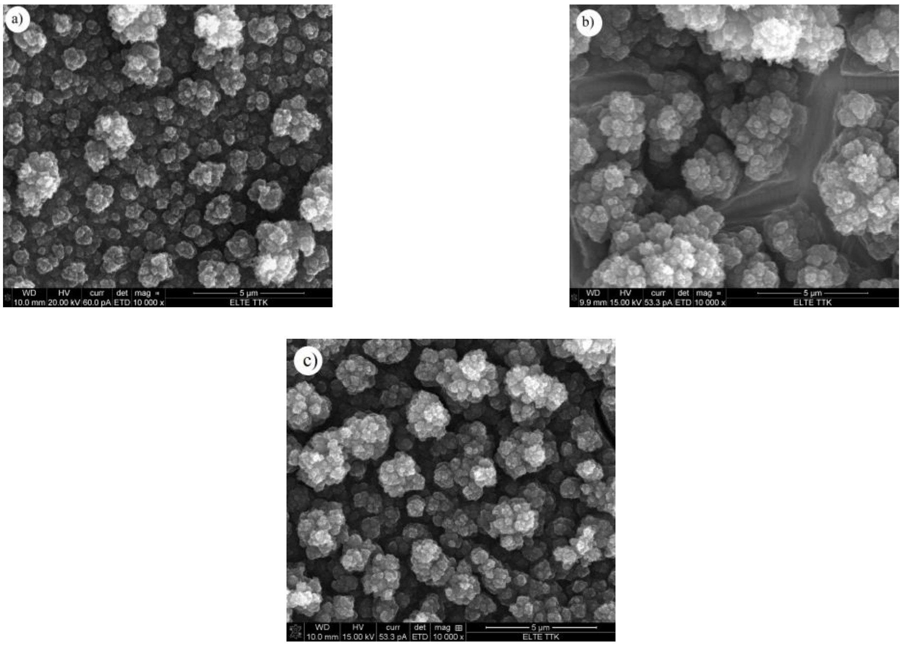

Figure 1: Secondary electron SEM images of freshly prepared PEDOT films. (a) About 0.4 µm PEDOT film on gold. (b) About 3.4 µm PEDOT film on gold. (c) About 2.0 µm PEDOT film on glassy carbon. The length of the vertical bar left to the images corresponds to 5 µm

Acknowledgement

Support from the National Research Development and Innovation Office – NKFI (OTKA K109036) is gratefully acknowledged.

References:

[1] *G.G. Láng, M. Ujvári, S. Vesztergom, V. Kondratiev, J. Gubicza, K. J. Szekeres: The Electrochemical Degradation of Poly(3,4-ethylenedioxythiophene) Films Electrodeposited from Aqueous Solutions, Zeitschrift für Physikalische Chemie 230 (2016) 1281-1302.*

OGN 203

Electrochemical insights on a key protein from *Geobacter sulfurreducens* crucial to bacterial electricity production

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Geobacter sulfurreducens, a Gram-negative bacterium, is the best studied *Geobacteraceae* organism and belongs to the δ–*Proteobacteria* family. This is a well-known microorganism for producing energy, interacting with inorganic electrodes and by using extracellular electron acceptors, besides being important agents in natural biogeochemical cycles where Fe(III) and Mn(IV) reductions are essential [1]. Analysis of the *G. sulfurreducens* genome revealed that more than one hundred genes encode for cytochrome *c* proteins [2], which act as terminal electron connections with Fe(III) and Mn(IV) oxides [1]. Some of these proteins are involved in the extracellular electron transfer processes, driving electrons from the inner membrane to the cell exterior [3]. OmcF is an outer-membrane associated protein required for the transcription of genes that are involved in the electricity production. [4]. OmcF has one heme group, 109 amino acids and a molecular mass of 9.4 kDa [5].

In this work, the electrochemical characterization of OmcF was attained by cyclic voltammetry experiments. The formal redox potentials were determined in the pH range of 3 to 9. The results obtained showed that the formal redox potentials are highly pH dependent between the pH values of 6 and 8 (Figure 1). Such dependence, designated redox-Bohr effect, might be physiological relevant as it is observed in the physiological pH range for *G. sulfurreducens* growth. The obtained pH dependence was fitted considering only one acid/base group model, yielding distinct pK_a values for the redox-Bohr centre in the reduced and oxidised forms of OmcF. The redox potential values at pH 6 and 8 obtained are, respectively +227 ± 6mV and +140 ± 18mV. Kinetic and thermodynamic data was also retrieved from the cyclic voltammetry results and will be discussed in terms of their relevance for extracellular electron transfer processes in *G. sulfurreducens*.

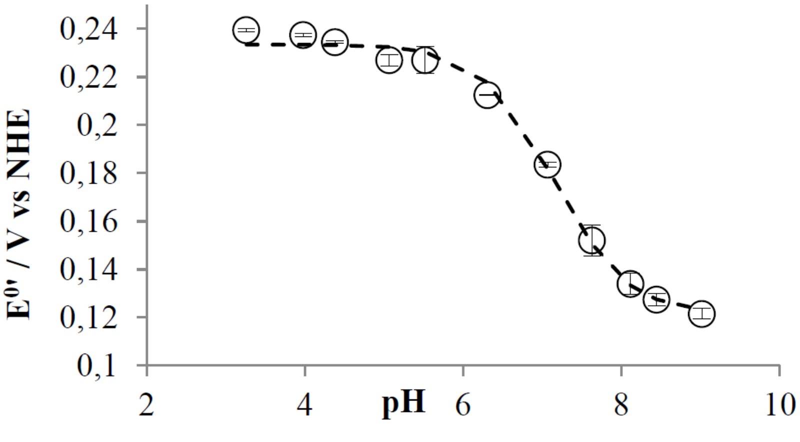

Figure 1: Plot of the OmcF redox center's pH dependence observed by cyclic voltammetry

Acknowledgements

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References:

[1] *Lovley, D. R., et al, (2011). Geobacter: the microbe electric's physiology, ecology, and practical applications. Advances in Microbial Physiology, 59, 1–100.*

[2] *Methé, B. A., et al, (2003). Genome of Geobacter sulfurreducens: metal reduction in subsurface environments. Science (New York, N.Y.), 302(5652), 1967–9.*

[3] *Reguera, G., et al, (2005). Extracellular electron transfer via microbial nanowires. Nature, 435(7045), 1098–101.*

[4] *Kim, B.-C., et al, (2008). Insights into genes involved in electricity generation in Geobacter sulfurreducens via whole genome microarray analysis of the OmcF-deficient mutant. Bioelectrochemistry, 73(1), 70–75.*

[5] *Pokkuluri, P. R., et al, (2009). Outer membrane cytochrome c, OmcF, from Geobacter sulfurreducens. Proteins: Structure, Function, and Bioinformatics, 74(1), 266–270.*

OGN 140

What happens to gold during the electrochemical reduction of the surface oxide layer?

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Rotating ring-disk electrode (RRDE) is an effective technique to detect and/or explore the behavior of intermediates and electroactive products of electrode reactions, since the potentials of the disk and the ring electrodes can be controlled independently. Any such electroactive species generated at the disk electrode is swept away to the ring where it can be detected by maintaining the ring electrode potential at a desired value. The method of dual dynamic voltammetry, i.e. applying dynamic potential programs to the generator and the collector electrodes of a generator-collector system simultaneously, is a promising new method for studying the mechanisms of complex electrochemical processes [1-3].

It is a widespread opinion that the electrochemical behavior of gold in aqueous media has been thoroughly studied, and the interface stress changes of gold can be explained by monolayer oxide formation/removal and adsorption phenomena. However, there are some peculiarities to consider. E.g. by applying the dual dynamic voltammetric method to an Au/Au rotating ring-disk electrode (RRDE) it could be shown that the sharp change in the slope of the interface stress vs. potential curve recorded in the oxide reduction region of gold in sulfuric acid solutions is accompanied by the formation of soluble, electrochemically reducible gold species which can be detected at the ring electrode.

It was found that the dissolution process is more pronounced in sulfuric acid than in perchloric acid. This is in agreement with the results obtained by the bending beam method.

Acknowledgement

Support from the National Research Development and Innovation Office – NKFI (OTKA K109036) is gratefully acknowledged.

References:

[1] *S. Vesztergom, M. Ujvári, G.G. Láng: Electrochemistry Communications 19 (2012) 1–4.*

[2] *N. Kovács, M. Ujvári, G.G. Láng, P. Broekmann, S. Vesztergom: Instrumentation Science and Technology 43 (2015) 633–648.*

[3] *S. Vesztergom, N. Barankai, N. Kovács, M. Ujvári, P. Broekmann, H. Siegenthaler, G.G. Láng: Electrochemistry Communications, 68 (2016) 54–58.*

[4] *G.G. Láng, C.A. Barbero: Laser Techniques for the Study of Electrode Processes, Springer-Verlag, Berlin, Heidelberg, 2012.*

KN 229

Electroanalytical methods in characterization of sulfur species in water environment

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Electrocanalytical methods provide simple measurements procedure and prompt response for relatively low cost. Combined with the high sensitivity and selectivity, along with possibility to conduct in-situ measurements, electroanalytical methods are strong analytical tool for characterization and quantification of different sulphur species [1-7]. Recently it was shown that electroanalytical methods can differentiate between truly dissolved, and particulate sulphur fractions including sulphur based nanoparticles (NPs) in water environment [4,5]. Features of electroanalytical methods, especially voltammetry, makes them appropriate for use as monitoring tools in assessment of water quality in natural environment with special emphasis for trace pollutant analyses (sulphur species [1-7], organic compounds [6-10], trace metals [1,7, 11,13], engineered and natural nanoparticles [4,5, 14-16].

Voltammetry is the only technique that allows speciation and determination of the dissolved sulphur and trace metal species without many sample handling. Speciation of these compounds affects their biogeochemical cycling processes as well as biological impacts. Thus, electroanalytical measurements in natural waters are essential in order to obtain complete information on the speciation and to fully understand the geochemical cycling and bioavailability (toxicity) of the studied species.

Strong interaction between mercury (Hg) electrode and sulphur species is a background for their electroanalytical characterization and determination at the Hg electrode (Figure 1). The methodology is based on the tendency of inorganic and organic reduced sulphur species (RSS) to deposit HgS layer during an accumulation step at the deposition potential, which is further reduced during the scanning potentials to more negative values at the hanging mercury drop electrode (HMDE). In solutions containing sulphide anions, insoluble HgS layer at the Hg electrode surface can be formed by the reversible process of two-electron-transfer oxidation of Hg at potentials more positive than -0.5 V vs. Ag/AgCl. RSS comprise a group of compounds that contain sulphur in nominally -2 and 0 oxidation states. Some of the most important members of this group in natural waters include sulphide, thiols, thiosulphate, sulphite, zero-valent sulphur present as dissolved S8 or incomporated in polythionates, inorganic and organic polysulphides and polysulphones, colloidal sulphur, as well as metal sulphide NPs. It was shown that along with sulphide this methodology can be used for organic sulphur compounds (thiourea, thiols, oxines), thioanions, labile chalcogenide NPs (CuS, PbS, HgS, FeS, Ag_2S), polysulphides and dissolved and colloidal suphur which deposit HgS layer at sufficiently positive potentials [2,4-7].

Voltammetric measurements in combination with electrochemical nanogravimetric measurements (EQCM), atomic force microscopy (AFM) and electrochemical scanning tunneling microscopy (EC-STM) on different electrode surfaces (Hg, Au) are shown to be beneficial in giving more details and information related to attachment, adsorption, deposition and interaction between selected sulfur species, including NPs and functionalized electrode surfaces [17]. Experiments designed to monitor in parallel with electrochemical measurements (voltammetric and amperometric) physico-chemical and surface characteristics (ζ – potential and size) of the studied metal sulphide NPs (FeS, PbS, Ag_2S, CdS) under same experimental conditions, showed that electrochemical signals of NPs depend on electrolyte concentration and composition as well as measured ζ - potential and size of the same NPs in dispersions, determined by DLS [16]. The measurements indicate significant relationship between ζ – potential and size of the studied metal sulphide NPs dispersions and recorded voltametric and amperometric response, indicating great potential of electroanalytical chemistry in characterization of physico-chemical and surface chemistry features of the sulphur based NPs in the water environment. The best electrochemical response is obtained in presence of the smaller NPs, < 100 nm.

In the frame of the project „The Sulphur and Carbon Dynamics in the Sea- and Fresh-water Environment“ (SPHERE), funded by Croatian science foundation, the sulphur (S) and carbon (C) dynamics between different environmental compartments (atmosphere, water, sediment, biota) of the sea- and fresh-water environment are studied. A main focus is given on distribution of S and C compounds between organic, inorganic, dissolved, colloidal and nanoparticulate fractions. Methodology that is developed in laboratory, in model water electrolyte conditions, is further tested and applied for the study of natural sea- and fresh-water samples that differ in environmental redox conditions. To gain better insight of interaction and transport at the air-water boundary, aerosols and rain precipitation were studied as well. Some of the obtained results will be presented and discussed.

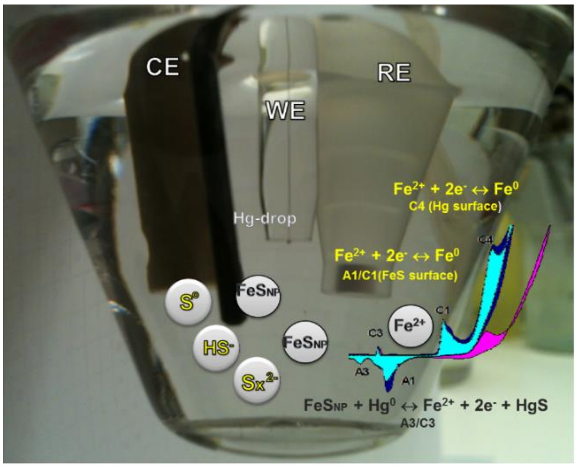

Figure 1: Illustration of electrochemical cell and Hg electrode processes with presence of dissolved and nanoparticulate reduced sulfur species

References:

[1] *G.W. Luther, A.E. Giblin, R. Varsolona, Limnol. Oceanogr.* **30** *(4) (1985) 727-736.*
[2] *N. Batina, I. Ciglenečki, B. Ćosović, Anal. Chim. Acta***267** *(1992) 157-164.*
[3] *E. Bura-Nakić, G.R. Helz, I. Ciglenečki, B. Ćosović,Geochim.Cosmochim.Acta***73** *(2009) 3738-3751.*
[4] *E. Bura-Nakić, E. Viollier, I. Ciglenečki, Environ. Sci. Technol.***43** *(2013) 741-749.*
[5] *I. Milanović, D. Krznarić, E. Bura-Nakić, I. Ciglenečki, Environ. Chem.* **11***(2014) 167-172.*
[6] *P. Orlović-Leko, K. Vidović, M. Plavšić, I. Ciglenečki, I. Šimunić, T. Minkina, J. Solid State Electrochem.,***20***(11) (2016) 3097-.*
[7] *P. Orlović-Leko, D. Omanović, I. Ciglenečki, K.Vidović, T. Brenko, Bulgarian Chem. Comm. 2017, in press.*
[8] *B. Ćosović, V. Vojvodić,Limnol. Oceanogr.***27** *(1982) 361-369*
[9] *B. Ćosović, V. Vojvodić, Electroanalysis***10** *(1998) 429-434.+*
[10] *B.Ćosović, Z.Kozarac, S.Frka, V.Vojvodić, Electroanalysis,* **22** *(17-18) (2010) 1994-2000.*
[11] *I. Pižeta, G. Billon, J-C. Fisher, M. Wartel, Electroanalysis***15** *(17) (2003) 1389-1396.*
[12] *G.W. Luther, B. Glazer, S. Ma, R. Trouwborst, B.R. Shultz, G. Druschel, C. Kraiya, Aquat. Geochem.* **9** *(2003) 87-111.*
[13] *C.B.Braungardt , E. Achterberg, B. Axelsson, J.Buffle, F.Graziottin, K.A. Howell , S. Illuminati, G. Scarponi, A.D.Tappin, M.-L. Tercier-Waeber, D.Turner D. Mar. Chem.***114** *(2009) 47-55*
[14] *Y. Zhou, N.V. Rees, J. Pillay, R. Tshikhudo, S. Vilakazi, R.G. Compton, Chem. Commun.* **48** *(2012) 224-226.*
[15] *E. Bura-Nakić, M. Marguš, I. Milanović, D. Jurašin, I. Ciglenečki, Environ.Chem.* **11** *(2014) 187-196.*
[16] *M. Marguš, I. Milanović, I. Ciglenečki, J. Solid State Electrochem.***20** *(11) (2016)2981–2989.*
[17] *M. Marguš, I. Morales-Reyes, E. Bura-Nakić, N. Batina, I. Ciglenečki, Cont. Shelf. Res.***109** *(2015) 24–34.*

EX 159

Cyclic voltammetry: Staircase CV vs. true analog CV

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Cyclic voltammetry (CV) is one of the most popular techniques used in electrochemical research. During the CV measurement, the voltage applied to the electrochemicall cell is scanned with a constant scan reate and the current response is monitored.

The current response of an electrochemical systems depends on the voltage and on the type of the waveform applied to the cell. Therefore, for getting accurate and reliable results, it is of crucial importance for the users to know and understand how a measurement is implemented in the instrumentation used for the measurement.

In this presentation we will compare 3 different types of cyclic voltammetry, based on the type of the potential scan applied and how the current response is sampled: CV-staircase, CV-analog and CV-current integration.

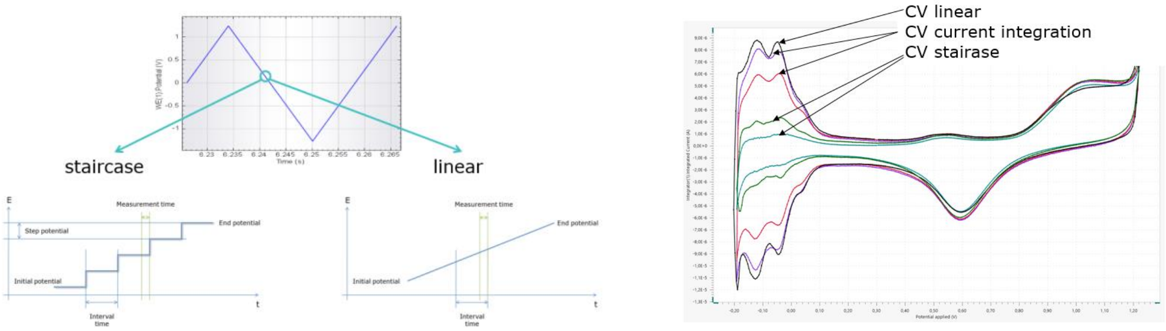

Figure 1: Potential profile of a staircase scan and analog scan (left) and the resulting CVs (right) measured in otherwise same conditions

EX 160

New electrochemical techniques in Nova: electrochemical frequency modulation and fully integrated spectroelectrochemistry

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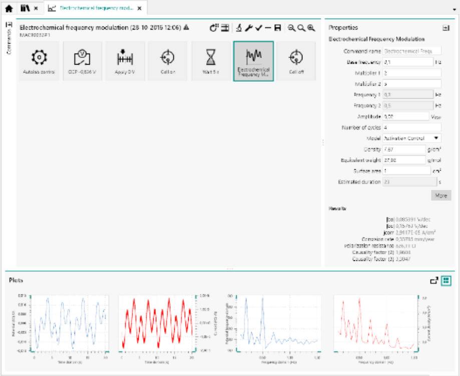
Nova is one of the most powerful electrochemical software available on the market which is used to perform measurements and data processing by using an Autolab potentiostat/galvanostat.

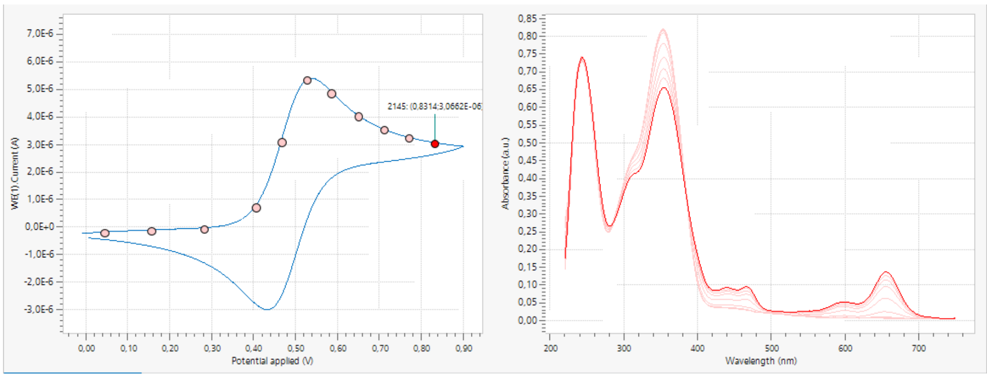
In this presentation, two of the newest additions to Nova will be shown:

I. Electrochemical Frequency Modulation (EFM). EFM is a novel AC technique used in corrosion applications in which two potential sine waves of different frequencies are applied simultaneously to the corroding system and the AC response of the current together with its harmonics are recorded and analyzed. The specific corrosion parameters such as the anodic and cathodic Tafel slopes, the corrosion current density and corrosion rate are automatically calculated.



II. Fully integrated Spectroelectrochemistry support. In-situ spectroelectrochemistry is one of the most popular hyphenated electrochemical techniques in which the optical (UV/VIS/NIR or Raman) spectra is recorded during an electrochemical measurement at well-defined potential values. The optical spectroscopic results are used as complementary information for the characterization of the electrochemically generated species (end products or intermediates). For this applications, of crucial importance is the accurate correlation of the optical results with the electrochemical data as well as the convenient control of the instruments and analysis of the results.

The Autolab Spectrophotometers are fully integrated in the Nova software, very conveniently controlled from the same interface as the electrochemical instruments and the optical data is acquired and directly correlated with the electrochemical data.



EX 221

A novel multi-sine excitation procedure for impedance spectroscopy supports automatic drift correction and online error determination

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The traditional way to measure impedance using single sine (monochromatic) excitation is the most transparent and robust way to find reliable EIS data. Compared to the time saving polychromatic (i.e. multi sine) excitation, the advantage is the unequivocal assignment of harmonic content in the response signal to unwanted interference. Systematic analysis of these harmonics allows for the determination of a reliable measurement variance for every single data sample immediately after raw data collection is complete. For decades such a procedure named "Weighted Harmonics Autocorrelation" has proven its benefit for the EIS instruments of the authors group [1]. Another helpful feature is owed to the periodicity of the monochromatic excitation: unwanted time drift contributions can be calculated from succeeding periods of the response signal for the reconstruction of the drift-free response. This allows for an automatic drift correction [2].

These valuable features are hardly achievable using standard multi sine techniques: here, even in the absence of interference the response signals are neither periodic nor free of harmonics.

In spite of the fact that monochromatic techniques have even the better relationship between information density and time effort [3], it is sometimes preferable to use multi sine whenever the total measurement time is crucial.

In this presentation, a novel multi sine excitation method will be presented that keeps the advantages of automatic drift correction and online error determination analogous to the monochromatic single sine procedure.

Keywords: EIS, error determination, drift correction, multi sine, batteries, fuel cells

References:

[1] *C.-A. Schiller, R. Kaus; Impedance Contributions Online 2008, 6, P4.1 - P4.13 (http://accessimpedance.eu/images/stories/ICO6_P4.pdf)*

[2] *C. A. Schiller, F. Richter, E. Gülzow, N. Wagner; J. Phys. Chem. Chem. Phys. 2001, 3, 374-378*

[3] *Ruben H. Milocco, Minimal measurement time in electrochemical impedance identification, Electrochim. Acta 1994, 39, 1433-1439*

OEN 148

Investigations on long-term behavior of bifunctional air electrodes for zinc-air flow batteries

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In order to counterbalance electricity fluctuations caused by an increasing share of electricity generated by renewable sources, i.e. wind and solar, higher energy storage capacities need to be implemented into the electricity grid. Electrochemical energy storage systems, such as stationary flow batteries, present one option, whereby the zinc-air flow battery (Eq. 3) is especially promising due to its use of the inexpensive, safe and abundant active storing metal zinc [1,2].

Zn electrode:	$Zn(OH)_4^{2-} + 2\,e^-$	$\rightleftarrows$	$Zn + 4\,OH^-$	Eq. 1
Air electrode:	$4\,OH^-$	$\rightleftarrows$	$O_2 + 2\,H_2O + 4e^-$	Eq. 2
Overall reaction:	$2\,Zn(OH)_4^{2-}$	$\rightleftarrows$	$2\,Zn + 4\,OH^- + O_2 + 2\,H_2O$	Eq. 3

As depicted in Eq. 1, zinc is dissolved into the flowing alkaline electrolyte during discharge and can then be stored in an external compartment. During charging, zinc is electrochemically redeposited on the electrode's surface. On the positive air electrode (Eq. 2), oxygen supplied from the surrounding air is reduced to hydroxide ions during discharge (oxygen reduction reaction – ORR) and generated again during charging (oxygen evolution reaction – OER) [1,2].

As summarized in Fig. 1 several key parameters are to be considered during manufacturing in order to achieve well-performing and stable bifunctional air electrodes. The main factors causing deteriorating performances are the highly oxidative potentials and the vigorous oxygen bubble formation during OER, which slowly degrade the electrode's porous structure and materials. The implementation of precious metal-free oxide catalysts into bifunctional air electrodes, which exhibit high long-term stability during prolonged charge and discharge cycling, and the effects leading to final electrode degradation were investigated.

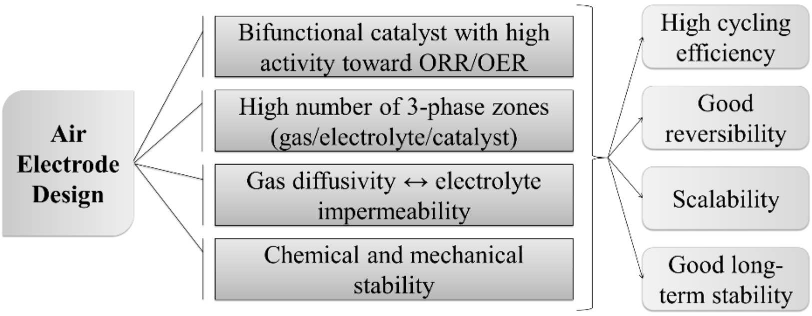

Figure 1: Schematic of the important parameters for obtaining stable and catalytically active air electrodes

For the manufacture of bifunctional air electrodes the catalysts were mixed with binder and conductivity additives, e.g. carbon nanofibers, and supported on nickel foam, which functions as current collector and mechanical backbone of the electrode. Electrochemical characterization was carried out by charge and discharge cyclization (1 h each) in half-cell configuration at current densities of 50 mA cm^{-2}, whereby stable ORR and OER potentials over a period of several hundred hours where achieved [3].

References:

- *[1] J. Fu, Z.P. Cano, M.G. Park, A. Yu, M. Fowler, Z. Chen, Electrically Rechargeable Zinc-Air Batteries: Progress, Challenges, and Perspectives, Adv. Mater. (2016).*
- *[2] L. Jörissen, Bifunctional oxygen/air electrodes, J. Power Sources. 155 (2006) 23–32.*
- *[3] B. Pichler, S. Weinberger, L. Reščec, I. Grimmer, F. Gebetsroither, B.Bitschnau, V. Hacker, Long-term behavior of bifunctional air electrodes with high stability during pulse charging for zinc-air flow batteries (submitted).*

OEN 145

Stable cathodic material for zinc-ion batteries based on Prussian blue derivatives for stationary applications

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In 2015, we introduced an aqueous zinc-ion battery based on copper hexacyanoferrate nanoparticles (CuHCF) for grid-scale energy storage devices with an operational discharge voltage of 1.73 V.[1] Later on, moderate cycle stability with a specific charge retention of 74.35% after 1000 cycles in 20 mM $ZnSO_4$ was achieved. Recently, we have shown that the current rate and the electrolyte (nature and concentration) greatly affect the performance and aging of the CuHCF. In particular, the aging of the cathodic active material occurred at a shorter number of cycles when the concentration of the electrolyte was higher and the current rate was lower.[2] In addition, we observed that the aging process of CuHCF in presence of Zn salts was caused by a phase transformation.[2]

For this reason, we modified the chemical composition of the Prussian Blue derivative in order to reach a longer cycle life and stabilize the system. Several materials were synthesized, in which Cu was partially substituted with Zn, namely with Cu:Zn ratios equal to 85:15, 90:10, 93:7, 95:5, and 98:2. Among them, the mixture with the Cu to Zn ratio of 93:7 has shown the best performance with the capacity fading of 85.5% after 1000 cycles, which is about 11% less than the capacity fading of pure CuHCF in the same electrolyte. Furthermore, there is no evidence of the phase transformation upon cycling the mixture of $KCu_{0.93}Zn_{0.07}HCF$ even after 1000 cycles in 20 mM $ZnSO_4$. The use of mixture CuZnHCF as an active material appears to be a very promising step forward in the application of aqueous zinc ion batteries for grid-scale energy storage.

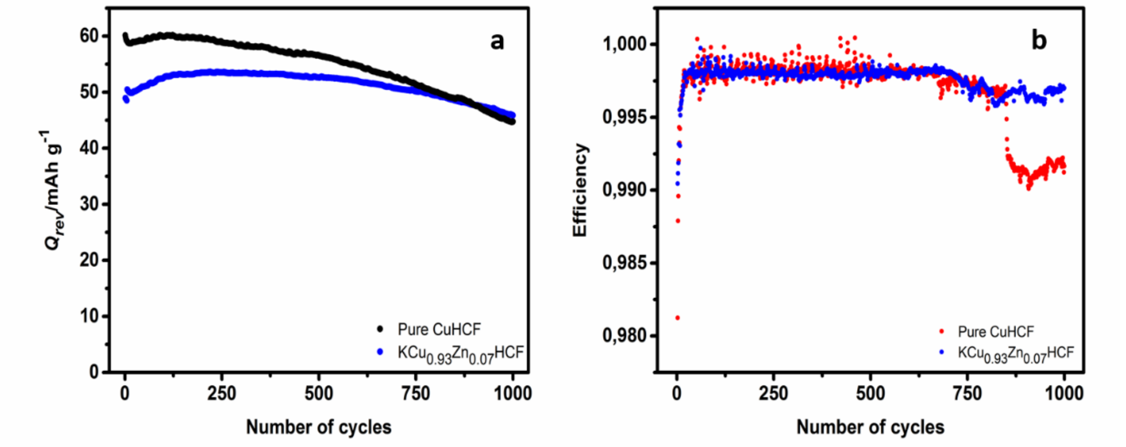

Figure 1: a) Reversible specific charge vs. number of cycles for pure CuHCF (black) and mixture of $KCu_{0.93}Zn_{0.07}HCF$ *(blue) at 1C current rate in 20 mM* $ZnSO_4$*, and b) Columbic efficiency vs. number of cycles for pure CuHCF (red) and mixture of* $KCu_{0.93}Zn_{0.07}HCF$ *(blue) at 1C current rate in 20 mM* $ZnSO_4$

References:

[1] *R. Trócoli, F. La, An Aqueous Zinc-Ion Battery Based on Copper Hexacyanoferrate, ChemSusChem. 8 (2015) 481–485. doi:10.1002/cssc.201403143.*

[2] *G. Kasiri, R. Trócoli, A.B. Hashemi, F. La Mantia, An electrochemical investigation of the aging of copper hexacyanoferrate during the operation in zinc-ion batteries, Electrochim. Acta. (2016). doi:10.1016/j.electacta.2016.10.155.*

OEN 195

Imaging the formation of $PtCu_3/C$ electrocatalyst by *in-situ* annealing transmission electron microscopy

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While vehicles with proton exchange membrane fuel cells (PEMFC) are already commercially available, its most vital part – the electrocatalysts still contains too high quantities of the very precious platinum. In order to make the electrocatalyst cheaper, one has to further enhance the kinetics of the slow oxygen reduction reaction (ORR) for instance by alloying Pt with other transition metals. In addition to improving the kinetics of the electrocatalyst, one has to also consider the scalability of the electrocatalyst synthesis. Record breaking specific and mass activities of Pt-based electrocatalysts in thin film rotating disc electrode setups (TF-RDE) are being reported on an annual basis. Although such materials show immense potential of Pt-based electrocatalysts for further commercialization of PEMFC, nearly all of their synthesis processes base on the same poorly scalable polyol synthesis with average scale of 30-50 mg per batch, and make them unsuitable for transition from TF-RDE to membrane electrode assembly (MEA).

Our in-house gram scale patented synthesis of a $PtCu_3/C$ catalyst [1] enables synthesis of up to 20 gram electrocatalyst batches. The process involves partial galvanic displacement of copper on carbon support (Cu/C) with platinum precursor salt (K_2PtCl_4). Obtained PtCuO/C composite (Fig. 1a) is then further annealed in order to form $PtCu_3$ nanoparticles with an ordered pm3m structure (Fig. 2a).[2] In this work, we reveal insight into the annealing step of our $PtCu_3/C$ catalyst by a highly advanced characterization method; *in-situ* annealing transmission electron microscopy (TEM). The results are further complimented by ex-situ X-ray diffraction (XRD) analysis and electrochemical measurements using TF-RDE.

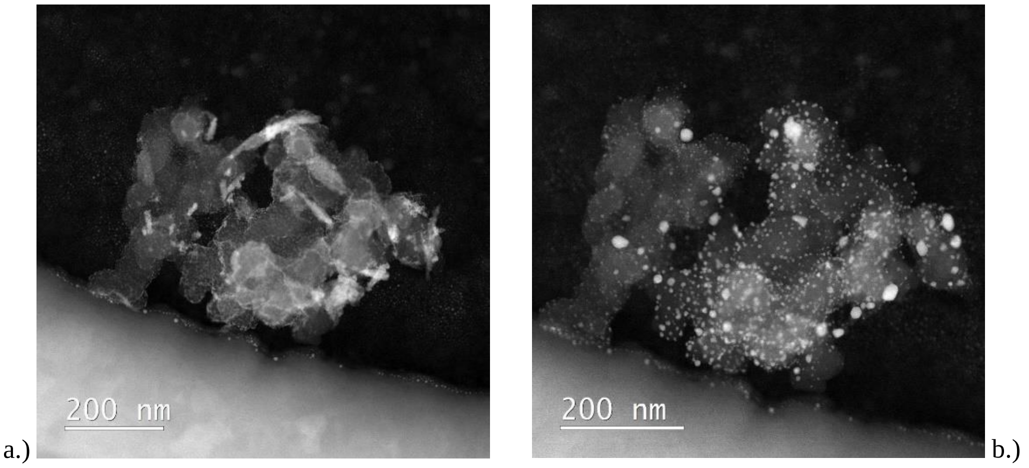
a.)
b.)

Figure 1: TEM image of the PtCuO/C composite (a) prior to thermal annealing step of the synthesis and (b) after thermal annealing step of the synthesis on the same location

References:

[1] *M. Bele, M. Gaberšček, G. Kapun, N. Hodnik, S. Hočevar, et al., Electrocatalytic composite (s), associated composition (s), and associated process (es), (2015).*

[2] *N. Hodnik, C. Jeyabharathi, J.C. Meier, A. Kostka, K.L. Phani, A. Rečnik, et al., Effect of ordering of* $PtCu_3$ *nanoparticle structure on the activity and stability for the oxygen reduction reaction, Phys. Chem. Chem. Phys. 16 (2014) 13610–13615.*

OEN 178

Over-discharge investigation of lead-acid batteries

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In recent decades, more and more systems (start-stop, drive-by-wire, brake-by-wire) are being developed in the automotive industry which use the car's electronic system therefore reliable power sources are necessary. It is essential to understand thoroughly the detailed behavior of the battery to increase its efficiency, stability and monitorability which is the most popular field nowadays.

Over-discharge plays an important role in aging because it increases the probability of initiation of grid corrosion, sulfation and loss of active mass. In this work the effects of over-discharge have been investigated via ohmic resistance increase, temperature change and the loss of capacity separately for the negative and the positive electrode. Most of the measurements were carried out in a prepared cell which contained a negative and a positive plate, an $Ag|Ag_2SO_4$ reference electrode, a shunt (for measuring current accurately), a dummy battery and electronic load (Figure 1).

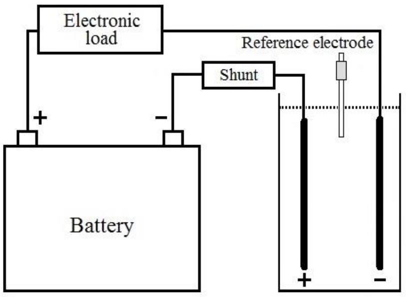

Figure 1: Experimental system

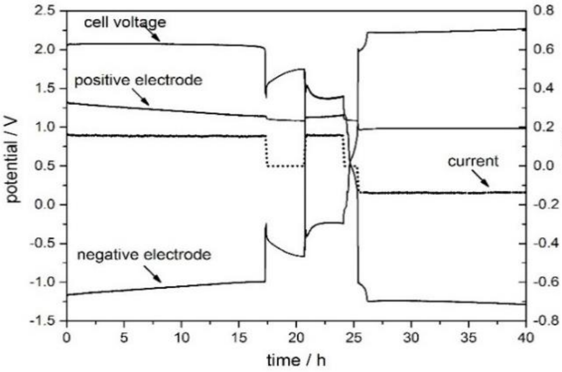

Figure 2: Over-discharge characteristic of cell

It was found that the ohmic resistance highly increased during the cell reversal. This process and also the increasing gas evolution [1] caused significant temperature rise inside the electrode. This phenomenon may have a very serious influence on aging specifically the loss of capacity because there is high temperature and gas flow at the same time.

The loss of capacity caused by over-discharge was also investigated. At first, a state of health measurement was executed and after that a certain percent of the cell's SOH was also discharged (depth of discharge) and this procedure was repeated four times (Figure 2). The results of these measurement are summarized in Table 1.

Table 1: Loss of capacity as a result of over-discharge in case of negative and positive electrode

Depth of discharge	State of health of negative electrode before i^th^ measurement			
	1st	2nd	3rd	4th
100 %	100 %	98 %	96 %	94 %
110 %	100 %	97 %	95 %	93 %
120 %	100 %	94 %	91 %	88 %
~	State of health of positive electrode before ith measurement			
120%	100 %	96 %	93 %	95 %

It is stated as the results of these measurements that the loss of capacity is very significant in case of negative electrode at high DOD level. The main reason of this may be that the expanders and other additives have been oxidized irreversibly during reverse charging.

References:

[1] J. Garche, A. Jossen, H. Döring, J. Power Sources 67 (1997) 201-212

OEN 119

Electrochemical nanogravimetric and conductivity studies on phtalocyanines

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Investigations of the electrochemical behavior of phthalocyanines (Pc) have been in the foreground of research during the last decades especially as a catalyst of the oxygen reduction reaction (ORR). However, these molecules have their own limits. These are organic compounds, therefore their conductance is much lower than in case of metallic catalysts. On the other hand, their conductive properties vary immensely with their redox states.

In this study the conductive behavior of Pcs was analyzed by measuring the 2-point and 4-point resistances of the Pc layers simultaneously (Fig 1. bottom half). Several Pcs (FePc, PdPc, polyCuPc and HPc) were measured at different pHs. These results combined with the cyclic voltammetry and the potential dependence of EQCN frequency can deliver fundamental information about the micro processes during electrochemical reactions.

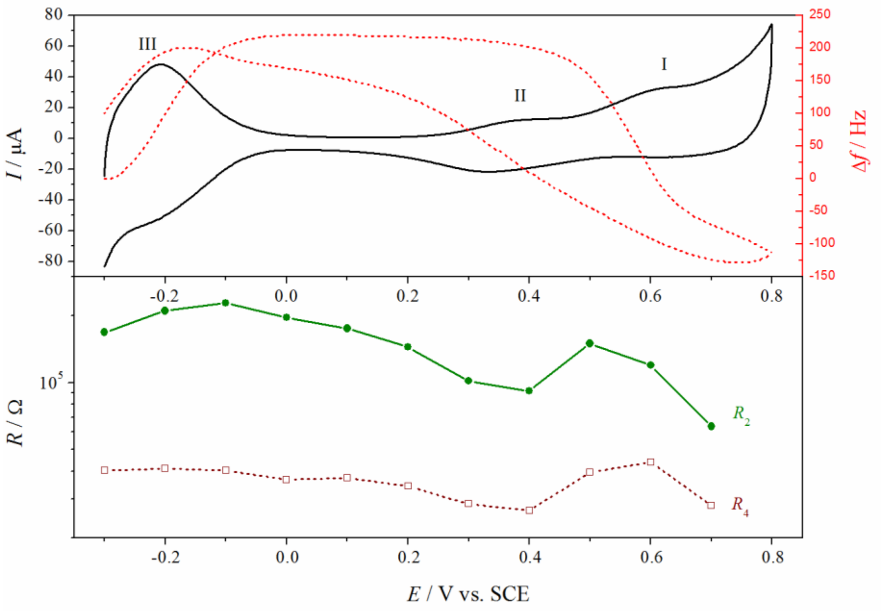

Figure 1: Cyclic voltammogram (black curve), EQCN frequency response (red dotted curve), the 2-point (green curve) and the 4-point resistance (wine dotted curve) of FePc microcrystals attached to gold surface. Electrolyte: 0.1 M deaerated H_2SO_4. Scan rate: 10 mV s^{-1}

It was found that Pcs have several conductive states. In neutral state the resistance is very high, and when protonation / deprotonation takes place the conductivity increases heavily. When counter ions enter the layer during the electrochemical reactions the resistance also decreases. The redox changes of the central ion also influence the properties of the layer.

These results can lead to better understanding of the redox behavior of phthalocyanine layers, which can help us developing better catalyst layers or sensors in the future.

OAN 181

Hyphenation of electrochemistry and mass spectrometry using disposable sensors

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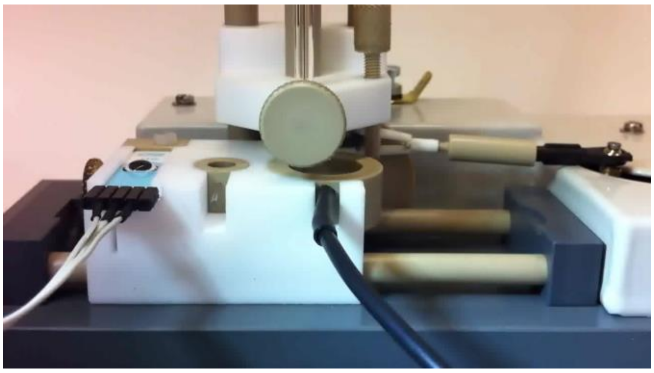
The hyphenation of electrochemistry (EC) with capillary electrophoresis (CE) was introduced in 2003 as a concept enabling the separation of neutral analytes via electrochemical generation of charged species during hydrodynamic sample injection [1]. The conventional approach for electromigrative separations of neutral analytes is the addition of surfactants forming micelles (micellar electrokinetic capillary chromatography). However, there is a limited compatibility of solutions containing surfactants with electrospray ionization mass spectrometry (ESI-MS). As an alternative EC-CE-MS can overcome this problem. Our group has developed and characterized several instrumental generations of EAI devices [2]. A fully automated EC-CE-MS system with integrated screen-printed electrodes is extensively used in our laboratory. This system allows a user-friendly operation. The strength of EC-CE-MS is particularly seen in cases where charged product species can be formed electrochemically. Bioanalytical studies can be undertaken under near physiological conditions in absence of organic solvents. [3, 4]. In case of neutral product species HPLC is the preferred separation technique. Very recent results concerned with EC-HPLC-MS will be presented.



Photograph of the automated system for the coupling of electrochemistry – capillary electrophoresis – mass spectrometry

References:

[1] F.-M. Matysik, Electrochem. Commun. 5 (2003) 1021-1024

[2] M. Cindric, F.-M. Matysik, Trends Anal. Chem. 70 (2015) 122-127

[3] R. Scholz, P. Palatzky, F.-M. Matysik, Anal. Bioanal. Chem. 406 (2014) 687-694

[4] M. Cindric, F.-M. Matysik, Electroanalysis 27 (2015) 234-241

OAN 120

Electrochemical determination of carotenoids in fish samples

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High quality aquaculture products must fulfil several requirements, including the adequate color and nutritional value. As fish cannot synthesize pigments, the coloring agents need to be incorporated into their diet. The most used coloring agents are carotenoids. Carotenoids are a diverse class of polyisoprenoid hydrocarbons (carotenes) and their oxygenated derivatives (xanthophylls) and have an important role as defenders from UV-Vis light, precursors of vitamin A and natural antioxidants. Due to the positive effects on health, various methods that would allow their easy and quick determination are researched.

Until now, electrochemical investigations of carotenoids have been performed in non-aqueous media [1] with an exception of some studies in micelle systems [2] and as self-assembled monolayers (SAM) in aqueous phase [3]. Voltammetric measurements for characterization of carotenoids in fish samples are also sparse in literature, so this approach could provide a better knowledge of their mechanism of action and input into their use in aquaculture and potentially beneficial effects on human health when consuming fish food.

In this study, relatively new voltammetric method for the characterization of carotenoids (astaxanthin, lutein and β-carotene) and their detection in fish samples named stripping voltammetry microprobe (SPV) [4] was applied. This method is based on a formation of a precipitate film of analyte on the electrode surface by pipetting 5 μL of analyte dissolved in organic solvent and allowing the solvent to evaporate in air. By means of this technique, lipophilic compounds could be analyzed in aqueous media.

Measurements were conducted on a paraffin impregnated graphite electrode (PIGE) using square-wave voltammetry (SWV) in a wide range of potential scan rates in 0.1 M $HClO_4$ aqueous electrolyte. Prior to the analysis, fish samples were macerated in acetone allowing the extraction of carotenoids present in samples.

The results revealed that the oxidation of different carotenoid standards is not similar. While β-carotene and lutein showed one irreversible peak at $E = 0.453$ V and $E = 0.687$ V, respectively, oxidation of astaxanthin turned out to be more complex process. It has one well defined reversible peak at $E = -0.350$ V followed by one poorly defined shoulder at $E = -0.109$ V and smaller reversible peak at $E = 0.470$ V. Analysis of fish samples precipitates on the surface of PIGE was performed using SWV under optimal experimental condition: $E_{SW} = 50$ mV, $f = 100$ Hz, d$E = 2$ mV. Both salmon and bass samples revealed a reversible peak at the same potential, $E = 0.960$ V.

Proposed method showed good sensitivity and applicability on real samples and has a potential of further development.

Acknowledgments

The authors wish to thank to the Croatian Foundation in the frame of the project number IP-11-2013-2072.

References:

[1] D. Liu, Y. Gao, L.D. Kispert, Journal of Electroanalytical Chemistry ***488*** *(2000) 140–150.*

[2] G. Ziyatdinova, E. Ziganshina, H. Budnikov, Talanta ***99*** *(2012) 1024–1029.*

[3] A. Ion, V. Partali, H.R. Sliwka, F.G. Banica, Electrochemistry Communications ***4*** *(2002) 674–678.*

[4] M. A. Gulppi, N. Vejar, L. Tamayo, M. I. Azocar, C. Vera, C. Silva, J. H. Zagal, F. Scholz, M. A. Páez, Electrochemistry Communications ***41*** *(2014) 8-11.*

OAN 172

Characterization of titanium(IV)-4-(2-Pyridylazo)resorcinol complex as an effective reagent for determining hydrogen peroxide in bioelectroanalysis

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In the course of our electrochemical studies in bioanalysis, sometimes we encountered with the need of an effective reagent for determining trace hydrogen peroxide. To meet such demand, we have so far developed some reagents to detect trace levels of hydrogen peroxide. The reagents should be highly sensitive and specific to hydrogen peroxide. Among them, 4-(2-pyridylazo)resorcinol-titanium(IV) complex, denoted as Ti-PAR reagent, was found to be quite promising, because titanium(IV) has strong chemical affinity to hydrogen peroxide and PAR ligand has intense light-absorbing property [1]. In this study, this complex was assessed as an effective reagent to determine hydrogen peroxide based on the experimental results and spectral analysis.

Method: Determination of hydrogen peroxide was made by measuring the absorption peak at 508 nm due to the formation of Ti-PAR-H_2O_2 complex. *Ab initio* calculations were performed by using Gaussian 98 Rev. A. 7 and Gaussian 03 Rev.D.02 with RHF/STO-3G basis set. UV-visible spectral analysis was made by ZINDO method.

Results and Discussion: Following the addition of hydrogen peroxide to the Ti-PAR reagent, the absorption peak appeared at 508 nm due to the formation of Ti-PAR-H_2O_2 complex. Its absorbance was proportional to the concentration of added hydrogen peroxide. It exhibits high sensitivity to hydrogen peroxide due to a considerable large absorbance of the PAR ligand moiety at 508 nm with an apparent molar absorptivity for hydrogen peroxide of 3.6×10^4 M^{-1} cm^{-1}. Using this reagent, we have attained highly sensitive analysis of hydrogen peroxide with the detection limit of 4 pmol per test. In the determination of hydrogen peroxide in various real samples using this reagent, inorganic ions and organic compounds, such as ascorbic acid, amino acids, were actually found to cause no significant interferences on the analytical results.

When we promoted the use of the Ti-PAR reagent as an effective reagent for determining hydrogen peroxide, an actual molecular structure of the Ti-PAR-H_2O_2 complex dissolved in a test solution was confronted with essential evidence, i.e. what species is an entity of the Ti-PAR-H_2O_2 complex giving the absorption peak at 508 nm. Although a structural model was tentatively proposed based on some experimental results [1], definite structure for the colored species at 508 nm remained unsolved from the viewpoint of theoretical calculation. To solve this problem, the molecular structure of this complex was confirmed by the UV-visible spectral simulations in the present study.

References

[1] *K. Takamura, C. Matsubara, Bull. Chem. Soc. Jpn.* ***76*** *(2003) 1873.*

OAN 175

Novel hydrazinium EDTA-based electrochemical gas sensor for benzaldehyde

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A disposable electrochemical sensor for convenient room temperature detection of gaseous benzaldehyde will be presented. The sensor is composed of a three-electrode screen printed system modified with a mixture of Nafion polymer membrane containing novel tetrahydrazinium EDTA salt. This mixture serves a dual purpose, i.e. as benzaldehyde accumulation/derivatisation medium, and as semi-solid polyelectrolyte enabling voltammetric measurements. These can provide for several unprecedented characteristics for electrochemical determination of gaseous benzaldehyde (Fig. 1a) such as: i) a wide linear response in the examined concentration range of 0.01–1 gm^{-3} of gaseous benzaldehyde in combination with 60 min accumulation time (Fig. 1b); ii) also sub-gm^{-3} concentration levels could be detected when the exposure period is sufficiently prolonged corresponding to the calculated limit of detection 0.005 gm^{-3}.

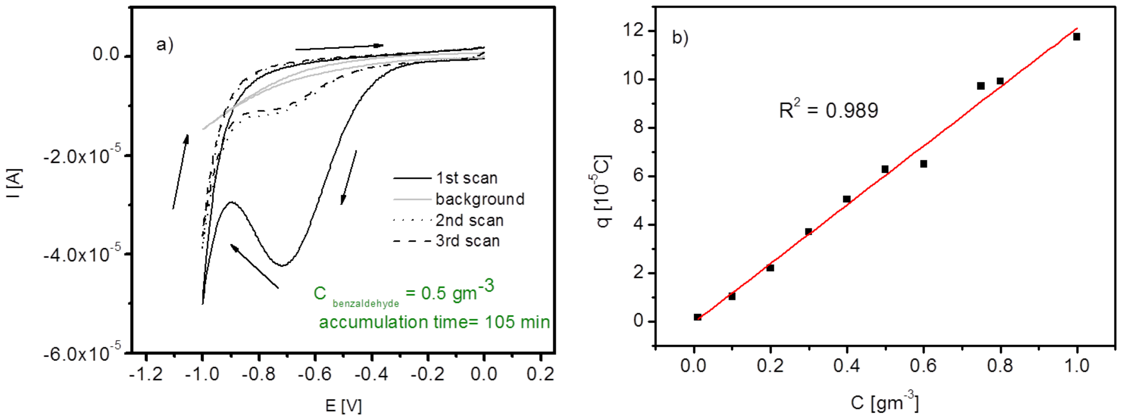

Figure 1: a) Cylovoltammetric (100 mVs^{-1}) response corresponding to reduction of benzyl hydrazone. Experimental conditions correspond to 0.5 gm-3 gaseous benzaldehyde and accumulation time of 105 min. b) Corresponding calibration curve

OAN 179

Glassy carbon electrode modified with nano-CeO_2 and Nafion for Malachite Green detection in aqueous solutions

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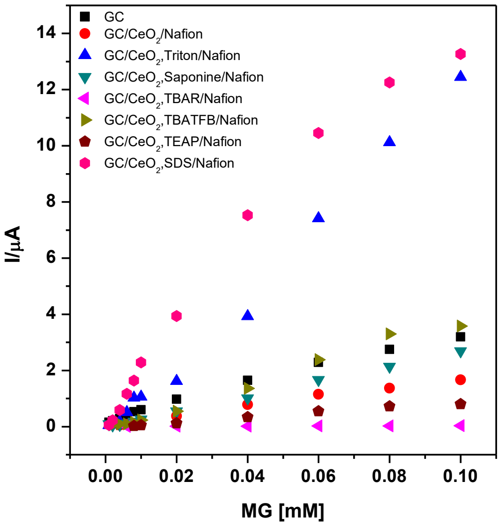
CeO_2 nanoparticles and Nafion have been employed to create a novel modified glassy carbon electrode for Malachite Green (MG) detection. The methods used for electrode characterization include square wave anodic stripping voltammetry (SWASV), batch amperometry and electrochemical impedance spectroscopy. FT-IR spectroscopy was carried out in solid state, bringing to light the electrostatic attractions that take place between MG and the polymer, making the electrode architecture very favorable.

Various surfactants (anionic, cationic and non-ionic) were used to prepare the CeO_2 nanoparticle suspension. Their effect on the response of the modified electrodes was studied, together with other parameters, such as CeO_2 suspension and Nafion solution concentrations. The optimum conditions were applied to detect MG in a real sample, a commercial product used in ornamental fish farming.



Influence of surfactants used for preparation of CeO_2 suspensions on the calibration curves for MG detection obtained by SWASV

Acknowledgements

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PL 113

Conducting polymers: Past, present, future

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The discovery or in a certain extent rediscovery of polymers possessing variable and high electronic conductivity launched a new field of research about 40 years ago. Electrochemistry has played a significant role in the preparation and characterization of these novel materials, which has served as a basis for many advanced applications in different areas spanning from the energy technologies to the health care. This lecture is intended to give an overview on the history of this field and on the achievements until now. The tasks for the future are also discussed. We focus on the electronically conducting polymers (shortly conducting polymers) but the redox polymers and the distinction between the two categories will also be discussed. The Nobel Prize in 2000 also helped to popularize these compounds. A simple Google search gave 4 680 000 entries on conducting polymers in January, 2017. A narrow search using the database of the ScienceDirect resulted in 271 483 hits. The far highest citation number can be found for polyaniline, polypyrrole has the silver medal, and these polymers are followed by PEDOT and polythiophene. It is worth to analyse the reason of the even increasing interest regarding these systems since the fundamental nature of charge propagation and the basic properties have already been clarified [1, 2]. The utilization based on the useful properties of conducting polymers has started even at the end of the last century, e.g., the variation of the conductivity in electronic devices including thin film transistors and insulated gate field effect transistors or in gas sensors; the color change in electrochromic display devices or in smart windows, the electroluminescence in light emitting devices, the swelling-deswelling accompanying the charging-discharging processes in artificial muscles, the charge storage capacity in energy technologies (batteries, supercapacitors), and corrosion protection. One of the most notable features of the conducting polymers is the potential-dependent variation of their charging state. It can be applied e.g., to remove ionic species from waste water via stripping, and release those by changing the charging state of the polymer layer. Similarly, it is possible to regulate the dosage of different medicines even in vivo. Conducting polymers with combination with other compounds (embedded enzymes, polyelectrolytes etc.) can be used for specific purposes, e.g., in biosensors.

In the last two decades the researchers have started to apply novel approaches. The new trend is the fabrication of composites including nanocomposites of polymers and other materials such as carbon nanotubes, graphene or inorganic compounds having special structure and properties. Microsystem technologies have been replacing by nanosystem technologies. The biocompatibility of several conducting polymers provides opportunity for the application in medicine as artificial muscles and limbs, as well as artificial nerves. More sophisticated and combined techniques have been developed, and have become widespread tools in the laboratories all around the world; e.g., scanning microscopies, or the new versions of electrochemical quartz crystal nanobalance. In the recent years we have reached a deeper level of understanding of the behavior of these systems that we can use to improve the performance of the devices based or use conducting polymers. The improvement occurs either by a fine-tuning of already promising systems or by using more sophisticated compositions and structures. The use of the derivatives of the monomers or copolymerization of different monomers may be an option to obtain conducting polymers, which are more flexible or rigid or even crystalline for e.g., heterojunction solar cells, as well as which are mechanically and chemically more stable, have a more advantageous processability etc. The functionalization of conducting polymers which lead to smart materials interacting and responding to their environment is also a great opportunity. The preparation of self-doped polymers is also a good way to overcome the problems of the ionic charge transport during redox switching and other limitations of the use of the polymer. The development in the field of conducting polymers is unbroken, and we still expect new discoveries and novel utilizations in several areas such as energy storage and power sources, photovoltaics, health care, and different technologies.

References

[1] Inzelt G (2011) Rise and rise of conducting polymers. J Solid State Electrochemistry 15 (7-8): 1711-1718

[2] Inzelt G (2012) Conducting polymers - A new era in electrochemistry. 2nd edn. In: Scholz F (ed) Monographs in electrochemistry. Springer, Heidelberg Berlin

KN 217

Insights into electrochemical dealloying of Pt-based nanoparticles at the sub-nano-scale

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The importance of electrocatalysis will be discussed in the broader context of the emerging hydrogen and circular economies. The future challenges will be boiled down to recent sub-nano-scale insights into how metal nanoparticles as electrocatalysts behave under chemical reaction conditions, which in turn are critical for the understanding and optimization of electrochemical (conversion) processes.

Dealloying is an electrochemical phenomenon where the less noble metal gets selectively leached out of a binary alloy leaving behind either a nano-porous or core-shell structure.[1, 2] Therefore dealloying has become one of the key strategies for producing electrocatalysts. In the case of Pt-alloys, which are considered highly promising cathode PEM fuel cell electrocatalysts, the activation procedure includes dealloying as an effective way to prepare very active surface. This causes structural, morphological and composition changes inside and on the surface of nanoparticles (Figure 1). At the sub-nano-scale many details are still missing. Known and less known phenomena are demonstrated on our home-made $PtCu_3$ nanoparticulate electrocatalysts with advanced characterization techniques such as High Resolution Identical Location Transmission Electron Microscopy (IL-TEM),[3] Electrochemical Flow Cell coupled to ICP-MS, Monte Carlo Simulations, etc.

A deeper understanding of the nano-scale electrochemical phenomena will eventually help us utilize various electrochemistry treatments to our advantage. As an example, a novel green platinum recycling concept will be proposed.

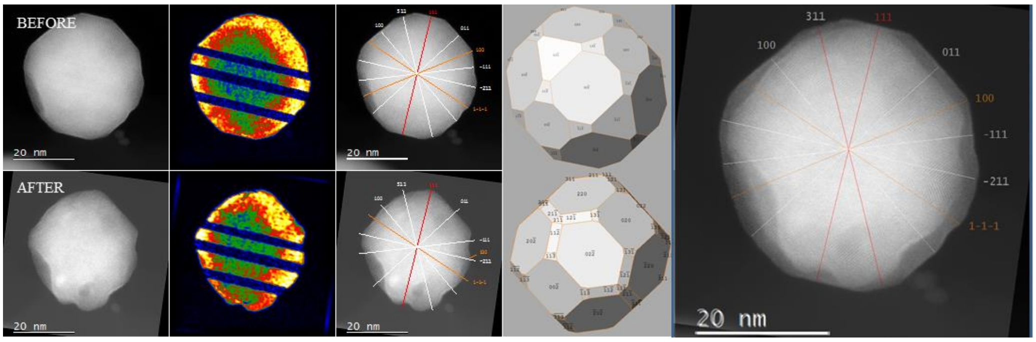

Figure 1: High resolution identical location TEM micrographs of $PtCu_3$ single nanoparticle before and after electrochemical activation

References:

[1] *M. K. Debe, Nature, 2012, **486**, 43-51.*
[2] *N. Hodnik, M. Zorko, M. Bele, S. Hočevar and M. Gaberšček, The Journal of Physical Chemistry C, 2012, **116**, 21326-21333.*
[3] *N. Hodnik, G. Dehm and K. J. J. Mayrhofer, Accounts of Chemical Research, 2016, **49**, 2015-2022.*

OEN 210

The capacitance properties of activated carbon obtained from biopolymers as the electrode material for electrochemical capacitors

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Porous carbons were prepared through KOH activation of biopolymers such as chitosan, pectin, starch or cellulose. The porosity and surface area strongly depend on the temperature of activation. Different electrolytes were tested to select the most suitable one for electrochemical capacitors. As the best was chosen 1 M H_2SO_4. Figure 1 presents dependence of capacitance values versus current load for activated carbon from pectin in various electrolytes. Lower but very stable values of capacitance during cyclability measurements were obtained for carbons operating in 1 M Na_2SO_4. All carbon electrode materials in alkaline electrolyte show decrease in capacitance as the current regime was increased. The activated carbon prepared from chitosan with the temperature of activation standing at 750°C exhibits the largest specific surface area and capacitance of 295 Fg^{-1} at a current density of 0.1 Ag^{-1} in the acidic medium. Moreover, the activated carbon from chitosan shows good rotation and excellent cycling stability (almost 99% capacitance retention over 5000 cycles).

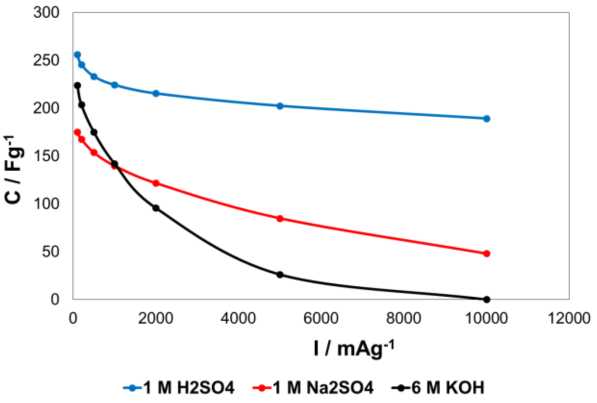

Figure 1: Capacitance values versus current load dependence for activated carbon from pectin

Applying different polysaccharides as precursors of activated carbons gives possibility to obtain carbons with well-developed surface area, which provide high capacitances probably as a result of suitable porosity and electrolyte ion dimensions. The activated carbons had a surface area more than 2800 m^2g^{-1}, with predominant contribution of micropores, where mainly the charging process of the electrical double layer took place. Furthermore, the polysaccharide-based activated carbons showed good charge propagation and excellent cycling stability.

Acknowledgements

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OEN 212

Comparison of electrochemical properties of activated carbons and graphene-like materials used as electrode materials in various energy storage devices

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Carbonaceous materials are well known and readily used in a broad range of applications. Owing to the well-developed porous structure and the presence of certain surface functional groups, these materials are commonly used as adsorbents for a wide range of contaminants from gaseous or liquids media. Currently, activated carbons are also widely used as the electrodes for electric double-layer capacitors because of their high surface area, chemical stability and acceptable price.

This work is focused on the carbon materials obtained from biopolymers such as lignin, cellulose and chitosan as precursors. The carbonization in nitrogen atmosphere followed by chemical activation in KOH was chosen as a synthesis method. The resulting carbon materials were characterized by well-developed surface area and microporous structure, beneficial for electric double-layer capacitors (EDLC) electrodes. In parallel, graphene-like materials obtained from graphite oxidation followed by thermal reduction were also synthesized.

The main goal of performed research tasks was to compare the electrochemical properties of carbon materials applied as electrode materials in different energy storage systems - electrochemical capacitors and in hydrogen storage systems. The special example taken into the consideration were hybrid capacitors composed of a battery-type electrode and a high surface area carbon electrode. This kind of configuration allows merging the advantages and reduces the drawback of redox and capacitive based systems. As one can see in Fig. 1, the same electrode material can give different electrochemical response depending on the type of device in which they are employed.

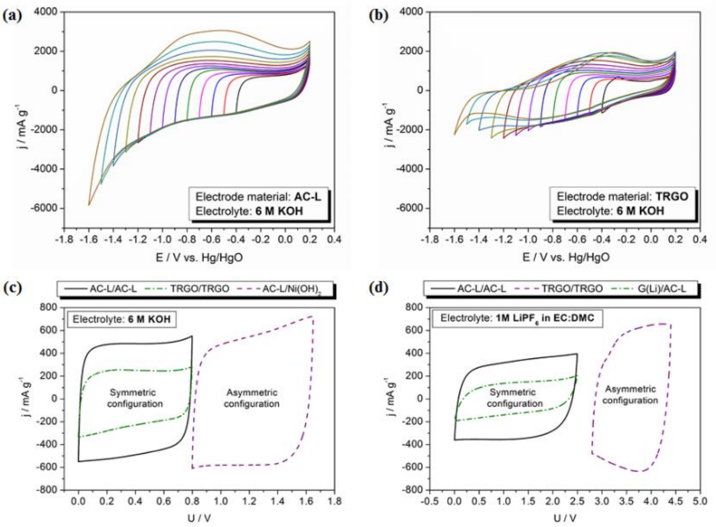

Figure 1: Cyclic voltammetry curves recorded for activated carbon (AC-L) and thermally reduced graphite oxide (TRGO), in different electrochemical systems: (a) and (b) hydrogen storage (Scan rate: 5 mV s^{-1}); (c) and (d) electrochemical capacitors with symmetric and asymmetric construction (Scan rate: 10 mV s^{-1})

This work will report on the influence of the physicochemical properties of carbon-based electrodes of various origin on their electrochemical response in various energy storage systems.

Acknowledgement

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OEN 155

High-power supercapacitor electrodes based on vertically aligned carbon nanotube layer

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Double layer capacitors (DLCs) are key components for energy storage systems, e.g. for economic hybrid electric vehicles. Due to their high power density and outstanding cycle stability, as compared to batteries, DLCs are advantageous in applications like energy recuperation from braking. However, comparatively low energy density and high costs limit their application and performance improvement is required. Within various possible electrode materials, vertically aligned carbon nano-tubes are expected to provide many advantageous properties towards next generation DLCs due to their unique structure and their electrical properties.

Authors have been involved in two FP7 projects, which objectives were the development of economic growth processes for aligned carbon nano-tubes on metal electrode surfaces. The aim of this lecture is to present electrochemical characteristics of supercapacitors, built form vertically aligned carbon nanotube (VA-CNT) grown on different substrate, such as nickel and aluminium foil, and carbon felt. Electrochemical cell configurations have been developed with high double layer capacity, and power density. Organic electrolytes are targeted to achieve high cell voltage and energy density. Application oriented tests were performed to demonstrate the improved charging efficiency, long-term stability and useful lifetime of the optimized devices.

The CNT electrodes were tested and evaluated in symmetric electrochemical test cell setups in various electrolytes. $TEABF_4$/acetonitrile being the standard electrolyte in commercial DLC cells was found to be suitable for CNT based supercaps as well. For characterization of supercapacitor performance, the following investigations were done on the samples: Impedance spectroscopy, cyclic voltammetry and galvanostatic charge-discharge.

Electrochemical testing revealed the huge potential of the CNT-films for energy storage applications. Specific capacities strongly depend on the specific surface area of the electrode material and thus are directly influenced by the CNT diameter. For samples with the lowest CNT diameter capacities of up to 60 F/g were obtained. Very low series resistance was measured indicating the excellent contacting of the aligned CNT forest to the metallic electrode and fast ion diffusion kinetics within the high aspect ratio 3D structured CNT films. The overall low resistance of CNT electrodes can be clearly attributed to their unique structural properties. While in active carbon based electrodes particle-particle resistance and complex micropore geometry add to limited charge and electrolyte ion transport, CNT electrodes profit from their completely different architecture.

- every single CNT is in direct contact to the current collector
- electronic resistance along the CNT is very low
- surface area is completely accessible
- intertube pores are larger then 10 nm and are directed towards the other electrode thereby leading to a very fast ionic transport.

Long-term tests demonstrated that the life-time of supercapacitors determined principally by the electrochemical stability of substrate material. Long-term stabiltity tests on supercapacitors built form VA-CNT on carbon felt electrodes up to 1.000.000 charge-discharge cycles demonstrate excellent stability of the CNT test cells.

Acknowledgements

The atmospheric pressure CVD process line was developed and VA-CNT electrodes were prepared by Susanne Dörfler, Benjamin Schumm, Althues Holger and Stefan Kaskel at the Fraunhofer Institute for Material and Beam Technology, IWS, Dresden, Germany. Financial assistance of the PLIANT (Process Line Implementation for Applied Surface Nanotechnologies) FP7 project (No. 309530) and OTKA K112034 is gratefully acknowledged.

OIF 154

On the nature of the electrochemical double layer

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Since Helmholtz's statement in 1879, the double layer has been regarded to be capacitive, implying instantaneous double layer structure changes following those of voltage. Accordingly, the vast majority of the double layer theories in the past hundred years have been of static nature; time or frequency do not appear in the resulting equations. In other words, the kinetics of the double layer rearrangement processes have always been out of the scope.

Recent advances of methodology enabled precise studies of the kinetics of double layer rearrangement processes. To be presented are results of impedance spectroscopy measurements, made in cooperation with colleagues at the Ulm University in the past decade. These experiments have been performed with systems which are very simple and well-defined from conceptual points of view – like CV and EIS measurements on Pt(100) in aqueous HCl solutions or on Au(100) and HOPG in ionic liquids. The results demonstrate that charging-discharging of the double layer is far from being immeasurably fast; in particular, in the case of the ionic liquids these processes are rather sluggish. These demonstration experiments are aimed to urge theoreticians to include slow adsorption-desorption and local transport processes in their double layer models.

References

[1] *T. Pajkossy, Impedance spectra of Pt(100) in aqueous H_2SO_4 and HCl solutions around the hydrogen adsorption-desorption peak, Z. Phys.Chem.,* **226** *(2012) 935-943*

[2] *C. Müller, K. Németh, S. Vesztergom, T. Pajkossy, and T. Jacob, The interface between HOPG and 1-butyl-3-methyl-imidazolium hexafluorophosphate, Phys.Chem.Chem.Phys.,* **18** *(2016) 916-925*

OIF 158

Electrochemical Flicker-noise of redox reactions

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Flicker noise is a low-frequency phenomenon which in many cases dominates the noise of electronic devices or sensors. There are classically three statements about flicker-noise that are considered to be valid, namely **a;** the power spectral density exhibits a $\sim 1/f^{\alpha}$ behavior, **b;** it is a typical non-equilibrium noise and **c;** even though there is no generally accepted model about flicker noise but it is in many cases attributed to surface inhomogeneities, without any real evidences.

Statement **a** and **b** do not show any conflict in the case of electronic devices since those normally show pure Ohmic behavior in the low frequency region. On the other hand, in electrochemistry the situation is just the opposite. Due to diffusion control or slow relaxation processes electrochemical immitance spectra exhibit significant reactance and thus frequency dependence even in thermodynamic equilibrium. Here we have to emphasize that noise and conductance (immitance) are strongly related phenomena since both are originated from the stochastic motion and reactions of the free charge carriers present in the systems. Strictly saying, there are no two different models for conductance and noise, a consistent stochastic model for a particular system must provide both the impedance and the noise of that system. The fluctuation-dissipation theorem of thermodynamics has one basic consequence, namely the real part of the immitance and the corresponding noise spectrum are in one-to-one correspondence in thermodynamic equilibrium:

$$S_U(\omega) = 4\mathbf{k}TZ'(\omega) \text{ or} \tag{1}$$

$$S_I(\omega) = 4\mathbf{k}TY'(\omega), \tag{2}$$

where $S_U(\omega)$ and $S_I(\omega)$ correspond to the power spectral density of the potential and current fluctuation, $Z'(\omega)$ and $Y'(\omega)$, mean the real part of impedance or admittance, respectively, $\mathbf{k}$ and T denote to the Boltzmann factor and absolute temperature.

An electrochemical cell may provide an immitance the real part of which exhibits $\sim 1/f^{\alpha}$ behavior even in thermodynamic equilibrium. Thus under the same condition the power spectrum density of the corresponding noise will also exhibit a $\sim 1/f^{\alpha}$ behavior. If we considered this latter to be flicker noise we would get into contradiction with statement **b** since we are still in thermodynamic equilibrium. To avoid this problem, we defined a new concept, the dimensionless relative noise spectrum:

$$S_{\mathrm{rel}}(\omega) = \frac{S_{\mathrm{U}}(\omega)}{4\mathbf{k}TZ'(\omega)} \equiv \frac{S_{\mathrm{I}}(\omega)}{4\mathbf{k}TY'(\omega)}, \tag{3}$$

which we consider to be the real measure of noise. $S_{\mathrm{rel}}(\omega)$ shows a constant unity value in thermodynamic equilibrium while out of equilibrium it may or may not show different values. We consider a noise to be flicker noise only if the relative noise spectrum exhibits a $\sim 1/f^{\alpha}$ behavior.

The most important theoretical question about flicker-noise is whether it can be attributed to surface or bulk-phase phenomena (see statement **c**). Electrochemistry offers a unique possibility to decide this question since as compared to solid-state systems it is much easier to exchange the composition of the bulk-phase (electrolyte) and surface properties (metal phase of the electrode) independently of each other.

Examples will be shown for different redox systems with different electrode materials. According to our experience out of equilibrium the relative noise spectra can be modeled with a simple ~ $1 / f^{\alpha}$ behavior while the mere power spectral density in each case need a more difficult model. We found that flicker noise primarily depend on the composition of the electrolyte and the applied external polarizing current. We concluded that flicker-noise in electrochemical redox systems can be attributed to bulk-phase phenomena such like diffusion and solution phase reactions of the electroactive species.

OCA 191

The electrochemical reduction of CO_2 in ionic liquid + water mixtures under diffusion control

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The electrochemical reduction of CO_2 is currently receiving global interest as one of the most promising solutions to mitigate and utilize CO_2 gas, which is regarded as one of the main components of greenhouse gases [1]. The main advantage of using an electrochemical approach for CO_2 conversion is that it can be combined with renewable energy resources (solar, wind, hydro) [2]. Efforts have been devoted to develop superior nanostructured electrocatalysts and search appropriate electrolyte solutions. Ionic liquids (ILs) have recently gained significant attention as electrolyte for CO_2 reduction due to the following advantages: (i) ILs exhibit a selective and relatively high absorption of CO_2; (ii) the solubility of CO_2 in ILs can be tuned by tailoring the structures of cations and anions; (iii) ILs decrease the overpotential of CO_2 reduction via the complexation of CO_2 radical anion with the imidazolium cation [3]. Therefore, ILs are proposed as alternative, more effective next generation solvents for CO_2 capture/sequestration and conversion. However, the mass transport of CO_2 in ILs is typically slow due to the relatively high viscosity of ILs. One possibility to improve mass transport in ILs is to decrease their viscosity by dilution with water.

In this work, we have chosen 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF_4]) as a model IL, to which defined amounts of water are added. Note that [BMIm][BF_4] is fully miscible with water. A DOSY-NMR method is used to determine the concentration and diffusion coefficients of CO_2 and of other solution components. The effect of water is further explored in the diffusion-controlled CO_2 electroreduction in [BMIm][BF_4] + water. The diffusion coefficients obtained from DOSY-NMR are compared with those obtained from electrochemical measurements. A silver working electrode is used due to its high selectivity and activity towards the formation of CO. The formation of CO in CO_2 electroreduction is confirmed by complementary analysis of products by online gas chromatography.

References:

[1] *J. Qiao, Y. Liu, F. Hong, J. Zhang, A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels, Chemical Society Reviews, 43 (2014) 631.*

[2] *J. Durst, A. Rudnev, A. Dutta, Y. Fu, J. Herranz, V. Kaliginedi, A. Kuzume, A.A. Permyakova, Y. Paratcha, P. Broekmann, T.J. Schmidt, Electrochemical CO_2 Reduction - A Critical View on Fundamentals, Materials and Applications, CHIMIA International Journal for Chemistry, 69 (2015) 769.*

[3] *B.A. Rosen, A. Salehi-Khojin, M.R. Thorson, W. Zhu, D.T. Whipple, P.J.A. Kenis, R.I. Masel, Ionic Liquid–Mediated Selective Conversion of CO_2 to CO at Low Overpotentials, Science, 334 (2011) 643.*

OCA 131

Highly efficient electrocatalysts by N-, S-doping of mesoporous carbons for enhanced oxygen reduction reaction

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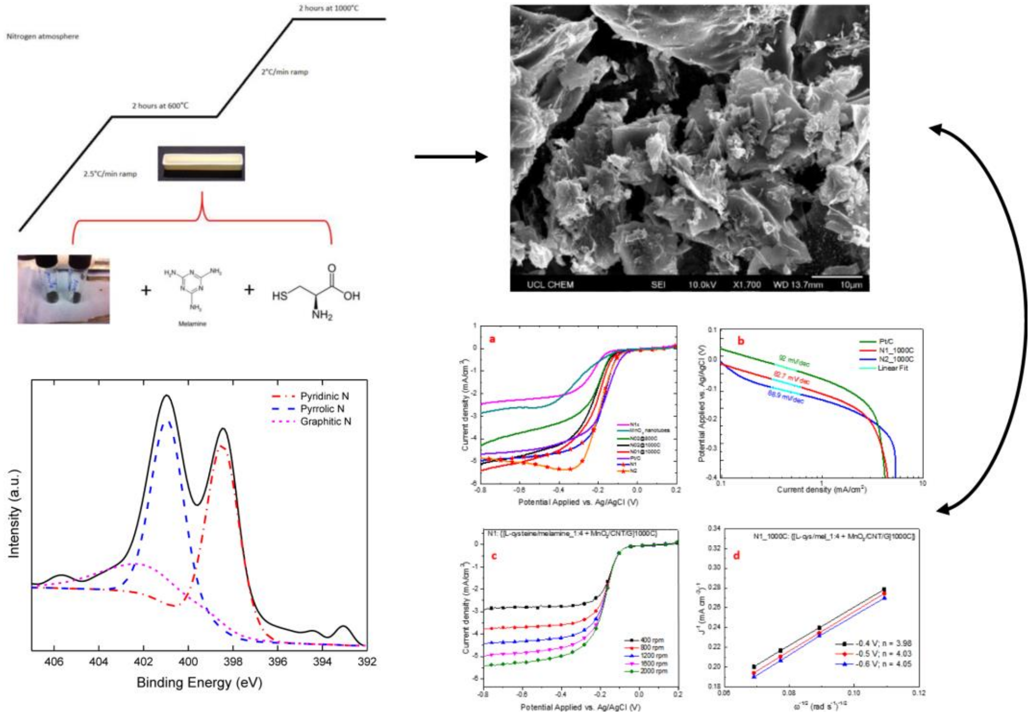
Multi-component composites made of MnO_2/CNT/G and carbonized L-cysteine/L-serine/melamine were synthesized and these showed excellent electrocatalytic properties including superb onset potentials and current densities. A carbonization process has proven to be a factor in increasing the porosity of the initial precursors. The mesopores present in the catalysts have shown to have an impactful effect on the oxygen reduction process. The N-doped carbon materials obtained after carbonization exhibit relatively high surface areas (BET) of 306 $m^2\,g^{-1}$ and 400 $m^2\,g^{-1}$, for N1_1000C and N2_1000C respectively, and notably large pore volumes of 1.078 $cm^3\,g^{-1}$ (N1_1000C) and 1.032 $cm^3\,g^{-1}$ (N2_1000C). These catalysts exhibited great performance towards oxygen reduction reaction (ORR) in alkaline media compared to MnO_2 nanotubes. Moreover, the different amounts of N-bonding formed at different carbonization temperatures has shown to influence the ORR. It has been shown that these N-, S-doped nanomaterials can attain large current densities and favorable ORR kinetics. The electron transfer numbers (≈ $4e^-$) showed that these mesoporous catalysts can achieve an excellent stability and performance towards ORR. Moreover, excellent Tafel slopes for ORR were obtained with 82.7 mV/dec (N1_1000C) and 88.9 mV/dec (N2_1000C) compared to around 92 mV/dec for Pt/C.



OCA 143

Multicomponent catalysts containing nonprecious metal for hydrogen and oxygen evolution reaction

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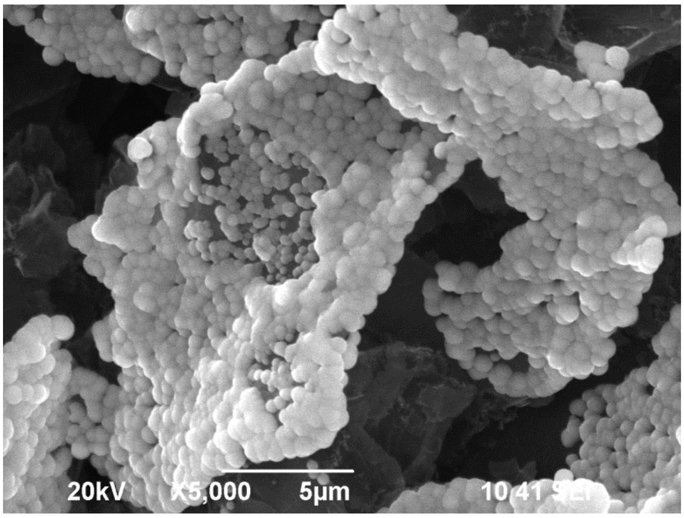
A new generation catalytic materials for hydrogen evolution reaction and oxygen evolution reaction containing transition elements of iron group (without precious metals) were produced to generate hydrogen as a clean fuel.

In order to improve the kinetic of electron transfer and hence the overall electrocatalytical behavior of the electrode material several multi-crystalline and amorphous electrochemical deposited alloys between Ni, Co, Fe, as *hyper-d* elements with typical *hypo-d* elements such as Zr, Mo, W and Re were obtained. Nonmetallic inclusion of P was used for formation of amorphous deposits. Alloys were deposited by methods including potentiostatic and galvanostatic modes of sophisticated electrolytes on carbon and non-carbon substrates. The alloys were characterized by X-ray fluorescence, scanning electron microscopy (SEM) with energy dispersive X-ray, X-ray diffraction and X-ray photoelectron spectroscopy methods. Polarization curves and electrochemical impedance spectroscopy measurements were used to study the electrocatalytic activity of the electrodes at room temperature. The results show that the obtained new catalytic alloys are promising electrode materials for electrochemical water splitting.



A typical SEM image of NiFeCoP alloy deposited on carbon paper

Acknowledgement

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OCA 197

Promotion effects of reduced graphene oxide on catalytic properties of nickel towards the hydrogen evolution reaction

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Catalytic activity of composites, obtained by the simultaneous reduction of graphene oxide (GO) and electrodeposition of nickel, towards the hydrogen evolution reaction was investigated in alkaline and acidic electrolyte. Graphene oxide, prepared by modified Hummers method, was drop-casted onto the copper substrates and reduced in the solution of Ni^{2+} ions. Duration of electrolysis was varied from very short times, sufficient for the reduction of all mass of the graphene oxide and formation of first nickel deposits to the prolonged times at which coalescence of nickel, hence coverage of all reduced graphene oxide (rGO) by nickel, occurs. Although all prepared surfaces showed improved electrocatalytic properties compared to the pure nickel surface, clear dependence between electrolysis time and electrocatalytic activity, reflected in appearance of maximum electrocatalytic activity for moderate electrolysis times, was observed. This observation indicates that rGO could have more than a simple supportive role and is discussed in terms of spillover of H_{ads} from Ni to the rGO at the Ni|rGO interface.

OCA 137

M_xPt/C electrocatalysts based on bimetallic nanoparticles with non-uniform distribution of components

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Platinum-supported electrocatalysts are a key component of the low-temperature fuel cell with polymer ion-exchanged membrane. A regulation of hierarchical structure of MxPt/C catalysts at different levels of the organization of such structure is the basic direction to enhance the functional characteristics of these materials. At the same time, the search for the optimal compositions and methods of synthesis for these catalysts is hampered by inhomogeneity of formed metal nanoparticles in the composition, size and architecture, as well as by features of their spatial distribution on the surface and in the pores of the carbon support particles [1,2].

The aims of this study were: obtaining of electrocatalysts based on bimetallic nanoparticles M_xPt (M = Cu, Co) of similar composition, but with different architecture and studying a microstructure of the catalysts; studying of electrochemical performance of M_xPt/C catalysts in the reactions of oxygen electroreduction (ORR) and methanol electrooxidation (MOR) in acidic media; an assessment the stability of the catalysts in the process of multiple repetition of the cyclic potential sweep.

Figure 1 shows the idealized architecture bimetallic nanoparticles, which we expected to obtain by the application of methods of joint or sequential chemical reduction of metal precursors in the carbon slurry.

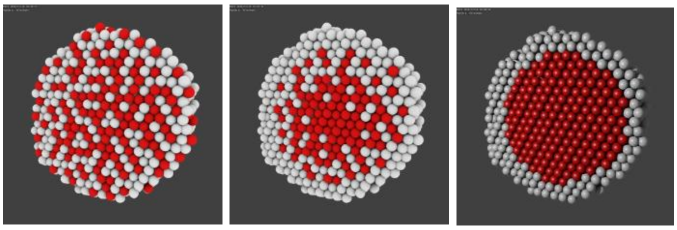

Figure 1: Schematic representation of M_xPt nanoparticles of different architectures: a solid solution, the gradient and the "core - shell" nanoparticles

It is found that the synthesis of MxPt nanoparticles by sequential reduction of metal's, and then - platinum precursors, could optimize structural characteristics of the materials. Thus, the samples of M_xPt/C electrocatalysts obtained, were not inferior commercial Pt/C samples in ORR activity and were superior in stability. Furthermore, M_xPt/C catalysts showed significantly higher tolerance to methanol and activity in MOR as compared with the commercial Pt/C catalyst with a similar Pt loading. The regimens of M_xPt/C catalysts thermo-treatment have been found, which improved their functional characteristics. Features of the electrochemical behavior of the synthesized materials are explained, considering the microstructure of metal-carbon materials and architecture of bimetallic nanoparticles.

Acknowledgement

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References:

[1] V.E. Guterman, S.V. Belenov, A.Yu. Pakharev, M. Min, N.Yu. Tabachkova, E.B. Mikheykina, L.L. Vysochina, T.A. Lastovina, Pt-M/C (M = Cu, Ag) electrocatalysts with inhomogeneous distribution of metals in the nanoparticles, Int. J. of Hydrogen Energy, 2016, 41 (3), pp. 1609 -1626.

[2] Vasiliy V. Pryadchenko, Vasiliy V. Srabionyan, Sergey V. Belenov, Vadim A. Volochaev, A.A. Kurzin, Leon A. Avakyan, Ivo Zizak, Vladimir E. Guterman, Lusegen A. Bugaev, Bimetallic PtCu Nanoparticles in PtCu/C Electrocatalysts: Structural and Electrochemical Characterization, Applied Catalysis A: General, 2016, 525, pp. 226 – 236.

KN 189

Component distribution in electrodeposited alloys and multilayers

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The importance of electrodeposited metals and multilayers keeps growing due to various properties of high technical relevance such as corrosion protection, mechanical and magnetic properties etc. In parallel, an immense improvement of the composition depth profiling methods took place in the last decades. Instead of just a simple bulk composition analysis (e.g., with the standard energy dispersive analysis in the scanning electron microscope), nowadays a large variety of instrument are available with the capability of nanometric in-depth resolution. In order to exploit the opportunity offered by these up-to-date instruments, a large variety of electrodeposited alloys and multilayers have been studied. The present lecture offers a comprehensive summary of these results. For sputtering-based depth profiling methods, the advantage of the application of the reverse depth profiling direction was also taken of, highlighting the composition variations in the near-substrate zone of the deposit that is normally not available with a sufficient resolution if the sputtering is carried out with the normal direction.

Samples studied were all prepared at room temperature with either galvanostatic plating or a two-pulse plating on silicon substrates previously covered with a Cr(5nm)/Cu(20nm) bilayer to provide both adhesion and conductivity. When the deposit was removed from the substrate, the deposit of interest was also plated with a nickel layer of a few micrometer in order to make the sample self-supporting. The Si/Cr/Cu cathodes were applied in two configurations: (i) facing upwards in the bottom of the cell with a stagnant electrolyte solution; (ii) as a rotating electrode facing downward. The composition depth profiling studies were performed with either Secondary Neutral Mass Spectrometry (SNMS) or Glow Discharge – Time-of-Flight Mass Spectrometry (GD-ToFMS), while elemental maps were also obtained in the Transmission Electron Microscope (TEM).

The general experience was that in stagnant solutions, the preferentially deposited component(s) of the electroplated alloy accumulate in the near-substrate zone as compared to the mean alloy composition achieved during the steady-state deposition. This accumulation trend proved to be independent of either the substrate or the alloying elements. In ternary systems, a correlation between the mole fraction of the preferentially deposited elements was found, which can be explained as an interplay of the deposition preference and the depletion of the electrolyte solution in the cathode vicinity. The correlation between the mole fraction of the preferentially deposited elements could be confirmed with direct TEM elemental map observations. When the hydrodynamic conditions during the deposition was well controlled (rotating electrode configuration), the near-substrate accumulation of the preferentially deposited metals could be suppressed.

For multilayers, the composition depth profiling analysis was helpful in observing two sample features that remain hidden in the bulk analysis. First, the development of the surface roughness could be taken into account in the elucidation of the composition depth profile data. Secondly, a strong correlation in the occurrence of the impurities was found, which draws the attention in the fundamental difference in the deposition of the specific layers in a multilayered deposit.

EX 150

Scanning electrochemical microscopy: New possibilities, new techniques

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The VersaSCAN is an Electrochemical scanning Microscopy single platform capable of providing spatial resolution to both electrochemical and materials-based measurements. Traditional electrochemical experiment measure an average response over the entire electrode/electrolyte interface. Rarely is a sample homogenous. Samples often consist of local sites of passivate/active nature or sites of anodic/cathodic character. This need to investigate localized phenomenon led to the emergence of scanning probe electrochemistry.

In collaboration with LEPA-EPFL, we offer the Soft Stylus Probe contact mode technique developed by Professor Hubert Girault and co-workers for constant distance SECM. The probe technology offers benefits like Constant distance SECM: SECM imaging without major topographic artefacts. Ideal for tilted, corrugated and rough samples.

EX 136

Portable electrochemistry: The new generation of portable electrochemical devices

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The potentiostat is still a young instrument, considering the average age of chemical methods and instruments. Less than 100 years ago the polarographic instrument was introduced (1922). In the 40’s the potentiostat was developed and in the 60’s the frequency response analyzer. These instruments allowed academics to investigate electrochemical processes in more detail. Analog potentiostats were bulky devices. In the 80’s digital potentiostats became available. These instruments were cheaper, easier to operate, and had the potential to be smaller. Convenient features, like auto-ranging, soon became a standard option. Today analog potentiostats are only used for very specific measurements. The majority of potentiostats are digital.

In the beginning of the new millennium PalmSens BV, at this time under the name Palm Instruments BV, was founded by Dr. Kees van Velzen. PalmSens BV developed a commercialized, pocket-sized potentiostat. This potentiostat was battery powered and was operated by a pocket PC, a PDA running on Windows CE. Together with the increasing research in and production of Screen Printed Electrodes (SPEs) the foundation for research focused on electrochemical point-of-care devices was laid. Electrochemistry could be performed anywhere.

Nowadays pocket sized high-tech electronic devices are ubiquitous and also the potentiostat has followed this development. Potentiostats have shrunk. PalmSens BV’s smallest potentiostat, EmStat3, has a footprint below 40 cm^2 and weighs only 85 g. Small potentiostats need small controllers thus smartphones or mini-computers such as Raspberry Pi are perfect computer replacements for mobile electrochemistry. The combination of an EmStat with a smartphone makes a rapidly developed point-of-care device.

We will present developments which make it easier for electrochemists and engineers to develop their own complete point-of-care system based on the EmStat platform.

Another important development in the field of portable electrochemistry was the capability to perform Electrochemical Impedance Spectroscopy (EIS). Thus portable potentiostats can compete with many desktop devices. Recently we launched the PalmSens4, a potentiostat, galvanostat, and impedance analyzer which offers high performance for field work, a flexible lab, a glove box, or wherever you need electrochemistry. The device and its specifications will be presented.

OIF 157

Investigations on the structure of PEO layers

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The Plasma electrolytic oxidation (PEO) is a type of high-voltage anodic oxidation capable to produce a thick oxide layer with a wide range of coating structures influenced by the electrolytic system. This process enables the combined adjustment of both characteristics, i.e. the morphology and chemical composition. Thus, the possibility exists to generate an individual structure and to form a crystalline surface in a single step respectively [1, 2]. A highly porous surface with a high crystalline content is ensured through the process of plasma electrolytic oxidation of pure titanium. In the present study the plasma electrolytic oxidized TiO2-layer were investigated about its crystallinity through the layer thickness. The layers were prepared with a high applied voltage to optimize the crystallinity of the PEO layer. Raman spectroscopy and electron backscattering diffractometry (EBSD) were selected to clarify the structure of the oxide layer in its crystallinity and phase composition. The composition of the TiO2-phases is more or less irregular distributed resulting from the higher energy input on the uppermost side of the layer. Scanning transmission electron microscopy (STEM) should provide a deeper understanding of the structure and the effects of plasma discharges on the layer. Therefore it is an indication that the plasma discharges have a strong influence on crystallite formation on top of the oxide layer.

References:

[1] *R.C. Petersen, Titanium Implant Osseointegration Problems with Alternate Solutions Using Epoxy/Carbon-Fiber-Reinforced Composite, Metals (Basel). 4 (2014) 549–569. doi:10.3390/met4040549.*

[2] *S. Stojadinović, R. Vasilić, M. Petković, B. Kasalica, I. Belča, A. Žekić, L. Zeković, Characterization of the plasma electrolytic oxidation of titanium in sodium metasilicate, Appl. Surf. Sci. 265 (2013) 226–233. doi:10.1016/j.apsusc.2012.10.183.*

OIF 187

What do laser-induced transient techniques reveal for the electrochemical systems?

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The great urgency of finding new energy sources resulted in an upsurge in the electrocatalysis and battery research. However, optimization and improvement of various energy conversion and storage systems require a better understanding of the electrochemical processes limiting their performance. Thus, further development of new in-situ characterization methodologies is of great importance. One of the methods providing a deeper insight into the electrode/electrolyte interface processes is the laser induced current transient (LICT) technique. This technique can be easily combined with other commonly used methods (i.e. cyclic voltammetry, electrochemical impedance spectroscopy and electrochemical nano-gravimetry), providing a powerful tool for detailed characterization of various systems.

The rapid illumination of the electrode surface results in an increase in its temperature directly influencing the inner Helmholtz plane of the electric double layer [1]. As a consequence, one observes current transients whose sign, in the simplest case, corresponds to the sign of the excess electrode surface charge. The LICT is also a relatively simple technique of evaluating the potential of maximum entropy (PME) and, closely related to it, the potential of zero charge (PZC)- the fundamental properties of the electric double layer.

We present for the first time the results of the in-situ LICT technique implementation for battery systems investigating $Na_2Ni[Fe(CN)_6]$ thin films as model electrodes. Surprisingly, the electrode surface charge stays positive within the whole potential range of intercalation/de-intercalation of sodium (**Figure 1**) and potassium cations from aqueous media. This indicates that the complexity of intercalation mechanisms of alkali metal cations into the films might be oversimplified. Further, we demon-strate the influence of the electrolyte pH on the net charge of the Pt(poly) electrode surface. Apparently, the be-havior of the system is not only governed by the concentration of H^+ cations but also by the metal cations present in the electrolyte.

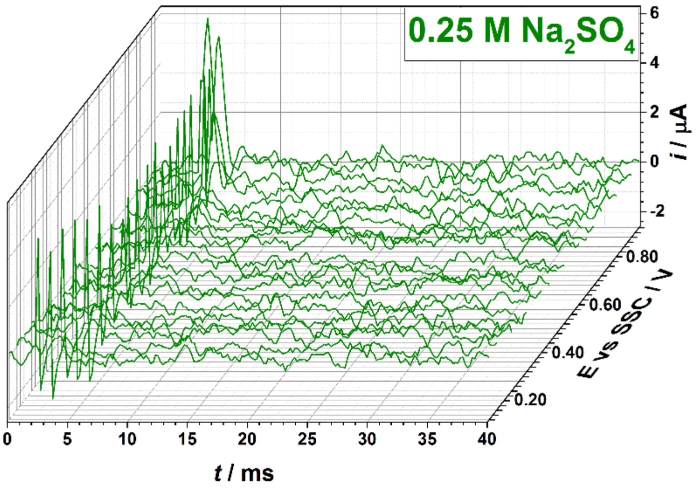

Figure 1: LICT characterization of the $Na_2Ni[Fe(CN)_6]$ film in aqueous 0.25 M Na_2SO_4

References:

[1] Garcia-Araez, N.; Climent, V.; Feliu, J. M. Evidence of Water Reorientation on Model Electrocatalytic Surfaces from Nanosecond-Laser-Pulsed Experiments. J. Am. Chem. Soc., ***2008****, 130, 3824-3833.*

OIF 186

Electrochemical and spectroelectrochemical studies on electron transfer reactions on transition metal complexes with π-acceptor ligands

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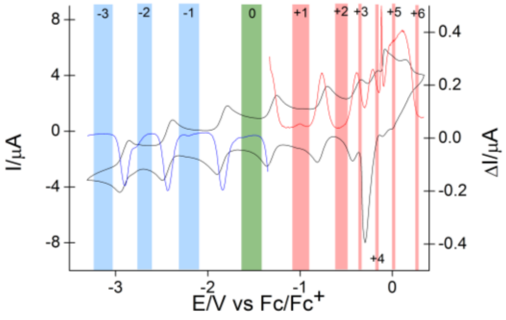
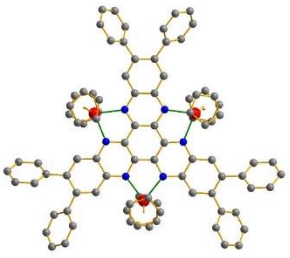
Multinuclear transition metal complexes bridged by ligands with extended π-electronic systems such as hexaphenyl-5,6,11,12,17,18-hexaaza-tribiscyclopentadienyl titaniumnaphtylene $[(Cp_2Ti)_3HATN(Ph)_6]$ show a variety of complicated electronic transitions and electron transfer reactions.[1] They are therefore intensively investigated as artificial analogues to a number of natural systems capable of converting light into chemical energy by translocating charges over large distances or to generate light efficiently.[1] While a systematic understanding of the photochemistry and electrochemistry has been atained for binuclear complexes,[1] much less is known about trinuclear and multinuclear complexes.[2]

Trinuclear titanocene(II) complexes include formally three titanocene(II) fragments with two d-electrons, i.e. they contain six potential d-electrons. The voltammogramm of $[(Cp_2Ti)_3HATN(Ph)_6]$ shows three reduction waves and six oxidation waves. Solution spectra of $[(Cp_2Ti)_3HATN(Ph)_6]$ as well as of its electrochemically formed products $[(Cp_2Ti)_3HATN(Ph)_6]^-$, $[(Cp_2Ti)_3HATN(Ph)_6]^+$ and $[(Cp_2Ti)_3HATN(Ph)_6]^{2+}$ show electronic transition in the UV, visible and NIR ranges.

The existance of a single occupied molecular orbital (SOMO) populated by a single electron transferred from one of the Ti(II) centers to the $HATN(Ph)_6$ ligand gives rise to several characteristic electronic transitions from which the most prominent is the intervalence charge transfer (IVCT) transition between the Ti(III) center and the remaining Ti(II) centers. IVCT is devided into two steps: first an electron transfers from metal to ligand (MLCT) and than from ligand to metal (LMCT). Another transition related to the SOMO is the ligand-centered SOMO-LUMO transition. When oxidized to $[(Cp_2Ti)_3HATN(Ph)_6]^+$, one Ti(II) center is transformed to Ti(III). The electronic configuration of the $HATN(Ph)_6$ ligand is not changed. If the complex is oxidized to $[(Cp_2Ti)_3HATN(Ph)_6]^{2+}$, one electron is extracted from the SOMO. A MLCT transition is still observed in the NIR absorption spectrum, initiated by a photoinduced electron transfer from the remaining Ti(II) center to the ligand. As there is no populated SOMO, all other transitions involving the SOMO, especially the SOMO-LUMO transition, are not found in the spectrum. For the reduced form $[(Cp_2Ti)_3HATN(Ph)_6]^-$, the "SOMO" is fully occupied and becomes the new HOMO. However, one can still observe HOMO-LUMO transition and MLCT and LMCT transitions.





$[(Cp_2Ti)_3HATN(Ph)_6]$

References:

[1] S. Kitagawa, S. Masaoka, Coord. Chem. Rev. 246 (2003) 73-88.

[2] I. M. Piglosiewicz, R. Beckhaus, W. Saak and D. Haase, J. Am. Chem. Soc., 127 (2005) 14190-14191

OIF 192

Atomistic insight into the bonding of silanol molecules to oxidized aluminum surfaces

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Hybrid sol-gel coatings, which combine the properties of organic and inorganic materials, are among the most promising novel corrosion resistant coatings, used for the protection of aluminum and its alloys. Novel solutions are needed because traditional high-performance chromate conversion coatings are toxic and cancerogenic. One of the precursors for the synthesis of hybrid sol-gel coatings are silanol molecules and it is assumed that they react with the surface primarily via a condensation mechanism, as shown in figure 1a.[1,2] To shed some new light on the atomistic bonding mechanism, the interactions of a simple silanol molecule (methylsilanetriol) with a model of the oxidized aluminum surface at the solid/vacuum interface, were studied within the framework of Density Functional Theory (DFT) utilizing periodic boundary conditions and the PBE exchange-correlation functional. The condensation reaction between two methylsilanetriols in the gas-phase (figure 1b) was compared to the condensation reaction between the molecule and the oxidized surface (figure 1a). According to the calculations both reaction energies are exothermic. The reaction of the molecule with the surface is by about 0.2 eV more exothermic, indicating that the bond between the molecule and the surface is slightly stronger than the bond between the silanol molecules themselves. Our calculations thus show that the currently proposed silanol–surface bonding mechanism is physically sound.

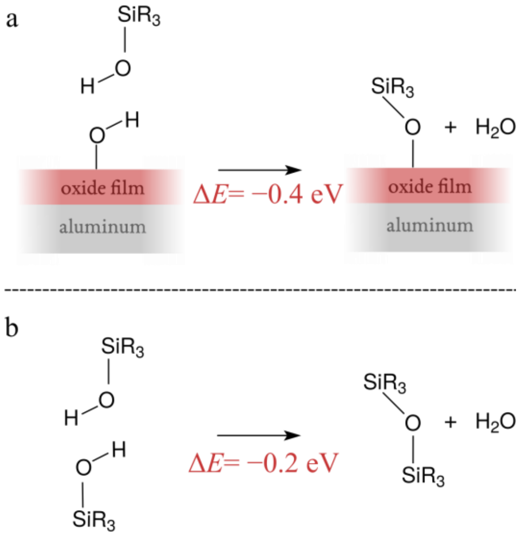

Figure 1: a) Reaction scheme and the calculated reaction energy (ΔE) of a silanol molecule reacting with the surface via the proposed condensation mechanism. b) Reaction scheme and the calculated ΔE of the dimerization reaction between two silanol molecules

References:

[1] *B. Arkles, J.R. Steinmetz, J. Zazyczny, P. Mehta, J. Adhesion Sci. Technol.* ***1992****, 6, 193–206.*

[2] *P. Rodič, J. Iskra, I. Milošev, J. Sol-Gel Sci. Technol.* ***2014****, 70, 90–103*

OIF 204

A method to compute the current transient generated by nucleation and growth of metal particles under mixed kinetic-diffusion control

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Metal electrodeposition on foreign substrates proceeds through the formation of nuclei at active sites randomly distributed over the electrode surface. Following the formation of nuclei, particles are grown by diffusion of metal ions to nuclei and successive charge transfer at the electrolyte/particle interface. Irrespective of the particle growth regime (diffusion, mixed kinetic-diffusion, kinetic control), particle size distribution and morphology are influenced by the nucleation rate A and by the saturation number density of nuclei N_0 [1]. Therefore, controlling the size and morphology of electrodeposited nanoparticles imposes to predict the dependence of A and N_0 on electrodeposition parameters. For this purpose, an effective method is to fit chronoamperometric current transients by models describing the dependence of the current transient on A and N_0 [1, 2]. In this framework, the application of the model proposed by Scharifker and Mostany (SM) [2] for electrochemical nucleation and three-dimensional diffusion controlled growth is the consolidated practice in the study of electrodeposition. However, the SM model can hardly be extended to cover deviations from three-dimensional diffusion control including, for example, mixed kinetic-diffusion control [1] or non-negligible contribution of surface diffusion to particle growth.

In this contribution, a novel method is presented to compute the current transient generated by electrochemical nucleation and three-dimensional growth of metal nanoparticles under the general case of mixed kinetic-diffusion control. The proposed method, which is derived from the integral formulation of the multi-particle diffusion problem [3], reduces the computation of the current transient to the solution of a set of integro-differential equations and can predict the average size of particles nucleating within any prescribed time interval. We demonstrate that the method can overcome the limits imposed by the application of the SM approach to mixed kinetic-diffusion control [1]. Preliminary results are illustrated in Fig.1. This compares the chronoamperometric current transients predicted by the proposed method with the detailed numerical solution of the multi-particle diffusion problem [3] for the case of instantaneous nucleation at different values of the dimensionless growth constant $K_{GD}=k_G/DN_0^{1/2}$, k_G and D denoting the charge transfer kinetic constant and the diffusion coefficient, respectively.

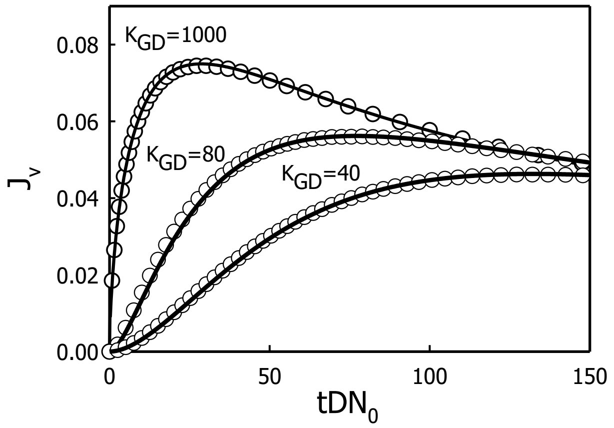

Figure 1: Comparison between the current transients predicted by the proposed method (solid lines) and by detailed numerical solution of the multi-particle diffusion problem (empty circles)

References:

[1] P. Altimari, F. Pagnanelli. Electrochim. Acta, 206 (2016) 116-126.

[2] B.R. Scharifker, J. Mostany. J, Electroanalytical. Chem., 177 (1984) 13-23.

[3] Y. Cao, A.C. West. J. Electrochem. Soc., 149 (2002) C223-C228.

OCA 146

Understanding Ru-Ti interplay in electrocatalysis

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Chlorine is produced electrochemically at annual rates of approx. 40 million tonnes of chlorine at the cost of 150 TWh (approx. 10% of the chemical industry consumption); producing more than 100 million tonnes of carbon dioxide. The net efficiency of the chlor-alkali industry is high (approx. 95%) with an estimated cost of 675 EUR per tonne of chlorine. An increase in efficiency by only 1% will result into savings of approx. 500 million EUR. [1]

Oxygen evolution reaction (OER) is a competing reaction, in the chlor-alkali industry, as it is thermodynamically favored but kinetically hindered. Therefore, OER is considered a parasitic reaction and a complete suppression is desired. State-of-the-art electrocatalysts for the chlor-alkali industry are based on Ru-Ti mixed oxides. Recent theoretical studies on the active sites in chlorine evolution [2] are opposing the general belief that RuO_2 is the active site.[3]

Herein, we present our recent findings on the attempt to identify the active sites for chlorine evolution on nanocrystalline oxides. Our electrochemical tests corroborated with structural characterization show that the concentration and position of Ti atoms can enhance or suppress the OER. X-ray absorption spectra points to a structural distortion of the expected rutile structure which we believe to be the cause for the OER enhancement.

References:

[1] *EuroChlor. Chlorine industry review 2014-2015. 2014.*

[2] *Karlsson RKB, Hansen H A, Bligaard T, Cornell A, Pettersson LGM. Ti atoms in Ru0.3Ti0.7O2 mixed oxides form active and selective sites for electrochemical chlorine evolution. Electrochim Acta 2014;146:733–40. doi:10.1016/j.electacta.2014.09.056.*

[3] *Trasatti S. Physical Electrochemistry of Ceramic Oxides. Electrochim Acta 1991;36:225–41.*

OCA 164

Influence of the thickness of Au sublayer on the catalytic properties of Ir films prepared by DCMS

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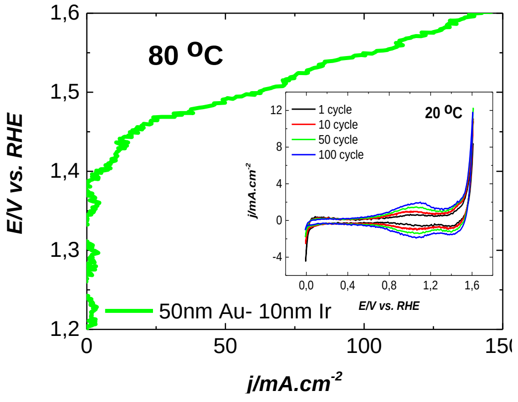
The PEM electrolysis of water is an attractive and efficient method for producing hydrogen and oxygen at low temperature. The development of proton exchange membrane water electrolyzers (PEMWE) has been held back by the cost of components such as the PEM (proton exchange membrane) and the precious metal electrocatalysts. Since there are still no non-noble metal electrocatalysts with satisfactory activities, it becomes vital to reduce production costs by improving the specific performance and durability of the well established noble metal electrocatalysts. On the hydrogen side of the cell, platinum provides the best performance and is commonly used for the PEMWE cathode. The most of the overpotential losses are related to the electrochemical processes at the anode, where the oxygen evolution reaction (OER) takes place. Therefore, the development and optimization of anode electrocatalysts is of great importance for PEMWE technology. The extensively studied catalysts for oxygen side are Ir, IrO_x, RuO_x.

In the last decade the method of magnetron sputtering (MS) it has been introduced as an alternative of the classical methods for catalysts preparation offering several advantages as homogeneous distribution of the metal particles and low metal loading (down to 10 μg cm^{-2}). The catalysts prepared by MS are deposited as thin compact (mono, bi- or poly- metallic, and/or oxide) films upon selected substrate material or even directly onto the polymer electrolyte membrane.



This work presents a research on the preparation of composite Au-Ir films deposited by direct current magnetron sputtering (DCMS) on glass and carbon substrates over 25nm Ti layer in various thickness combinations and evaluation of their catalytic activity toward oxygen evolution reaction (OER) in water electrolyzers. The composition, surface structure, and morphology of the deposited sputtered films are characterized by XRD and XPS analysis. The catalytic efficiency is evaluated in acid aqueous solution (0.5M H_2SO_4) using a standard three electrode cell and PEM cell using the conventional electrochemical methods of cyclic voltammetry and steady state polarization curves (the figure presents measurements in PEM cell). It is found that by proper variations in the films thickness it is possible to realize synergetic effects leading to essential decrease in Ir loading and the cost of catalysis without sacrifice in efficiency. The research also proves that the method of DCMS could be used as precise technique for deposition of multilayered catalysts with controlled thickness and tailored synergetic effects between the components.

OCA 184

Electrooxidation compositional mapping of copper-based thin film combinatorial libraries for sensor applications

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Combinatorial approaches for development of new materials are the most efficient ways toward identifying compositions with enhanced properties. Thin film combinatorial libraries are obtained from vapor phase using multiple source geometries where each alloying source is purposefully positioned off axis with respect to the substrate center. The obtained compositional spread along the substrate is screened and compositional mappings of the property of interest are performed [1]. Copper and Cu alloys are presenting a widely varied field of application. Besides the predominant use of pure Cu for electrical conductors a number of alloys possess high industrial importance due to their high mechanical strength, good thermal conductivity and excellent corrosion resistance. In the present work Cu-Ni, Cu-Zn and Cu-Pd thin film combinatorial libraries are evaluated for use in electrooxidative sensing [2-4]. Enhanced electrocatalytic activity was identified in each library for certain compositions during the oxidation of formaldehyde and glucose. After a compositional mapping, for all analyzed Cu-based libraries compositionally induced microstructural and crystallographic changes were identified and their influence on the sensing behavior was evaluated. In part (a) of Figure 1 the principle of glucose detection via electrooxidation is schematically presented. The same principle is used for formaldehyde detection.

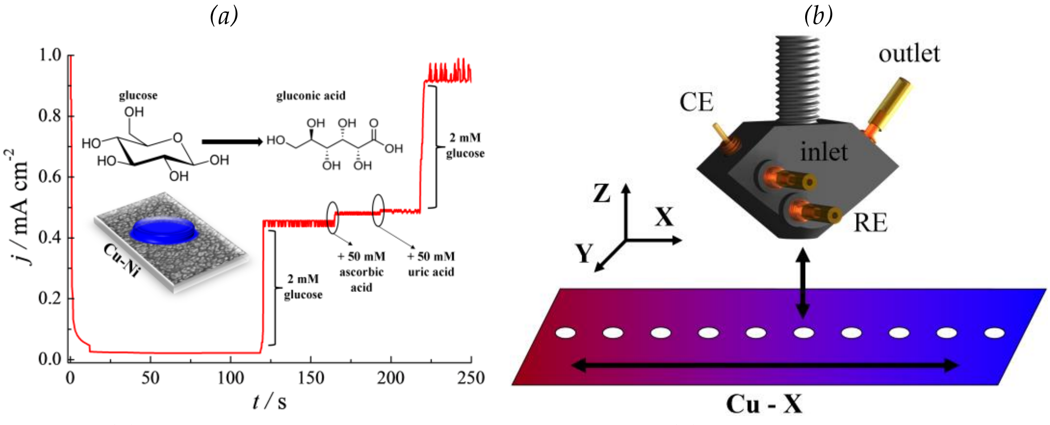

Figure 1: (a) Glucose detection via electrooxidation *(b) Flow-type scanning droplet cell*

The electrochemical response to both formaldehyde and glucose was investigated using scanning droplet cell microscopy with flowing electrolyte (FT-SDCM). The technique allows for localized addressing of a well defined area on the surface of the library due to its contact operation mode. Using 3D printing the body of the flow cell was realized accommodating a counter electrode (CE) and a reference electrode (RE) together with the electrolyte inlet and outlet as shown in part (b) of Figure 1. At the tip of the cell a predefined opening allows the electrolyte to come in contact with the investigated surface and the sealing is ensured by using a patterned silicone O-ring. The diameter of the area addressed for a single measurement can vary in a wide range from 50 µm to several mm providing a very good spatial resolution. All Cu-based thin film libraries were scanned in this way with high compositional resolution allowing a precise identification of interesting alloys to be further used for actual sensors development.

References:

[1] A.I. Mardare, A. Ludwig, A. Savan, A.W. Hassel, Sci. Technol. Adv. Mater., ***15*** *(2014) 015006.*

[2] I. Pötzelberger, A.I. Mardare, A.W. Hassel, Phys. Status Solidi A, 212, (2015) 1184–1190.

[3] I. Pötzelberger, A.I. Mardare, A.W. Hassel, Appl. Surf. Sci. ***In Press****, (2017)*

[4] I. Pötzelberger, C.C. Mardare, L.M. Uiberlacker, S. Hild, A.I. Mardare, A.W. Hassel, RSC Adv. ***7*** *(2017) 6031-6039*

OCA 194

Carbon catalysts for hydrogen peroxide production by oxygen electroreduction

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It is well known that the oxygen reduction reaction can proceed through two pathways: the four-electron and the two-electron one, which result in the formation of water or H_2O_2, respectively. The former has been in the focus of research in electrocatalysis recently because of its significance for fuel cells and batteries. However, it is important to note that hydrogen peroxide is an important industrial chemical. It is an environmentally friendly oxidant, important for water disinfection, bleaching and synthesis, its annual production reaching about 3 000 000t [1]. H_2O_2 is currently produced in the anthraquinone process, which is a sequential batch process requiring large-scale facilities and a large amounts of energy. The electrochemical production of H_2O_2 would be more attractive, allowing on-site production requiring only air, water, and electricity (which could be supplied by renewable sources). At DTU Physics a class of catalyst materials based on Pt and Pd alloyed with Hg have been developed, which are highly active and selective for H_2O_2 generation by oxygen reduction [2,3]. However, the use of mercury limits the potential application of these materials due to its toxicity. Conversely, carbon-based materials, which are inexpensive and environment-friendly, are a promising alternative. In this work, we examine different carbon black materials as catalysts for the electroreduction of molecular oxygen to H_2O_2. The faradaic efficiencies of these materials for the desired reaction, which is competing with the four-electron pathway, are vastly different, ranging 18-81%. In order to elucidate the source of the difference in the electrocatalytic properties of these materials a series of investigations were undertaken including XPS, TEM imaging, BET surface area determination, coupled with electrochemical measurements and the modification of the materials by wet oxidation, high temperature treatments, etc. The results show that their ORR selectivity likely depends on several factors, notably the specific surface area (Figure 1A) and the ratio of carbon and oxygen atoms on the surface (Figure 1B), as well as the presence of trace elements. The results show that the 2-electron oxygen electroreduction pathway is facilitated on carbons with high surface area and an intermediate amount of surface-bound oxygen. The observed dependencies could potentially be used to design new carbon catalysts with higher faradaic efficiencies for H_2O_2 generation by oxygen electroreduction.

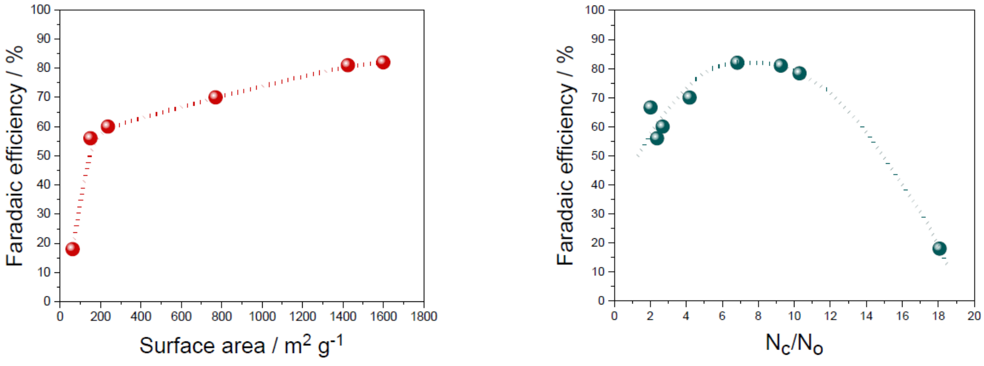

Figure 1: Dependence of the faradaic efficiency on (A) the surface area determined from BET adsorption isotherms (B) the ratio of C and O atoms on the surface determined by XPS. The dotted lines are presented as guides for the eyes

References:

[1] J.M. Campos-Martin, G. Blanco-Brieva, J.L.G. Fierro, Angew. Chem.-Int. Edit., 2006, 45, 6962.

[2] S. Siahrostami, A. Verdaguer-Casadevall, M. Karamad, D. Deiana, P. Malacrida, B. Wickman, M. Escudero-Escribano, E.A. Paoli, R. Frydendal, T.W. Hansen, I. Chorkendorff, I.E.L. Stephens, J. Rossmeisl, Nat. Mat., 2013, 12, 1137.

[3] A. Verdaguer-Casadevall, D. Deiana, M. Karamad, S. Siahrostami, P. Malacrida, T.W. Hansen, J. Rossmeisl, I. Chorkendorff, I.E.L. Stephens, Nano Lett., 2014, 14, 1603.

PL 228

Electrochemical deposition of rhenium-based alloys as thermal barrier coatings

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Rhenium (Re) is a refractory metal with a unique combination of properties. It has high melting point and excellent wear properties, it does not form carbides and does not have a ductile to brittle transition, it has excellent mechanical properties at high temperatures, and attractive catalytic properties. For these reasons, Re and its alloys have attracted much interest in many industrial applications, such as aerospace, nuclear, electrical, chemical, and biomedical.

In this presentation, I will review our six-year study of the electrodeposition and electroless plating of Re-based alloys. Issues such as the catalytic effect of iron-group metals on the deposition of rhenium, the early stages of deposition, the effects of bath deposition and pulse plating, electroless plating on carbons, and the microstructure of thin films, will be discussed.

Acknowledgements

This work was funded by the U.S. AFOSR (grant FA9550–10-1-0520) and the Israel DoD (grant number 4440258441). Atom-probe tomography (APT) characterization was conducted in collaboration with Prof. David Seidman from the Department of Materials Science and Engineering at Northwestern University.

KN 114

Electrochemical determination of selected pharmaceutical compounds combined with different analytical methods

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Electrochemical techniques are powerful and versatile analytical techniques that offer high sensitivity, accuracy, and precision with relatively low-cost instrumentation. The most common electrochemical techniques used for the analysis of pharmaceuticals and biological samples are: Cyclic Voltammetry widely used for the study of redox reactions as well as Stripping voltammetry and Pulse Voltammetry mostly used for the quantitative determination. The choice and application of most preferred electrochemical techniques is closely related to physicochemical properties of the organic functional groups that comprise drug structure, especially on redox properties of the pharmaceuticals and biomolecules in real samples.

Electrochemical techniques have been applied for the determination of pharmaceutical compounds in dosage forms such as tablets and biological samples (real and spiked urine samples, blood and serum). Various types of pharmaceutical compounds are analyzed by electrochemical techniques like: anticonvulsant drugs (derivatives of hydantoin), antibiotics (anisomycin and azithromycin), antidepressant, cardiovascular drug usually used in therapy for erectile dysfunction (sildenafil citrate) and mixture of anticonvulsant and analgesic drugs (phenobarbital sodium and paracetamol).

Electrochemical investigation of selected pharmaceutical compounds in correlation with analytical methods gave a possibility for structural identification of oxidation products and based on that to propose the oxidation mechanisms as was performed for hydantoin and anisomycin. In the case of azithromycin the electrocatalytic degradation was successfully performed by indirect oxidation revealing that electroanalytical method can be an alternative to chromatographic method in determination of azithromycin in electrolytes containing chlorine.

The obtained data show that different electrochemical methods combined with spectroscopic, spectrometric and chromatographic techniques provide fast quantitative and qualitative response of the investigated standards and commercial drugs. Some advantages of electroanalytical methods are underline such as the short analysis time, need of small volumes of investigated samples, sensitivity for the simultaneous determination of trace substances, measuring a very low concentration of analyte (nM) facilitating wide linear range. Besides, with the drug analysis in biological samples important data are collected enabling further clinical investigations.

OFM 121

Electrochemical impedance spectroscopy of cathode material modified by conducting polymer PEDOT:PSS

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Simple and mixed metal olivine type compounds such as $LiFePO_4$ and $LiFe_{0.4}Mn_{0.6}PO_4$ are considered as a promising cathode materials for lithium ion batteries. However, both compounds has low conductivity, which usually can be improved by ultra thin carbon shell coating and by nanostructuring of active particles. Recently it has been shown that PEDOT and other conducting polymers additives can positively effect on the electrochemical performance of electrode materials for lithium ion batteries. In particular, the use of PEDOT:PSS dispersion as conductive binder for olivine type cathode materials showed an increased specific capacity and high rate capability of materials [1,2].

High rate performance of electrode materials is determined by kinetics of interfacial charge transfer and Li-ion diffusion in the bulk of materials. Therefore, the investigations of the influence of different components of composition on the kinetics of interfacial charge transfer and bulk Li^+ ion transport are the issues of primary importance for understanding the intrinsic limitations for fast charge-discharge of LFP batteries and finding the rational strategy for improvement of material.

In this work we present new results on the investigations of electrochemical performance of LFP/PEDOT:PSS and LFMP/PEDOT:PSS cathodes, obtained by traditional way with PVDF binder and electrodes with the same initial cathode material modified by different conductive binders (PEDOT:PSS, CMC and their combination) with and without carbon black.

The morphology and structure of prepared composites were characterized by X-ray diffraction measurement and scanning electron microscopy. EDX analysis was performed with an energy-dispersive X-ray spectrometer X-act (Oxford Instruments, United Kingdom). All the samples showed well-defined characteristic reflections for the orthorhombic olivine-type structure of LFP and LFMP before and after mixing with PEDOT:PSS polymer dispersion, that confirm the maintenance of highly crystalline structure.

In order to get more deep insight into charge transfer and transport processes occurring in the cathode materials the systematic EIS measurements were performed and the characteristic parameters were derived by fitting to equivalent electrical circuits. The obtained kinetic parameters (interfacial resistances, effective Li^+ diffusion coefficients) allow to reveal the role of different components in electrochemical performance of LFP/PEDOT:PSS and LFMP/PEDOT:PSS materials. The comparison of the functional properties of different LFP and LFMP based materials and kinetic parameters derived was performed. It was found that the decrease of resistance Rct and increase of effective diffusion coefficients D_{eff} are main factors, responsible for observed positive effects. The observed influence of conduction polymer modification on the improvement of electrochemical performance of LFP and LFMP based cathode materials and possible reasons underlying in this effect well be discussed.

Acknowledgements

The authors are thankful to the colleagues from Interdisciplinary Resource centre for Nanotechnology and Resource centre "Physical methods of surface investigation" of St. Petersburg State University for providing common SEM, EDX, XPS and XRD analysis. Financial support from Russian Foundation for Basic Research (grants № 16-03-00457 and № 17-53-12029) is gratefully acknowledged.

References:

[1] S.N. Eliseeva, O.V. Levin, E.G. Tolstopjatova, E.V. Alekseeva, R.V. Apraksin, V.V. Kondratiev, Mater. Lett., 161(2015) 117.

[2] R.V. Apraksin, S.N.Eliseeva, E.G.Tolstopjatova, A.M.Rumyantsev, V.V.Zhdanov, V.V. Kondratiev, Mater. Lett. 176 (2016) 248.

OFM 133

Electroless deposition of metal particles on conducting polymer layers

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Metal deposition on conducting polymer (CP) substrates is intensively studied in view of the numerous applications of metal particles-modified electrodes, e.g. in the fields of electrocatalysis, electroanalysis and electrochemical sensing. The main approach used to deposit metal particles on supported CP layers consists in electrocrystallisation carried out under potentiostatic, pulse-potentiostatic or galvanostatic conditions. There is also another most specific opportunity to deposit metal particles on CPs by using the intrinsic redox properties of the polymer material. In this approach pre-reduced CP layers are put in contact with solutions of metal ions and a spontaneous process based on the coupling of metal ions reduction and CP oxidation takes place. This process is self-confined and depends markedly on a number of factors such as thickness and doping ions of the CP layers, concentration and ionic state (cations or anion complexes) of the source for metal reduction ([1-5] and literature cited therein). An overview of results obtained in the case of electroless deposition of silver and palladium on poly(3,4-ethylenedioxythiphene) (PEDOT)-coated electrodes will be given.

PEDOT layers are obtained by electrochemical polymerization of the monomer in the presence of perchlorate, dodecylsulfate or polysterensulfate ions. Two different electrode substrates (glassy carbon,- GCE or spectral graphite, SGE) are used for the polymerization of EDOT. It is found that depending on the doping ions of PEDOT there are marked differences with respect to the polymerization kinetics, surface morphology and finally amount of deposited metal. In all studied cases use of SDS-doped PEDOT results in larger amounts of the obtained metallic phase.

It is established that the electrode substrate plays a significant role for the polymerisation of PEDOT-PSS with delayed formation of the PEDOT layers observed on GCE in comparison to SGE. For PEDOT with one and the same polymerization charge obtained at both types of electrodes the coupled metal ions reduction/CP oxidation proceeds in completely different ways. A steep OCP increase for GCE in contrast to much slower and gradual OCP change for SGE is observed and results in ten times larger amount of palladium deposited at PEDOT-PSS/SGE. Palladium electroless deposition for both PSS-doped and SDS-doped PEDOT results in the formation of Pd nanoparticles with mean size of about 5 nm and homogeneous distribution over the polymer surface with larger amount of metal obtained in the PEDOT/SDS case.

References:

[1] *S. Ivanov, V. Tsakova,* Electrochimica Acta, *50 (2005) 5616-5623.*

[2] *V. Lyutov, V. Tsakova, J. Solid State Electrochem., 15 (2011) 2553-2562.*

[3] *V. Lyutov, V. Tsakova, J. Electroanal. Chem., 661 (2011) 186-191.*

[4] *M. Ilieva, A. Nakova, V. Tsakova, J. Solid State Electrochem., 20 (2016) 3015-3023.*

[5] *V. Karabozhikova, V. Tsakova, Chemical Papers, 71 (2017) 339-346.*

OFM 167

Novel Li-ion capacitor having an ultra-high specific capacity comparable to that of Li-ion batteries

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In an attempt to create an ultra-high capacity capacitor, we examined the application of a "nanoionics mechanism" proposed by J. Maier by the use of activated carbon fiber. The preparation process involved vacuum-deposition of Sn on the surface of activated carbon fiber (Kuractive #2000, Kureha Chemicals made, specific surface area: 2000 m^2 g^{-1}), followed by oxidation by heating in the presence of oxygen (to form SnO_2) and immersion into an organic solvent containing 1 M of $LiClO_4$. We measured the specific capacity under a constant current charging/discharging of 1C rate. The measured capacity was as high as 250 mAh/g, i, e., the same as that of a Li-ion battery. Apart from Sn we also examined Pd, Cu, In and Ag, and obtained comparable results.

When these metals were vacuum-deposited on the surface of activated carbon fiber, followed by heating in the presence of low pressure of oxygen, the cyclic voltammograms of the treated activated carbon fiber was successfully stabilized due to the formation of a thin metal oxide film at the surface.

Reference:

[1] *P. Balaya, A.j. Bhattacharyya, J. Jamnik, Yu.F. Zhukovskii, E.A. Kotomin, and J. Maier, J. Power Sources., 159(1), (2006) 171-178.*

OFM 180

Colloidal coatings with improved corrosion inhibition properties

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A number of different methods have been used to prevent metal corrosion, such as coating, electroplating, cathodic protection and use of inhibitors. The protection of metal surfaces with porous sol-gel coatings create an opportunity to further improve corrosion protection by impregnating the pores with corrosion inhibitors. These entrapped molecules can be released upon damage of the protected surface. The released molecules can provide a self-healing effect by either sealing the damaged area (forming a mono/multilayer film or an insoluble complex on the corrosion site) or by getting adsorbed on the metal surface, acting as an intelligent coating and hindering corrosion at the damaged area.

Due to the fact that the accumulation and release of the inhibitors in the porous systems is problematic to follow, in this study, different dyes with inhibiting properties (methylene blue and indigo carmine) entrapped in mesoporous coatings were used as model systems for self-healing coatings. It is important that the hydrophobic layers entrap the dyes indefinitely so that release only occurs upon damage to the surface.

Mesoporous silica coatings were produced using the dip-coating method with a non-ionic (Pluronic P-123) and cationic (cetyltrimethylammonium bromide) surfactants as templates. After thermal treatment, the porous silica coatings were impregnated with methylene blue dye. The inhibitor was trapped in the pores by rendering the coating hydrophobic by silylation.

A similar system was produced with a chitosan layer impregnated with indigo carmine dye. Although the chitosan layers are not stable in acidic environments, an inhibitor impregnated chitosan layer could provide good temporary corrosion protection

The dye release, its accumulation in the layers and the film thickness were studied in model experiments on glass surfaces by using UV- Vis spectrophotometry. The hydrophobic properties of the coatings have been examined by wettability measurements by using the sessile drop method and drop-build-up technique. Corrosion protective properties have been studied on Zn plates using electrochemical methods.

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References:

K. Palanisamy, A. Sekar, Investigation of Corrosion Protection Efficiency of Indigo Carmine on Carbon Steel in Acidic Environment, Journal of Advanced Electrochemistry 2 (4) (2016) 126-129

E.E. Oguzie, Corrosion inhibition of mild steel in hydrochloric acid solution by methylene blue dye, Materials Letters 59 (2005) 1076-1079

E. Hild, A. Deák, L. Naszályi, Ö. Sepsi, N. Ábrahám, Z. Hórvölgyi, Use of the optical admittance function and its WKB approximation to simulate and evaluate transmittance spectra of graded-index colloidal films, Journal of Optics A: Pure and Applied Optics, 9, 920-930 (2007).

E. Albert, N. Cotolan, N. Nagy, Gy. Sáfrán, G. Szabó, L.M. Mureşan, Z. Hórvölgyi, Mesoporous silica coatings with improved corrosion protection properties, Microporous and and Mesoporous Materials, 206 (2015) 102-113

OCR 207

Alkyl and perfluoro compounds as corrosion inhibitors for aluminium alloys containing Si

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Aluminium and its alloys are widely used in numerous applications due to their remarkable properties which enable these materials to be engineered to the demands of specific applications. Suitable mechanical properties are often achieved by alloying aluminium with silicon, copper, magnesium, zinc or manganese. The presence of alloying elements, however, renders the alloys susceptible to localized corrosion, which represents a serious drawback especially in chloride containing environment and should be additionally protected against corrosion. Development of new corrosion protection should be in accordance with environmentally friendly yet efficient technologies.

The basic idea of the current research study is to design multifunctional compounds by integrating corrosion inhibitors and hydrophobic agents with lipophilic or fluorous properties into hybrid matrices so as to produce a corrosion resistant hydrophobic coating that display good adhesion to Al substrates, i.e. AlSi7Mg0.3 and AlSi9Cu3. The first step is to test potential candidates for (i) hydrophobic compounds and (ii) corrosion inhibitor compounds. Alkyl and perfluoro chains of defined chain length were regarded with and without addition of various functional groups: carboxylic, azide, imidazole, disulphide, thiol, and thiocyanate. Compounds were commercially available or synthesized in our laboratories. These compounds were tested in the form of self-assembled coatings formed by immersion of Al substrate in ethanol solution. Related corrosion testing included immersion in 0.6 M NaCl for 1 week and electrochemical testing through potentiodynamic polarization curves in NaCl solution.

Based on the results obtained the candidates for further incorporation in corrosion resistant coatings will be tested.

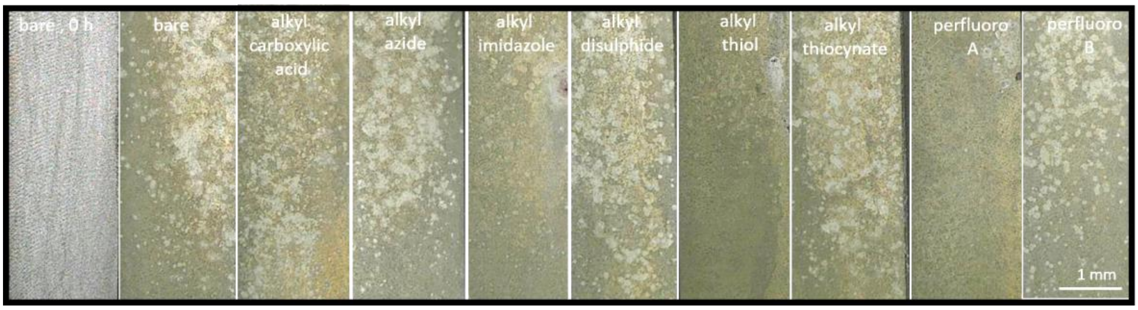

Figure 1: Images of bare AlSi9Cu3 aluminium alloy before immersion, bare alloy after immersion, and alloys coated with different types of inhibitor coatings after immersion for 7 days in 0.6 M NaCl

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OCR 123

Investigation of titanium dissolution in acidic media with rotating ring-disk electrodes by using dual dynamic potential control

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Titanium and titanium based alloys are widely applied in the medical area as prostheses and implants due to their outstanding biocompatibility and corrosion resistance. However, in aqueous solutions under certain conditions i.e. in the presence of fluoride ions [1] or in case of acidic media [2], the dissolution of the titanium based implants occurs. Since in case of dental implants these conditions are particularly frequent the investigation of the products resulting in these reactions is very important. One of the most convenient possibility for this purpose is using a rotating ring-disk electrode (RRDE).

RRDEs are commonly applied examples of generator-collector systems, which are experimental devices for detecting the intermediates of electrode processes. In our laboratory we constructed a unique electrochemical workstation which allows independent, simultaneous and dynamic potential control of the disk and ring electrodes. This fully dynamic control improves the sensitivity and usability of RRDEs to a great extent. During our experiments we used a Ti disk Pt ring RRDE.

In our work we examined the active and passive dissolution processes of titanium in acidic media applying dual potentiodynamic control. We used the so-called "dual cyclic voltammetry" [3] for the examination of the dissolution process at negative potentials in solutions with different fluoride concentrations. By applying digital signal processing techniques, these measurements provide a possibility of creating three dimensional "electrochemical maps" (see Fig. 1), showing the formation of different products during the polarization of the titanium disk electrode in different electrolytes. The dissolution process occurring during the oxide formation was examined applying suitable potential steps on the Ti disk electrode. The formation of a reducible product on the disk electrode as a result of the potential step was detected on the ring electrode.

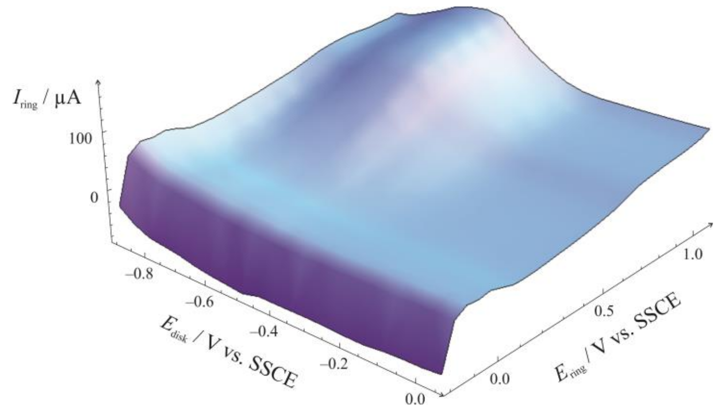

Figure 1: Three dimensional "electro-chemical map": current measured on the ring electrode (I_{ring}) as a function of the disk and ring potentials (E_{disk} and E_{ring}) in 1 M H_2SO_4 20 mM NaF aqueous solution. The titanium disk was polarized from 100 mV vs. SSCE to the negative potentials at 1 mV/s sweep rate while several cyclic voltammograms were recorded at 100 mV/s sweep rate on the platinum ring. The electrode tip was rotated at 500 min^{-1}

Acknowledgement

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References:

[1] *De-Sheng Kong: The influence of fluoride on the physicochemical properties of anodic oxide films formed on titanium surfaces. Langmuir 24 (2008), 5324–5331.*

[2] *R.D. Armstrong, J.A. Harrison, H.R. Thirsk, R. Whitfield: The anodic dissolution of titanium in sulphuric acid. J. Electrochem. Soc. 117 (1970), 1003–1006.*

[3] *S. Vesztergom, M. Ujvári, G.G. Láng: RRDE experiments with independent potential scans at the ring and disk electrodes – 3D map of intermediates and products of electrode processes, Electrochemistry Communications 19 (2012) 1.*

OCR 174

Simple and fast fabrication of superhydrophobic and corrosion resistant coatings based on fluoroalkyl silanes

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We have developed a relatively simple and fast procedure for preparation of superhydrophobic and corrosion resistant coatings based on fluoroalkyl silanes on aluminium substrate.

Formation of superhydrophobic surface on metals with a water contact angle greater than 150° and sliding angle less than 10° have attracted tremendous attention over the last decade in both academic and industrial areas, because the modified surfaces often show self-cleaning, anti-icing and anti-corrosion properties [1].

Such a high water repellency is due to rough surface microstructure and low surface energy. Nowadays the research on superhydrophobic surface has been mainly focused on fluoroalkyl silanes [1, 2]. They have been widely used as surface modification agents because of their high hydrophobic properties. Coatings containing fluorochemicals with a C–F bond find applications in many fields in electronics, optics and, recently, in barrier corrosion protection. The high resistance to solvents, acids and bases and ability to significantly reduce the frictions are main advantage of these coatings.

Aluminium holds an important position in modern industry because of superior physical and mechanical properties. Its corrosion resistance is based on compact and chemically stable oxide film that is spontaneously formed on the surface. However, when aluminium is subjected to some harsh environment such as Cl^- containing solution, it is prone to corrosion. Therefore it crucial to improve its anticorrosion properties. One of the options is surface modification to obtain superhydrophobic surface [1].

Alkyl and fluoroalkyl silanes with different chain length were studied to investigate the effect of C–F and C–H groups on hydrophobicity and corrosion resistance. Superhydrophobic coating formed by fluoroalkyl silane (FAS) provides a highly efficient corrosion-resistant coating during immersion in an aqueous solution of 0.5 M NaCl solution. The corrosion properties were elaborated also using electrochemical measurements. The surface characterization was performed using contact profilometer, scanning electron microscopy, IR spectroscopy and water contact angle. The stability was tested according to standard protocol for assessing durability of superhydrophobic surfaces, which also confirmed improvement in self-cleaning and anti-icing properties [3].

Keywords: aluminium, superhydrophobic coatings, corrosion protection, self-cleaning, anti-icing.

References:

[1] *N. J. Shirtcliffe, G. McHale, S. Atherton, M. I. Newton, (2010), An introduction to superhydrophobicity, Advances in Colloid and Interface Science, 161, 124–138.*

[2] *I. Bernagozzi, C. Antonini, F. Villa, M. Marengo, (2014), Fabricating superhydrophobic aluminum: An optimized one-step wet synthesis using fluoroalkyl silane, Colloids and Surfaces A: Physicochem. Eng. Aspects, 441, 919–924.*

[3] *I. Malavasi, I. Bernagozzi, C. Antonini, M. Marengo, (2015), Towards a standard protocol for assessing durability of superhydrophobic surfaces, Surface Innovations, 3, 49–60.*

OCR 122

Piperine for corrosion protection of iron B 500 in acidic media

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Corrosion control of metals is of technical, economic, environmental, and aesthetical importance. The use of inhibitors is one of the best options of protecting metals and alloys against corrosion. The environmental toxicity of organic corrosion inhibitors has prompted the search for green corrosion inhibitors as they are biodegradable, do not contain heavy metals or other toxic compounds. As in addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable. We have used piperine extracted by black pepper as corrosion inhibitor. The material under investigation is Iron B 500 usually applied to concrete as reinforcing bars. The inhibition effect of piperine on the corrosion behavior of iron is investigation in sulfuric acid in presence of chloride ions, in form of NaCl (H_2SO_4 1M + Cl^- 10^{-3}M). Potentiodynamic polarization method and mass loss measurements are used for inhibitor efficiency testing. Both methods show that inhibition efficiency increases with the increasing concentration of the inhibitors and corrosion rate decreases with the increasing concentration of the inhibitors. Piperine for potentiodynamic polarization method and mass loss measurements gave respectively 84% and 58% inhibition efficiencies in concentration 1.0 g/l.

Keywords: green inhibitors, corrosion, iron B 500, piperine

OCR 185

Self-healing effect of $Ce(NO_3)_3$ in coating based on GPTMS, TEOS and SiO_2 nanoparticles applied on aluminium alloy 7075-T6

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Aluminium alloy AA7075 is the most commonly used in aircraft and automotive industry. Due to the presence of intermetallic particles AA7075 is susceptible to localized corrosion in chloride solution. In the present work hybrid sol-gel coatings, based on silane precursors 3-glycidyloxypropyl(trimethoxysilane) (GPTMS) and tetraethoxysilane (TEOS) were used to protect AA7075-T6 against the corrosion. To enrich the barrier properties of coating, SiO_2 nanoparticles were added to the final solution. Self-healing effect was achieved by the incorporation of corrosion inhibitor cerium nitrate ($Ce(NO_3)_3$) into the coating. Due to oxygen reduction on cathodic sites OH^- ions causing the local increase in pH thus enabling the precipitation of cerium oxide/hydroxide. Ce^{3+} ions can further oxidize into Ce^{4+} ions and insoluble Ce(IV) oxide/hydroxide may be formed to protect cathodic sites. In the present work a multi-layer system of two sols was applied on the AA7075, where the first layer was doped with $Ce(NO_3)_3$ and the second was undoped. Self-healing effect of coatings was confirmed using different techniques such as electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy (XPS), ultraviolet-visible spectroscopy (UV-vis) and scanning electron microscopy (SEM) with chemical analysis (EDS).

According to the EIS, self-healing effect was effective after 4 days of immersion in 0.1 M NaCl (Fig. 1). The samples remained virtually undamaged for 60 days immersion in 0.1 M NaCl. Corrosion products were noticed only after 80 days of immersion, primarily at the sample borders (Fig. 2).

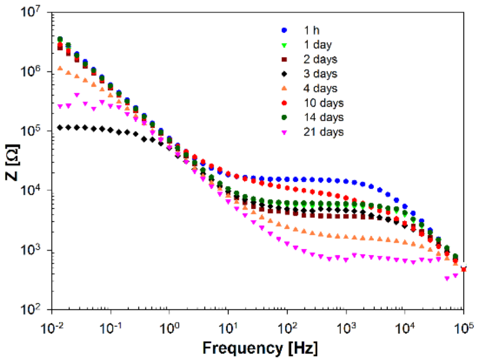

Figure 1: Electrochemical impedance measurements of AA7075 coated with multi-layer system after 1 hour, 1, 2, 3, 4, 10, 14 and 21 days of immersion in 0.1 M NaCl

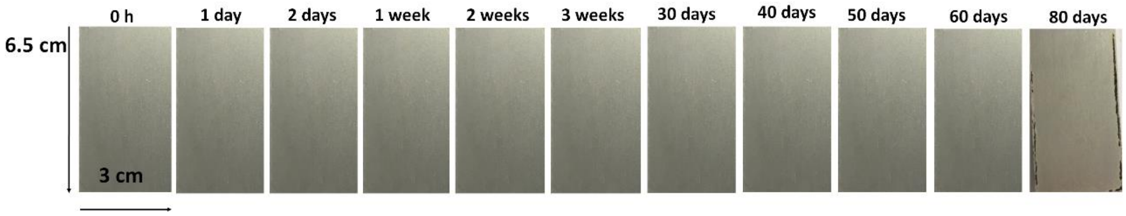

Figure 2: Images of AA7075 coated with multi-layer system, where first layer was doped with cerium and second was undoped

PL 225

Bifunctional oxygen reduction/evolution reaction (ORR/OER) catalysts for rechargeable metal-air batteries and regenerative fuel cells

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Development of active, durable and cost-efficient bifunctional electrocatalysts for oxygen reduction and evolution reactions (ORR and OER) is of outmost importance to realize the full potential of rechargeable metal-air batteries (e.g., Zn-air, Al-air, Mg-air, Li-air) and regenerative H_2-O_2 fuel cells. Manganese oxides (MnO_x) have been intensely studied especially for alkaline ORR electrocatalysis. Regarding the bifunctional ORR and OER electrocatalytic performance of MnO_x, however, improvements in activity and durability are required for implementation in commercial energy storage and conversion systems. Novel approaches are presented to enhance the bifunctional activity and durability by tuning the MnO_2 catalyst structure with co-catalyst addition, potassium ion doping and support effect (e.g., graphene and N-doped graphene). The combination of MnO_2 with a structurally different oxide co-catalyst such as perovskite ($LaCoO_3$) or fluorite-type oxide (Nd_3IrO_7) produces a synergistic catalytic effect improving the activity compared to the individual oxides. Doping of the oxide catalyst with potassium ions, either by long-term exposure to 6 M KOH or potential driven insertion (PDI), increases further the activity and durability as revealed in accelerated degradation experiments.[1,2] The effect of MnO_2 morphology on the bifunctional performance is demonstrated using a comprehensive statistically designed MnO_2 electrodeposition study. Optimizing the MnO_2 electrodeposition conditions can produce nanostructured morphologies that are favorable for bifunctional activity.[3] The electrochemical results are supported by extensive surface analysis (SEM, TEM, XPS, EDX, EELS) and explanation of the results is provided based on the scaling relationship between the binding energies of HO* and HOO* species.

References:

[1] P. H. Benhangi, A. Alfantazi and E. Gyenge, Electrochim. Acta, 123, 42 (2014).

[2] P. Hosseini-Benhangi, M. A. Garcia-Contreras, A. Alfantazi and E. L. Gyenge, J. Electrochem. Soc., 162, F1356 (2015).

[3] P. Hosseini-Benhangi, C.H. Kung, A. Alfantazi and E.L. Gyenge, submitted ACS Appl.Mat.Interfaces (2017).

KN 144

New polyazulene-based materials for heavy metal ions detection

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Azulene derivatives have been rarely used to the metal ions electroanalysis. Our study concerns the synthesis and electrochemical characterization of new azulene based monomers. Each monomer (**L**) has been used to obtain modified electrodes by electrochemical polymerization. Poly**L** films modified electrodes have been obtained and characterized by cyclic voltammetry, differential pulse-voltammetry, electrochemical impedance spectroscopy, and scanning electron microscopy, atomis force microscopy. The complexing properties of poly**L** based functional materials have been investigated towards heavy metals (Pb, Cd Hg, Cu) by preconcentration – anodic stripping technique in order to analyze their content from water samples. Derivatives of (5-[(azulen-1-yl) methylene]-2-thioxothiazolidin-4-one were found to be good ligands for heavy metals in homogeneous solutions and in heterogeneous systems based on chemically modified electrodes. Quantum mechanical calculations on azulene compounds have been performed in order to test their ability to coordinate heavy metals.

Acknowledgments

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References:

[1] Z Essaidi et al 2011 Optical Materials 33 1387

[2] T Osaka et al J. 1987 Electrochem. Soc. 134 2645

[3] P Szlachcic et al 2015 Dyes and Pigments 114 184

[4] G Buica et al 2013 J. Electroanal. Chem. 693 67

KN 103

On the electrolysis of dilute solutions of strong acids

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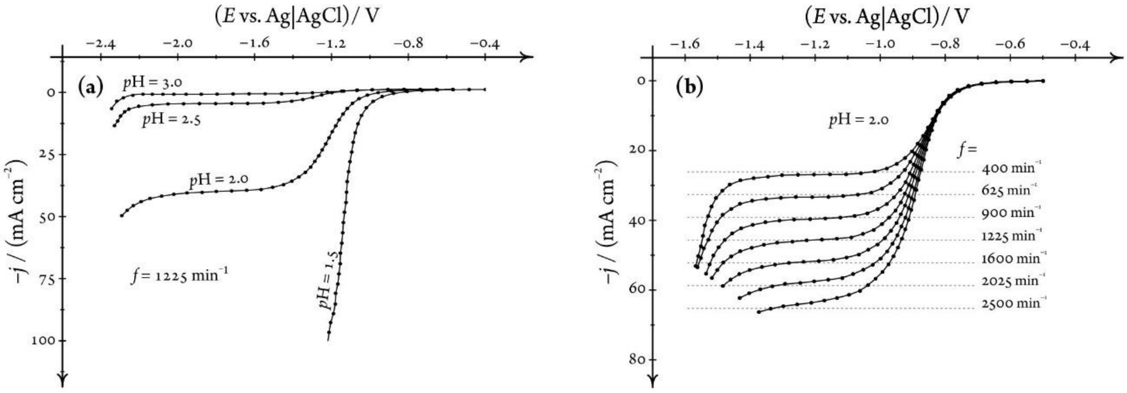
We study the effect of H^+ and OH^- diffusion on the hydrogen evolution reaction in unbuffered aqueous electrolyte solutions of mildly acidic *p*H. We demonstrate that the cathodic polarization curves measured on a Ni rotating disk electrode (RDE) in these solutions can be modeled by assuming two irreversible reactions, the reduction of H^+ and that of water molecules, both following Erdey-Grúz–Volmer–Butler kinetics.

The reduction of H^+ yields a transport-limited and thus, rotation rate-dependent current at not very negative potentials. At more cathodic potentials the polarization curves are dominated by the reduction of water and no mass transfer limitation seems to apply for this reaction. Although *prima facie* the two processes may seem to proceed independently, by the means of finite-element digital simulations we show that a strong coupling (due to the recombination of H^+ and OH^- to water molecules) exists between them. We also develop an analytical model that can well describe polarization curves at various values of *p*H and rotation rates.

The key indication of both models is that hydroxide ions can have an infinite diffusion rate in the proximity of the electrode surface, a feature that can be explained by assuming a directed Grotthuss-like shuttling mechanism of transport.



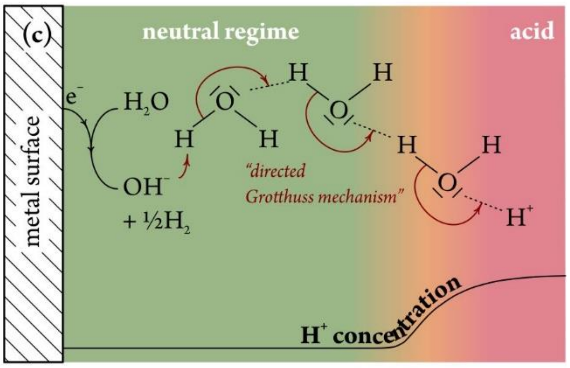


Figure 1: Polarization curves (a, b) measured on a Ni RDE immersed into solutions prepared by mixing KOH and $HClO_4$. Curves measured at different pH values and at a fixed rotation rate of 1225 min^{-1} are shown in (a); curves measured at a fixed level of pH = 2.0 and different rotation rates are shown in (b). The scheme of a "directed Grotthuss mechanism" explaining the establishment of a neutral near-surface solution layer when water reduction takes place at the interface is shown in (c). Based on this mechanism, an analytical model describing the polarization curves can be built

Acknowledgements

This research was supported by the European Union and the State of Hungary, co-financed by the European Social Fund in the framework of TÁMOP 4.2.4.A/1–11–1–2012–0001 "National Excellence" Program. Financial support from the Hungarian Scientific Research Fund (OTKA–K109036) and from the Swiss National Science Foundation (SNSF–200020–149224/1) is gratefully acknowledged.

OFM 169

Determination of the charge transfer resistance of poly(3,4-ethylenedioxythiophene) modified electrodes immediately after overoxidation

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Cyclic voltammetry and electrochemical impedance spectroscopy were used for the investigation of the electrochemical behavior of poly(3,4-ethylenedioxytiophene) (PEDOT) films. It is known that if the polarization potential exceeds a critical value an oxidation peak without corresponding reduction peak appears in the cyclic voltammograms [1]. The oxidative degradation of conductive polymer films is known as overoxidation. The impedance spectra of overoxidized PEDOT films on gold or glassy carbon recorded in aqueous sulphuric acid solutions differ considerably from those measured for freshly prepared films: after overoxidation, at both high and medium frequencies the complex-plane impedance plot is characterized by a well pronounced capacitive arc (or depressed semicircle), while the low frequency part indicates capacitive behavior. The decreasing capacitance and the increasing charge transfer resistance suggest that during overoxidation the electrochemical activity of the film decreases and the charge transfer process at the metal/film interface becomes more hindered than in the case of pristine films. However, the complex plane plots clearly indicate that the system is nonstationary. E.g. it can be inferred from the shapes of the sequentially recorded impedance spectra that the charge transfer resistance at the substrate/polymer film interface decreases continuously over several hours.

It is beyond doubt that the knowledge of the "initial" charge transfer resistance is essential for the better understanding of the degradation process that may also have an impact on practical applications. Due to measurement technology limitations it is impossible to record an impedance spectrum immediately after the overoxidation process, however, by using the four-dimensional analysis & cubic spline interpolation method [2] (Fig.1) the initial charge transfer resistance could be well estimated [3].

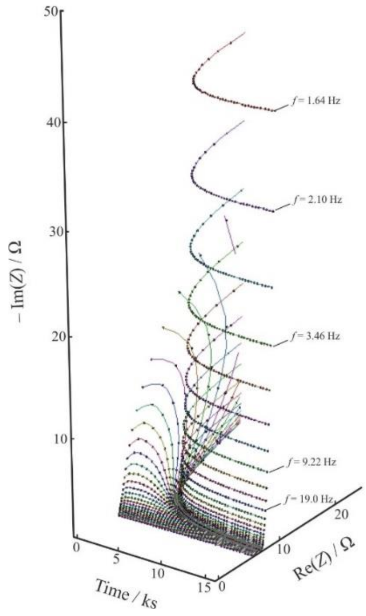

Figure 1: The measured impedance spectra of Au | PEDOT in 0.1 M H_2SO_4 and some isofrequential space curves created by spline interpolation shown in a three-dimensional (time dependent) complex plane representation

Acknowledgement

Support from the National Research Development and Innovation Office (OTKA No. K109036) is gratefully acknowledged.

References:

[1] *G.G. Láng, M. Ujvári, S. Vesztergom, V. Kondratiev, J. Gubicza, K. J. Szekeres: The electrochemical degradation of poly(3,4-ethylenedioxythiophene) films electrodeposited from aqueous solutions, Zeitschrift für Physikalische Chemie 230 (2016) 1281-1302.*

[2] *Z. Stoynov, B. Savova-Stoynov: Impedance study of non-stationary systems: four-dimensional analysis, Journal of Electroanalytical Chemistry 183 (1985) 133-144.*

[3] *M. Ujvári, D. Zalka, S. Vesztergom, S. Eliseeva, V. Kondratiev, G.G. Láng: Electrochemical impedance measurements in non-stationary systems – Application of the 4-dimensional analysis method for the impedance analysis of overoxidized poly(3,4-ethylenedioxythiophene)-modified electrodes, Bulgarian Chemical Communications 49 (2017) 106-113.*

OFM 176

Electrochemical approach for exfoliation of graphite and graphene production

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Different methods have been developed for graphene production such as chemical vapour deposition, epitaxial growth on SiC, wet chemical or electrochemical exfoliation of graphite, liquid phase exfoliation and carbon nanotube unzipping [1]. The selection of the appropriate method depends on required purity of material, sheet size, number of defects, price and possibility to use the method for mass production of graphene. Electrochemical exfoliation of graphite is one of the promising methods. Compared to the other techniques it is simple, operates at ambient temperature and pressure, and can be easily scaled up [2]. Using this method it is possible to obtain graphene of relatively high quality considering number of defects and sheet size.

The electrochemical exfoliation is a result of a different processes taking place at polarised graphite electrode such as ion and water intercalation, gas evolution and oxidation of carbon. In such a way the pressure achieved within the graphite structure is sufficiently high to exfoliate graphite resulting in the graphene production. In the case of anodic polarisation the graphite will be oxidized and structural defects will be created, however, careful selection of anodic potentials open up the possibility of tuneable level of oxidation and tailoring of different graphene structures [3].

The aim of this work was to obtain graphene sheets by graphite electrode polarisation in sodium dodecyl sulfate (SDS), sodium dodecyl benzenesulfonate (SDBS) and 1,1′-bi-2-naphthol (BINOL) electrolyte solutions. Graphite electrode was anodically and cathodically polarised in different electrolyte solutions in order to determine the optimal conditions for this process. Experiments were carried out in two electrode system by applying voltage values ranging from 2.5 to 3.2 V between a graphite electrode and Pt-foil. The exfoliation progress was monitored by using chronoamperometry while electrochemical behaviour and morphology characteristic of electrode were determined by means of cyclic voltammetry and scanning electron microscopy (SEM) techniques. The obtained product was also successfully isolated and characterized by employing Fourier transformed infrared spectroscopy (FTIR), ultraviolet-visible spectrophotometry (UV-Vis) and atomic force microscopy (AFM).

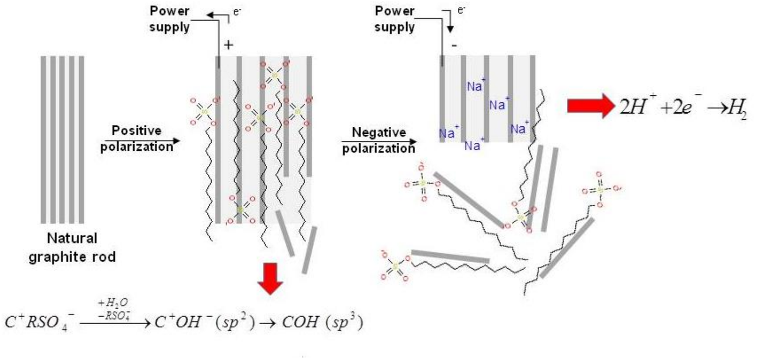

Figure 1: Schematic illustration of electrochemical exfoliation mechanism in the presence of surfactant

References:

[1] *C.T.J. Low, F.C. Walsh, M.H. Chakrabarti, M.A. Hashim, M. A. Hussain, Carbon, 54 (2013) 1-21.*

[2] *G. Wang, B. Wang, J. Park, Y. Wang, B. Sun, and J. Yao, Carbon 47 (2009) 3242–3246.*

[3] *Z. Y. Xia, S. Pezzini, E. Treossi, G. Giambastiani, F. Corticelli, V. Morandi, A. Zanelli, V. Bellani, V. Palermo, Advanced Funcional Materials 23 (2013) 4684-4693.*

OFM 211

PEMECs with Ir/MMT as anode material

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Polymer electrolyte membrane water electrolysis cell (PEMEC) is considered as one of the key technologies that can be powered by renewable energy sources and used for the large scale production of clean hydrogen. The partial hydrogen (HER) and oxygen (OER) evolution reactions are of special importance in both fundamental and applied electrochemistry. The OER takes place at high potentials which in combination with the intensive gassing, high humidity and elevated temperatures creates critical operative conditions, prohibiting the use of carbon-based materials as catalyst support

The best performing catalysts in acidic conditions for OER are Ir and Ru-based materials. They have excellent activity, but also lower stability. Later on, it was proven that iridium (IrO_2) and ruthenium (RuO_2) oxides are the most representative and effective OER electrocatalysts. Oxide nanoparticles are much more stable than metallic ones.

The usual approach to decrease the cost of the catalysis and thus, the capital expense of PEMEC, is to synthesize complex catalytic compositions mixing IrO_2 with inexpensive and electrochemically inert materials such as TiO_2, SnO_2, Ta_2O etc. catalyst layer in order to form Ir-based mixed oxides.

The purpose of this work has been to investigate one natural mineral (Montmorillonite, MMT) as catalytic support and to assess the efficiency of the composite MMT-supported IrO_2 toward OER in acidic electrochemical water splitting. MMT is a phyllosilicate layered clay with 2:1 type sheet structure, high cation exchange capacity, high surface area and low cost. Chemically, it is a complex mixture of hydrated phyllosilicates, having rather complex general chemical formula: $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \bullet nH_2O$. To our knowledge, MMT by now has not been investigated as catalytic support.

In the present research has been loaded with 10-20-30 wt.% noble metal Ir-acetylacetonate ($(Ir(C_5H_7O_2)_n)_m$ by the well established sol gel technique. The obtained MMT-supported catalysts have been characterized by EDX, SEM, DTG/TA and XRD techniques. Their electrochemical performance and OER catalytic efficiency have been investigated by cyclic voltammetry and steady state polarization techniques in 0.5 M H_2SO_4 standard tree electrode electrochemical cell and in PEMWE cell at temperature interval of 20°C and 80°C

The results obtained have shown that the catalysts under study possess superior performance in regard to both activity and durability compared to the previously studied iridium catalysts supported on commercial electrically conductive ceramic supports such as Magnelli phase titania

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ABSTRACTS OF THE POSTERS

P1 CR01

Imidazole-based compounds with different functional groups as corrosion inhibitors for copper and zinc

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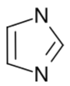
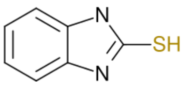
Minimization or prevention of corrosion is an important goal of the society since the corrosion of metal structures results in enormous economic costs worldwide. Corrosion inhibitors are one of the most common methods for reducing the corrosion of copper, zinc and their alloys. Hitherto the most effective inhibitor of copper corrosion was benzotriazole [1], which has been used for decades. In order to find less toxic compounds with similar inhibition efficiency the research is focused on alternative corrosion inhibitors for copper and its alloys. In our previous studies the effect of mercapto, benzene and methyl groups of imidazoles in the corrosion inhibition of copper [2,3] and aluminium-copper- and aluminium-zinc based alloys [4] was studied.

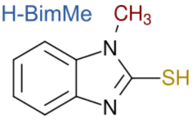
ImiH



SH-BimH



SH-BimMe



The basic idea of this research project is to design corrosion resistant copper-based alloy systems using corrosion inhibitors and to increase the impact of ICME (Integrated Computational Materials Engineering) for more rational and powerful prediction of inhibition efficiency using modelling and simulation, chemical synthesis, multi-scale experimental analysis, testing and validation. The first step is to test the corrosion protection performance of potential corrosion inhibitor candidates on copper and zinc substrates.

Three imidazole-type inhibitors were tested at the concentrations of 0.1 and 1 mM: imidazole (ImiH), 2-mercapto-benzimidazole (SH-BimH) and 2-mercapto-1-methyl-benzimidazole (SH-BimMe). Electrochemical measurements were performed in a three-electrode corrosion cell at room temperature in 3 wt. % NaCl solution. Prior to the electrochemical measurement the samples were stabilized for 1 hour at open circuit potential (OCP) and the potential was measured as a function of time. Polarization resistance, R_p, was then measured followed by the measurements of potentiodynamic polarization curves in the broad potential region.

According to the electrochemical results the presence of mercapto and benzene groups in imidazole beneficially affects the inhibition efficiency of both Cu and Zn. The following order of inhibitor efficiency expressed as increasing polarization resistance in solution with or without inhibitors added was obtained for both Cu and Zn:

NaCl < NaCl + ImiH << NaCl + SH-BimH < NaCl + SH-BimMe.

Increasing polarization resistance, or decreasing corrosion current density, reflects an increasing corrosion protection of the metal. In the presence of inhibitors the cathodic and, especially, anodic current densities are reduced indicating that these inhibitors act as mixed inhibitors with a more pronounced effect on the anodic side. In addition to electrochemical polarization measurements, immersion tests were performed for a duration of 1 month in order to address the long-term performance of these inhibitors.

Acknowledgments

This work is a part of M.ERA-NET project entitled “Corrosion inhibiton and dealloying descriptors”, acronym COINDESC. The financial support of the project by MESS (Ministry of Education, Science and Sport of Republic of Slovenia, Programmes of International Scientific Cooperation) and NWO (Nederlandse Organisatie voor Wetenschappelijk Onderzoek) is acknowledged.

References:

[1] M. Finšgar and I. Milošev, Corros. Sci., 52 (2010) 2737–2749

[2] Milošev, N. Kovačević, J. Kovač and A. Kokalj, Corros. Sci., 98 (2015) 107–118

[3] N. Kovačević, I. Milošev and A. Kokalj, Corros. Sci., 98 (2015) 457–470

[4] T. G. Harvey, S. G. Hardin, A. E. Hughes, T. H. Muster, P. A. White, T. A. Markley, P. A. Corrigan, J. Mardel, S. J. Garcia, J. M. C. Mol and A. M. Glenn, Corros. Sci., 53 (2011) 2184–2190

P1 CR02

Investigation of corrosion behavior of aluminum alloy ENAC-$AlSi_7Mg_{0.3}$ in artifical sea water with addition of inorganic sulfides

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Corrosion of aluminium alloy ENAC-$AlSi_7Mg_{0.3}$ in artifical sea water (ASW, Burkhoder's formulation B) [1], with concentration of 0 ppm, 20 ppm, 50 ppm, 100 ppm of sodium sulfide, was investigated by immersion tests up to 42 days in the accordance with standard NACE TM0169/G31 - 12a [2]. During the course of immersion tests samples were taken out from immersion solution in period of 1, 2, 3, 5, 7, 10, 14, 21, 28 and 42 days. Surface-analytical and electrochemical characterization of these samples were performed in order to address the compositional, morphological and electrochemical properties of the surface after being exposed to artificial sea. Surface characterization was performed using scanning electron microscopy with chemical analysis (SEM/EDX) and X-ray photoelectron spectroscopy (XPS) techniques. Electrochemical characterization of the samples carried out in fresh artificial sea water (pH=7.45)included the measurements of open circuit potential, electrochemical impedance spectroscopy, linear polarization resistance and potentiodynamic polarization curves. In addition, corrosion rate was monitored by measuring concentration of dissolved metal ions in immersion solution using inductively coupled plasma mass spectroscopy (ICP-MS). Corrosion current density, j_{corr}, deduced from potentiodynamic polarization curves by Tafel slope method is presented in Fig. 1. In the first 10 days of exposure to the ASW, the lowest j_{corr} values were obtained in the presence of 100 ppm Na_2S, and the highest in the pure ASW. Between 10 and 42 days of immersion, however, the trend changed and the greatest j_{corr} was in ASW containing 50 ppm Na_2S, whilst in ASW in the presence of 20 and 100 ppm Na_2S corrosion was still inhibited. After final immersion period the corrosion current density of samples immersed in sulfide-containing artificial sear was still reduced compared to that in solution without sulfide. Electrochemical results will be interpreted in relation to surface-analytical data.

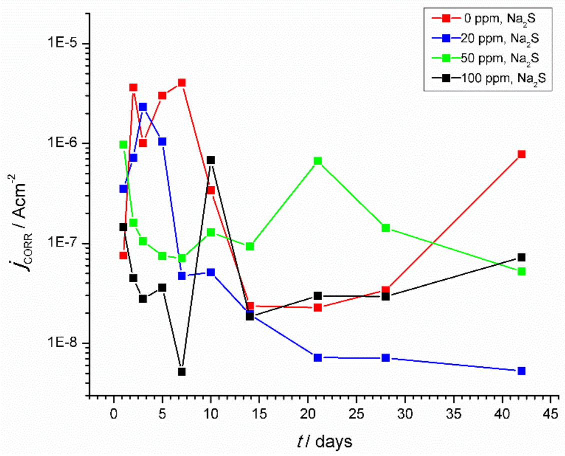

Figure 1: Change of corrosion current density with time of immersion in artificial sea water containing different concentrations of sodium sulfide

References:

[1] J.P. Bidwell, S. Spotte, Simulated Seawaters: Formulas and Methods, Jones and Bartlett Publishers, Boston, 1985.

[2] Standard Guide for Laboratory Immersion Corrosion Testing of Metals, NACE TM0169/G31-12a

P1 CR03

Localized corrosion of an austenitic stainless steel pipeline

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Unexpected local corrosion degradation was identified in an austenitic stainless steel pipeline after an incubation time ranging to several decades. The degradation spots could be found mainly, but by far not exclusively, in the vicinity of the welded joints of the pipeline parts, typically spread out into the flow direction. Horizontal sections of the pipeline system were particularly rich in the damage spots, indicating the possible role of the sediments. The operation of the branches of the system had a great influence on the distribution of the damaged areas, the parts often filled up with stagnant solution for a long time being highly endangered.

The morphology of the damages was versatile, ranging from microscopic cavities to elongated holes beneath the internal surface. The latter damage type occasionally could also cause a pipe failure by fully penetrating the pipe wall.

A comprehensive study has been carried out in order to reveal the possible origin(s) of the corrosion damage. The examinations all have been performed for (i) pipe sections cut from the operation site; (ii) pipe sections stored since the site construction that were not exposed to the operation conditions but are surely identical in structure and composition to the damaged ones; and (iii) stainless steel pipes of the same grade from a recently manufactured batch. Beside composition analysis, metallographic studies and mechanical test, electrochemical experiments made a core part of the investigation. The electrochemical study included a long-term corrosion potential measurement of the samples under alternating aerated and de-aerated conditions, analysis of the Tafel plots of slow-rate polarization measurements for the estimation of the average corrosion rate, cyclic voltammetric measurements in the presence of chloride ions to establish the inclination of the samples to pitting corrosion, and electrochemical impedance measurements.

The results of all sorts of investigation showed that the pipe material was conformal to the manufacturing standards. There was essentially no difference between the old and recently produced materials of the same grade, and the exposure to the operation conditions did not modify the properties of the pipe material where no damage happened. The electrochemical study revealed no sign of the inclination to pitting corrosion, and data obtained with both voltammetric and impedance measurements were fully in accord with a passivated surface.

The final conclusion of the study was that the corrosion damage was caused by the coincidence of several factors, neither of which being able alone to lead to the severe corrosion damage observed. While the imperfect protection of the welded joints were identified as the major initiation spots of the corrosion damage, the differential ventilation conditions of the extended pipeline system originating from the alternating operation of the branches certainly contributed to the large-scale local battery effect. These factors were surely strengthened by the corrosive action of the sediments and microbiologic effects. The maintenance of a clean system and a decrease in the possibility of the development of the differential ventilation condition were suggested as key measures for the prevention of further damages.

P1 CR04

Protective properties of epoxy coatings containing CeO_2 and ZrO_2 nanoparticles

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Corrosion could be efficiently delayed by application of inhibitors, metallic and/or organic coatings and by application of cathodic or anodic protection. Combining beneficial properties of both inhibitors and organic coatings in a single layer seems as a potentially effective design of a novel protective coating system. In this work an attempt was made to produce a protective system based on epoxy coating doped with CeO_2 and/or ZrO_2 nanoparticles, as the source of corrosion inhibitors. Deposition was carried out on AA6060 cataforetically from epoxy resin emulsion containing stable aqueous colloidal dispersions (sols) of ceria (CeO_2) and zirconia (ZrO_2). The optimal amount of sols (5.0 mM), providing stable epoxy suspensions, was determined on the basis of particles surface charge (zeta potential) and particle size values. The influence of Ce and Zr on the corrosion stability of epoxy coatings was evaluated by electrochemical impedance spectroscopy, during immersion in 0.5 M NaCl solution. All inhibitor containing coatings showed better corrosion stability than pure epoxy coating. The influence of the type of the inhibitor during 45 days of exposure to 0.5 M NaCl is shown in Figure 1. Zirconia proved to be more efficient inhibitor than ceria and the combination of both inhibitors seem not to show pronounced synergetic effect, during these time interval.

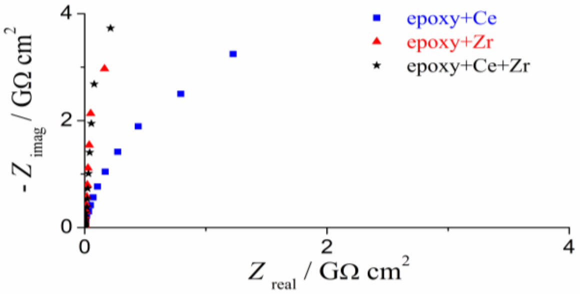

Figure 1: Nyquist plots for epoxy coatings containing different inhibitors (5.0 mM Ce or 5.0 mM Zr or 2.5 mM of both Ce and Zr) after 45 days of exposure to 0.5 M NaCl solution

The results of the long term exposure to a corrosion agent were compared with the ones performed during shorter period of time on samples with artificial defect. Making an artificial defect on the protective coating is a standard method for the determination of protective properties of coatings with fillers, enabling getting information on the coating behaviour in a shorter period of time. The increase of the charge-transfer resistance (R_{ct}) values of inhibitor containing coatings was ascribed to the self-healing ability of Ce and/or Zr. The R_{ct} values were, for instance, about five times greater for epoxy coating containing Zr than pure epoxy coating.

Since R_{ct} is a parameter inversely proportional to the corrosion rate, the corrosion protection provided by Ce and Zr loading is evident. EIS results were combined with adhesion strength and FTIR measurements and the role of inhibitors was examined from the standpoint of the kinetics of the barrier properties degradation of different protective systems.

P1 EN01

Electrodeposited Ag-Pd alloys as the catalysts for oxygen reduction reaction

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The Ag-Pd alloys were electrodeposited onto Au and glassy carbon rotating disc electrodes from the solution containing 0.001 M $PdCl_2$ + 0.04 M AgCl + 0.1 M HCl + 12 M LiCl under the conditions of non-stationary (RPM = 0) and convective diffusion (RPM = 1000), to the different constant amounts of charge (0.05 C cm^{-2} to 3 C cm^{-2}) and at a constant current densities (in the range of -0.178 mA cm^{-2} to -0.415 mA cm^{-2}) to the constant amount of charge (-0.2 C cm^{-2}). Electrodeposited alloy layers were characterized by the anodic linear sweep voltammetry (ALSV), transmission electron microscopy (TEM), X-ray techniques (XRD) and X-ray photoelectron spectroscopy (XPS). The ALSV analysis indicated the presence of Ag, Pd and two additional phases. Physical-chemical characterization was performed by TEM, XRD and XPS analysis, confirming the presence of the mentioned phases. Oxygen reduction reaction (ORR) on pure metals and Ag-Pd alloys was investigated by linear sweep voltammetry in 0.1 mol dm^{-3} NaOH solution at 25^{0}C, at the rotating disc electrode. To design an active alloy catalyst with a low content of a highly active precious noble metal and a second less active metal, it would be desirable to achieve strong ligand and ensemble effects [1]. For the ORR in alkaline media, less-expensive precious metals such as Ag exhibit good ORR activity, especially for HO_2– disproportionation [1]. The Pd–Ag alloys are expected to exhibit a higher ORR activity at room temperature, compared to Pd [2]. The determined ORR activities were expressed in terms of kinetic current densities per real electrochemically active surface area. It was revealed that ORR activity had been strongly influenced by the alloy composition. The alloys catalytic activities were compared to the corresponding values at the pure Ag and Pd, as well as to state of the art Pd based catalysts for alkaline fuel cells applications.

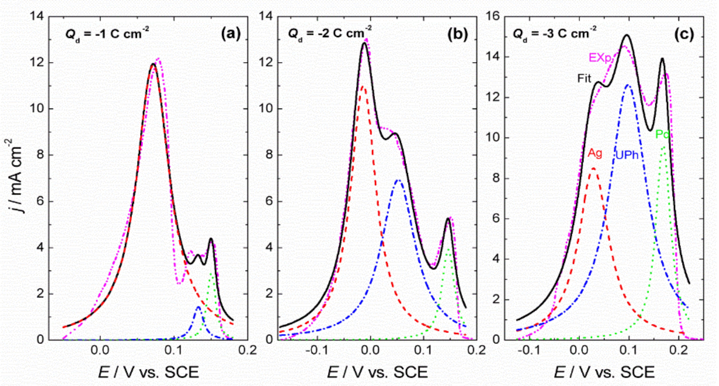

Figure 1: Results of fitting ALSVs of the Ag-Pd alloys electrodeposited at RPM=1000: (a) j_d = -5 mA cm^{-2}, Q_d = -1.0 C cm^{-2}; (b) j_d = -5 mA cm^{-2}, Q_d = -2.0 C cm^{-2}; (c) (a) j_d = -7 mA cm^{-2}, Q_d = -3.0 C cm^{-2}. Fitting lines (black solid lines); experimental lines (magenta dash-dot-dot lines); Ag lines (red dashed lines); Pd lines (green dotted lines); Phase 1 lines (blue dash-dot lines)

Acknowledgement

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References:

[1] D. A. Slanac, W.G. Hardin, K. P. Johnston, K. J. Stevenson, J. Am. Chem. Soc. 2012, 134, 9812–9819.

[2] M.C. Oliveira, R. Rego, L.S. Fernandes, P.B. Tavares, Journal of Power Sources 196 (2011) 6092.

P1 EN02

Nanostructured PtAu catalysts for formic acid electrooxidation

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Platinum-based nanomaterials have been widely employed as catalysts for fuel cell applications. Alloying Pt with another element can improve its catalytic properties, due to the effect that the other element can have on Pt (bifunctional, ensemble or electronic). PtAu alloy is known as a good catalyst for formic acid oxidation (FAO), as it enables the reaction to occur mostly via direct mechanism, which is not the case with pure Pt nanoparticles. Avoiding the indirect mechanism and the formation of CO as catalytic poison leads to the creation of a catalyst with improved properties, in terms of its stability and effectiveness.

In this study water in oil microemulsion method was used to synthesize carbon supported PtAu nanoparticles. With BRIJ 30 as a surfactant, simultaneous reduction of H_2PtCl_6 and $HAuCl_4$ precursors with $NaBH_4$ was performed. In one sample a capping agent (HCl) was added in the water phase to influence particle shape, while the other sample was free of HCl.

The catalysts were characterized electrochemically, with CO stripping voltammetry and by cycling voltammetry in the supporting electrolyte. Also, high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS) were employed to investigate the composition and structural properties of the catalyst powders. These analyses indicated the presence of metal nanoparticles from 4 to 7 nm in diameter on the carbon support, with equal shares of both elements (1:1) (Fig.1). The voltammograms recorded in the supporting electrolyte indicate no presence of Au on the surface (the Au reduction peak is not present), but its electronic effect on Pt is evident (the hydrogen region of the voltammogram has no well-defined hydrogen desorption peaks; CO oxidation peak is shifted for 200mV in comparison to Pt/C nanocatalyst (Fig.2). The catalysts were tested for formic acid electrooxidation, in terms of its activity and stability. The reaction takes place through direct mechanism, which is indicated by the shape of the positive-going voltammogram (Fig.3). The figures below represent results obtained for the sample with capping agent present during synthesis. Catalysts displayed improved activity and stability (chronoamperometry and long-term cycling) compared to Pt/C catalyst synthesized in the same way (w/o microemulsion method) and with similar particle size.

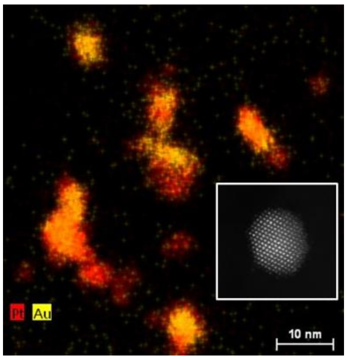

Figure 1: EDS map of PtAu/C with TEM image inset

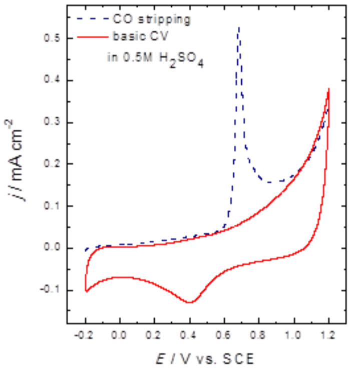

Figure 2: CVs in supporting electrolyte with CO stripping curve, v=50mVs^{-1}

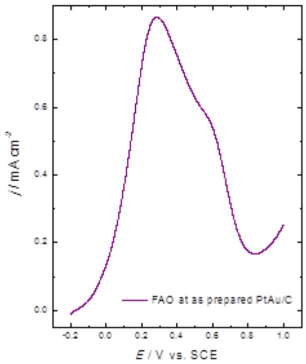

Figure 3: Anodic scan of FAO at PtAu/C in sup.el. + 0.5 M HCOOH, v=50mVs^{-1}

Acknowledgements

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172060). The authors would like to acknowledge the COST MP 1407 action for networking support.

P1 EN03

Improvement of electrochemical performance of $Li_4Ti_5O_{12}$ electrode material with conducting PEDOT:PSS binder

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Recently it has been shown that PEDOT and other conducting polymers additives can positively effect on the electrochemical performance of electrode materials for lithium ion batteries. In particular, the use of PEDOT:PSS dispersion as conductive binder for olivine type cathode materials showed an increased specific capacity and high rate capability of materials [1,2]. Introduction of conducting polymer can make impact in the improvement of electronic conductivity and provide more reliable, elastic contact between active grains due to the damping of structural - volume change (material breathing).

Anode materials based on spinel $Li_4Ti_5O_{12}$ are considered as promising energy storage material for Lithium-Ion Batteries for various applications, especially for portable electronic devices, electric vehicles. To improve the high rate capability of materials for powerful application the reducing of particles size and carbon coatings were proposed as a main strategy. In this work we have shown than additional improvement of the electrochemical performance of $Li_4Ti_5O_{12}$ can be achieved with employment of poly-3,4-ethylene-dioxythiophene: poly(styrene sulfonate) (PEDOT:PSS), and carboxymethlcellulose (CMC) binders. The results were compared with conventional composition of $Li_4Ti_5O_{12}$ with PVDF binder.

Conventional type of electrode were prepared with use of LTO, CB and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10. Modified electrodes contains of LTO, CB and poly-3,4-thylenedioxythiophene (PEDOT) and carboxymethlcellulose in a weight ratio of 80:10:10.The electrochemical coin-type cells 2032 contained conventional and modified $Li_4Ti_5O_{12}$ based materials were assembled with use Li foil as electrode, porous polypropylene film as separator, and 1MLiPF6 in a 1:2 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC).

Cyclic voltammograms of $Li_4Ti_5O_{12}$ containing electrodes with PVDF or PEDOT/CMC as binders were obtained at different scan rates (0.05 – 1 mV/s) in potential range 1.0-3.0 V. One sharp reduction peak at around 1.5 V and one sharp anodic peak at 1.6V was observed for both types of electrodes , indicating the good reversibility of lithium intercalation processes during phase transition between $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$.

Galvanostatic charge-discharge profiles of different in composition $Li_4Ti_5O_{12}$ containing samples were systematically investigated in a coin-type cell. The obtained results shows that the use of PEDOT/CMC as binder allows to obtain the higher discharge capacity values compared with the Li4Ti5O12 composite based on PVDF binder. Electrochemical impedance spectra of $Li_4Ti_5O_{12}$ based conventional and polymer modified materials were examined and analyzed. It was found that the decrease of R_{ct} and increase of D_{eff} are main factors, responsible for positive effects of conducting polymer binder on the electrochemical performance of $Li_4Ti_5O_{12}$/PEDOT electrodes.

Acknowledgements

The authors are thankful to the colleagues from Interdisciplinary Resource centre for Nanotechnology and Resource centre "Physical methods of surface investigation" of St. Petersburg State University for providing common SEM, EDX, XPS and XRD analysis. Financial support from Russian Foundation for Basic Research (grants №16-03-00457 and 17-53-12029) is gratefully acknowledged.

References:

[1] *S.N. Eliseeva, O.V. Levin, E.G. Tolstopjatova, E.V. Alekseeva, R.V. Apraksin, V.V. Kondratiev, Materials Letters, 161(2015) 117.*

[2] *R.V. Apraksin, S.N.Eliseeva, E.G.Tolstopjatova, A.M.Rumyantsev, V.V.Zhdanov, V.V. Kondratiev, Mater. Lett. 176 (2016) 248.*

P1 EN04

Influence of the electrode preparation conditions on the performance of the activated carbon symmetric supercapacitors

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Main properties of supercapacitors are its capacitance, nominal voltage, energy and power density. The nominal voltage of capacitor is determined by the chemical stability of the electrolyte, while the capacitance and energy density depend on the amount of charge that can be stored inside the supercapacitor. Another important characteristic of the supercapacitor is a power density which represents the rate of energy delivery. In order to achieve the best performance it is important to select a porous electrode with very large surface area, good electric conductivity and high electrochemical stability. It is desirable that the mechanism of charge storage throughout such electrode has fast kinetics as well as the reversibility and reproducibility which provide high stability and cycle life. Supercapacitor charging and discharging rate is determined by its internal resistance which can originate from active material, electrolyte and current collector.

The electrode material is mainly composed of three substances; an active material having the role of charge storage, a carbonaceous material which increases the electric conductivity of active material and the polymer binder responsible for mechanical properties of electrode. So far, lots of attention has been dedicated to a preparation of electrode material by improving its structural and chemical properties [1,2], enhancing the contact between electrode material and current collector [3] and studying the effect of electrolyte system such as the size, charge, and mobility of the ions [4,5].

The objective of this work was to optimize the electrode composition and the preparation conditions, in terms of temperature and pressure, resulting in the lowest internal resistance and highest capacitance possible. The electrode material was prepared by mixing various weight percentage of activated carbon (Norit DLC Supra 30, S_{BET} = 1900 m^2/g) (60-95 wt%), carbon black (Timcal Super C45) (3-20 wt%) and polyvinylidene fluoride (PVDF) (Sigma Aldrich) (2-20 wt%). N-Methyl-2-pyrrolidone (NMP) was used as a solvent. Electrodes were fabricated by coating the obtained slurry onto Al- foil current collector coated with thin layer of carbon (Galon) and dried at 60 °C in the vacuum furnace overnight. Dried electrodes were cut to area of 2 cm^2 with thickness of 50 or 100 μm and mass loading of 6 mg/cm^2 or 20 mg/cm^2, respectively. Such electrodes were hot pressed at temperatures of 80 or 200 °C, and pressure of 10 or 100 MPa. The symmetric supercapacitors were assembled in the glove box containing two electrodes separated with glass fiber membrane soaked with 0.25 M NEt_4BF_4 in acetonitrile. Supercapacitors were tested by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge method (GCD). Specific capacitance of supercapacitors was evaluated from the slope of discharge curve, while the internal resistance was obtained from IR-drop of discharge curve. The EIS spectra provided a better understanding of electrode behavior regarding all types of resistances present in the supercapacitor assembly. The results showed that behavior of electrodes, in terms of internal resistance and specific capacitance, largely depend on both temperature and pressure applied to the electrodes during preparation, likewise the electrode composition. The higher pressing temperature and pressure had the beneficial effect to the activated carbon/carbon black interparticle contacts, as well as to the reduction of overall ohmic resistance.

References:

[1] *K-C. Tsay, L. Zhang, J. Zhang, Electrochimica Acta 60 (2012) 428-436*

[2] *K.Fic, M. Meller, E. Frackowiak, Electrochimica Acta 128 (2014) 210-217*

[3] *C. Portet, P.L. Taberna, P. Simon, E. Flahaut, C. Laberty-Robert, Electrochmical Acta 50 (2005) 4174-4181*

[4] *R.Lin, P.L. Taberna, J. Chmiola, D. Guay, Y. Gogotsi, P. Simon, Journal of Electrochemical Society 156 (1) A7-A12 (2009)*

[5] *Juan C. Icaza, Ramesh K. Guduru, Journal of Power Sources 336 (2016) 360-366*

P1 EN05

Microwave-assisted synthesis of graphene/SnO_2 composite material and its supercapacitive properties

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Supercapacitors attract significant attention due to their promising properties for the energy storage and power supply. Charge storage mechanism in supercapacitors is based on the electrochemical double layer charging/discharging and therefore the capacitance is usually limited by the active surface area. To overcome this limitation there are efforts to increase capacitance by using the metal oxides or the conductive polymers where the charging/discharging mechanism includes fast redox reaction of the material and, as a result, much higher specific capacitance is obtained [1]. Considering the charge storage mechanism of metal oxide these materials are classified as ″pseudocapacitors″. The aim of this work was to study capacitive property of graphene/SnO_2 composite material. Metal oxides electrochemical behaviour can be significantly improved by the presence of graphene due to its properties, such as high electrical conductivity, high surface area and flexibility. On the other hand SnO_2 prevents agglomeration of the graphene sheets that results in graphene with high surface area. Therefore, synergistic effect of these two constituents is expected to enhance overall capacitive properties and improve these materials for supercapacitor application [2, 3].

In this work simple simultaneous synthesis of the SnO_2 and reduction of the graphene oxide (GO) was carried out by using microwave-assisted hydrothermal synthesis. This method was selected due to its effects such as rapid volumetric heating, increased reaction rates and shortened reaction time. Hydrothermal synthesis and microwave assisted hydrothermal synthesis are useful for accelerating the de-protonation reaction of $Sn(H_2O)_x(OH^-)_y^{(4-y)+}$ to SnO_2 x nH_2O offering good control of both particle size and particle distribution [4]. By using cyclic voltammetry it was shown that obtained material had good capacitive/pseudocapacitive properties suitable for supercapacitor application and specific capacitance values up to 93 F g^{-1} were determined. Obtained materials were additionally characterised by scanning electron microscopy (SEM) and Fourier transformed infrared spectroscopy (FTIR) that revealed presence of SnO_2 and successful reduction of GO to reduced form (rGO).

References:

[1] *C. D. Lokhande, D. P. Dubal, O. S. Joo, Curr. Appl. Phys. 11 (2011) 255*

[2] *M. Ara, K. Wadumesthrige, T. Meng, S. O. Salley, K. Y. S. Ng, RSC Adv. 4 (2014) 20540*

[3] *H. N. Lim, R. Nurzulaikha, I. Harrison, S. S. Lim, W. T. Tan, M. C. Yeo, M. A. Yarmo, N. M. Huang, Ceram. Int. 38 (2012) 4209*

[4] *Y. Wang, J. Y. Lee, J. Power Sources 144 (2005) 220*

P1 EN06

Maricite-type $NaFePO_4$ as cathode material for sodium-ion battery

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In order to satisfy a growing demand for energy storage devices and to create safer and less expensive batteries with high capacity, materials based on easily accessible and environmentally friendly elements with comparatively low atomic weights, such as sodium and iron, have to be used. A thermodynamically stable maricite-type phase of sodium iron phosphate $NaFePO_4$ (m-NFP) has been considered electrochemically inactive; however, recent studies have questioned this assertion. In this study, we propose an approach to a scalable synthesis of nanosized m-NFP and its composites with carbon. Maricite-type $NaFePO_4$ and its composites with carbon were synthesized via Pechini approaches. We assumed that in order to achieve high capacities, high defect concentration should be provided, facilitating sodium ion diffusion. For this purpose, the ball-milling of the materials was used. Ball-milling of the material was performed using a Fritsch Pulverisette 7 ball mill equipped with agate grinding bowls (inner volume 45 ml) and ten agate balls (⌀ = 10 mm) per bowl. As follows from the X-ray diffraction data, the obtained m-NFP samples contained a single phase, which corresponded to the maricite structure, *Pnma* space group. According to the inductively coupled plasma mass spectrometry (ICP-MS), the composition of the synthesized samples corresponded to $NaFePO_4$. According to the scanning electron microscopy (SEM) images the Pechini method allowed to obtain agglomerated m-NFP/C particles of 20-30 nm in diameter. Carbon was formed during the synthesis due to the carbonization of organic reagents. To prepare the working electrodes, 80% $NaFePO_4$/C composites were mixed with 10% carbon black and 10% PVDF binder dissolved in N-methyl-2-pyrrolidone. The obtained paste was thoroughly mixed and deposited on Al foil with 2.5 mg/cm^2 mass loading. The resulting electrode was pressed at 100 MPa for 1 min and vacuum-dried at 120 °C for 8 h. 1M $NaPF_6$ dissolved in ethylene carbonate and propylene carbonate mixture (V/V 1:1) was used as electrolyte. The experiments were performed using sealed three-electrode Teflon cells. Sodium metal served as counter and reference electrodes. Surface area of the working electrodes was 2.25 cm^2. The cells were assembled in a glove box under argon atmosphere with O_2 and H_2O content below 10 ppm.

The ball-milling led to a dramatic increase in the m-NFP capacity, which rose up to ~150 mA h g^{-1} at 15 mA g^{-1} charge-discharge rate (~0.1 C) and ~60 mA h g^{-1} at 1200 mA g^{-1} charge-discharge rate (~8 C). Specific discharge capacity, calculated by integrating cathodic parts of cyclic voltammograms (CVs) amounts to 142, 131, 119 и 103 mAh g^{-1} for υ = 0.1, 0.2, 0.4 and 0.9 mV s^{-1}, respectively. The dependences of currents in maxima of CVs on square root from scan rate are linear and pass the coordinate origin, that gives a possibility estimating effective diffusion coefficient of sodium (D_{eff}) in m-NFP with using the Randles-Ševćik equation. Estimating the effective diffusion coefficients of sodium, we used surface area calculated from particles sizes based on coherent scattering region. In this case $D_{eff} \approx 1.5*10^{-15}$ cm^2/s and $8.3*10^{-16}$ cm^2/s for sodium insertion and extraction, respectively.

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P1 EN07

MnO_2 and $MnFe_2O_4$ as electrode materials for hybrid supercapacitors

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The interest to the hybrid supercapacitors is determined by combining the high power characteristics of the electrochemical double-layer supercapacitors with the high energy density of the batteries. Among different metal oxides, manganese oxide (MnO_2) has been recognized as one of promising inorganic materials due to its easy synthesis process, low cost and excellent electrochemical properties. However, MnO_2 suffers from low electronic conductivity and poor cation diffusivity and this requires the nanoscale MnO_2 structures to include highly porous and electrically conductive materials to form a composite nanostructure for electrode materials. So it is most important to develop alternative low cost and novel electrode materials as next generation of supercapacitors that can charge and discharge in less time while delivering enhanced power density.In recent years many studies have been focused on the synthesis of metal oxide ($MnFe_2O_4$) nanoparticles because of their unusual optical, electrical and magnetic properties.

The objective of the present work is to developa hybrid battery supercapacitor based on $MnFe_2O_4$/active carbon (AC) nanocompositein aqueous alkaline electrolytes (6M KOH) and compare itselectrochemical performance with the properties of supercapacitator with MnO_2 in the composite electrode.

$MnFe_2O_4$nanosized powders were prepared by solution combustion synthesis. The mole ratio of the initial compounds was calculated in the way that the ratio of oxidizing to reducing power of the components of the combustion reaction is 1:1. AC (TDA Research, USA) and MnO_2(Fluka, USA) are commercial products.

The morphological and structured characterizations of the both Mn-oxides were carried out through X-Ray diffraction, transmission and scanning electron microscopy (TEM and SEM)and low-temperature nitrogen adsorption.

The hybrid supercapacitor cell is composed by a positive electrode – a composite of activated carbon and $MnFe_2O_4$or MnO_2in concentration range 30 – 80 wt.%, and a negative electrode of activated carbon. PTFE and ABG1000 are used as additives and Viledon 700/18F- as separator. The carbon and composite electrodes are fabricated in the form of disk in 6M KOH.The cells thus assembled are subjected to electrochemical charge/discharge cycling under galvanostatic conditions at different current loads (30 – 420 mAg^{-1}) using Arbin BT2000 apparatus.

The assembled supercapacitor cells with $MnFe_2O_4$show stable cycleability at prolong cycling (up to 500 cycles) and high efficiency (90%), as the highest value of capacity in the whole concentration rangewas observed at 30wt.%$MnFe_2O_4$(60 Fg^{-1}).

The capacitance on $MnFe_2O_4$is lower than that obtained for MnO_2 (100 Fg^{-1}, 50wt.% MnO_2) which can be explained by the different structure and morphology of the both oxides.For example, the particles of the $MnFe_2O_4$ are irregular in shape with mean size about 8 nm, while these of the $MnO_2$are approximately the same (5-6 nm) and with homogeneous structure.

However the results are promising and prove the possibility of application of $MnFe_2O_4$as electrochemically active material for hybrid lithium battery – supercapacitor systems.

Acknowledgement

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P1 EN08

Preparation and characterization of an Ir-TiO_2 composite

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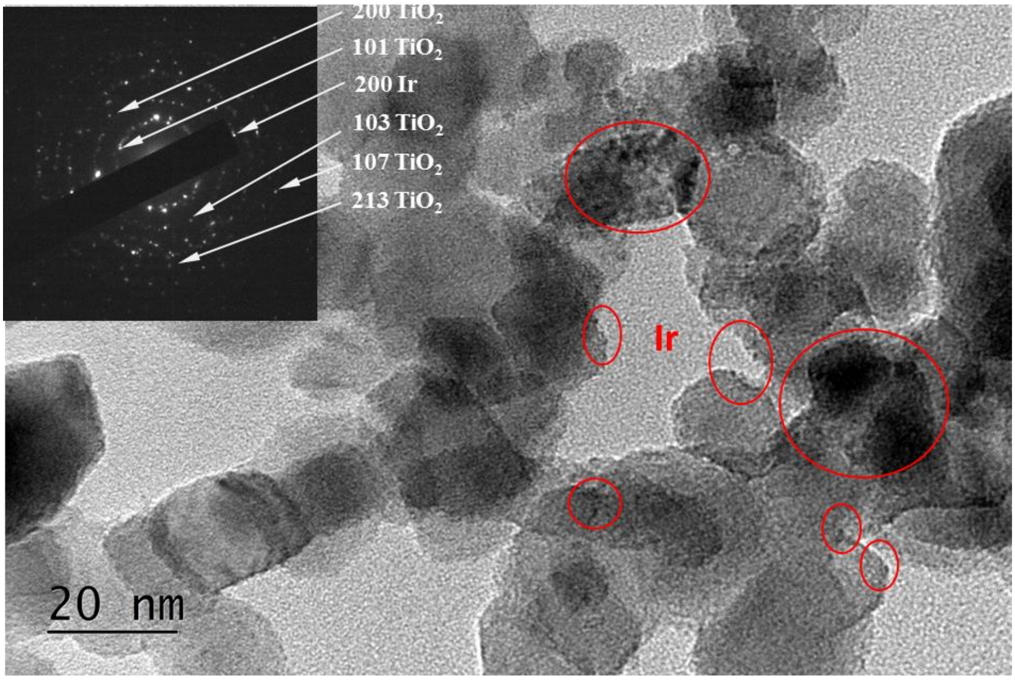
In an attempt to combine the photocatalytic activity of TiO_2 with the electrocatalytic activity of IrO_2 towards oxygen evolution, the surface of TiO_2 powder has been modified with Ir by UV photodeposition from appropriate Ir salt aqueous solutions. The resulting Ir-TiO_2 composite has been characterized by transmission electron microscopy (TEM), energy-dispersive spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS). A non-homogeneous Ir particle size distribution was observed, ranging from small, separated and very well dispersed crystallites to aggregates of different sizes. Depending on preparation conditions, both metallic and oxide forms of IrO_2 were detected. The electrochemical characterization of the resulting Ir-TiO_2 material was carried out by cyclic voltammetry (to identify the surface electrochemistry of the catalyst) and linear sweep voltammetry / photovoltammetry (to test oxygen evolution/water splitting activity).



TEM micrograph and SAED image of Ir/TiO_2 catalyst

P1 EN09

Pt(Cu) catalyst for methanol oxidation prepared by galvanic replacement on TiO_2 powder support

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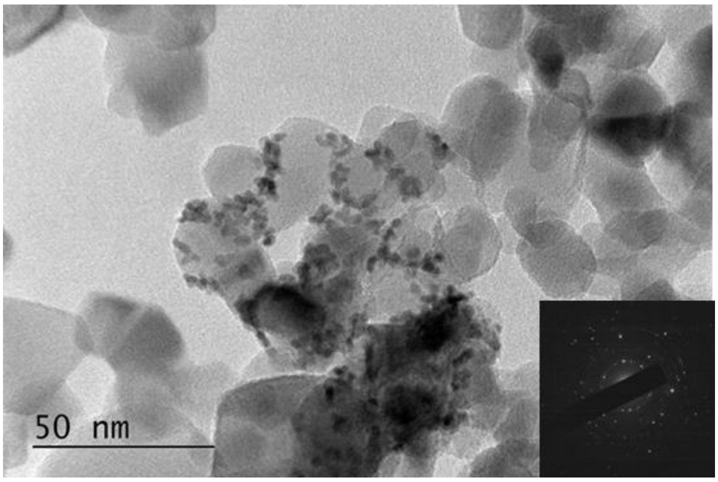
Pt(Cu) catalyst was prepared by photodeposition of Cu on TiO_2 powder support, followed by partial galvanic replacement of Cu by Pt in a chloroplatinate solution. Pt/TiO_2 catalyst was prepared by a direct photodeposition of Pt on TiO_2 support for comparison. The surface morphology and composition of the samples were characterized by transmission electron microscopy (TEM), energy-dispersive spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS). The crystal structure of the Pt(Cu)/TiO_2 and Pt/TiO_2 catalysts was examined by X-ray diffraction (XRD). The electrochemical and photoelectrochemical behavior of both platinized TiO_2 catalysts was evaluated by cyclic voltammetry, linear sweep voltammetry and chronoamperometry experiments in the dark and under UV light illumination. The electrocatalytic activity of the Pt(Cu)/TiO_2 catalyst towards methanol oxidation was evaluated and compared to Pt/TiO_2 catalyst. The Pt(Cu)/TiO_2 catalyst showed 5 times higher mass catalytic activity for methanol oxidation than a Pt/TiO_2 catalyst, further enhanced under UV light illumination. The increased catalytic activity is associated with more effective dispersion and better utilization of Pt, deposited by galvanic replacement of Cu, as well as with enhanced electron-hole separation efficiency.



TEM micrograph and SAED image of Pt(Cu)/TiO_2 catalyst

P1 EN10

PtSn versus PtSnO₂ carbon supported catalysts for methanol oxidation

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Number of studies has pointed out to increased activity of Pt alloyed with various metals for different reactions relevant for fuel cells. Oxidation of alcohols (for example methanol and ethanol) is improved at PtRu, PtRh, PtSn catalysts, oxygen reduction at PtNi, PtCo, PtFe, formic acid oxidation at PtAu, PtBi etc. Among these Pt based bimetallic catalysts Pt-Sn is one of the most extensively studied. It has been shown that Pt based catalysts containing significant amount of SnO_2 manifest high activity for CO oxidation as well [1]. One of the possible ways to obtain SnO_2 rich PtSn catalyst is to use polyol synthesis method [1]. Recently, using microwave assisted polyol method we prepared PtSn/C catalyst highly active or CO and ethanol oxidation [2]. Applying the same procedure this time we prepared $PtSnO_2$ carbon supported catalysts and examined both catalysts for methanol oxidation.

While for the synthesis of PtSn nanoparticles one step procedure was used, stabile $PtSnO_2$ nanoparticles were prepared in two-steps successive mode. First SnO_2 nanoparticles were synthesised and then H_2PtCl_6 was added. The catalysts were characterized by TGA, XRD, STM, TEM and EDX techniques. The major difference between the catalysts is revealed by XRD analysis which shows that PtSn/C is composed of Pt and small portion of Pt_3Sn phase. The rest of Sn is present in a form of very small tin oxide particles connected to Pt particles. $PtSnO_2$/C however contains pure Pt and SnO_2.

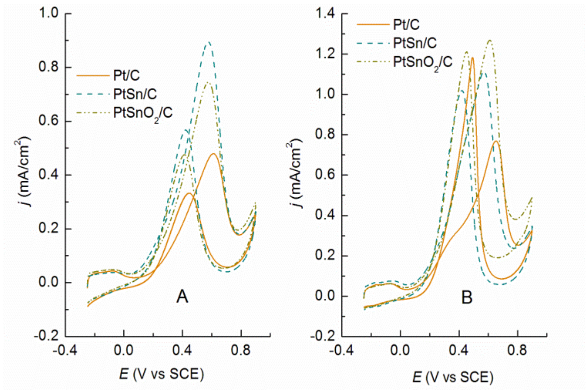

Figure 1: Potentiodynamic curves for the 0.5 M CH_3OH oxidation in 0.1 M $HClO_4$ at Pt/C, PtSn/C and $PtSnO_2$/C: A) as prepared and B) oxide annealed (v = 50 mV/s)

The catalysts were examined without previous treatment (as prepared) and after potential cycling up to 1.0 V vs SCE (oxide-annealed) in which case no alloyed Sn but only SnO_2 in contact with Pt should be present on the surface of both catalysts. The results obtained show that for all catalysts oxide annealed surfaces are more active (Fig. 1). The role of SnO_2 is confirmed and the significance of alloyed Sn and its electronic effect is revealed.

References:

[1] E. Lee, et al.: J. Electroanal. Chem., 659 (2011) 168.

[2] S. Stevanović, et a.l: J. Solid State Electrochemistry. 16 (2012) 3147

P1 EN11

Solution combustion synthesis of spinel ferrites as electrode materials in asymmetric supercapacitors

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In recent years many studies have been focused on the synthesis of metal oxide nanomaterials (especially these with complex composition and structure like MFe_2O_4 (Me^{2+}=Mn, Co, Ni, Cu, Zn) spinels because of their unusual optical, electrical, magnetic and electrochemical properties. They can be used as catalysts, as adsorbents for removing heavy metals in water, as ferrofluids, in biomedicine, in energy storage devices and others.

The solution combustion synthesis is widely used for the preparation of nanosized spinel materials. As was shown the type of fuel used in the solution combustion synthesis strongly influences the particle size, morphology and materials properties. In the present study a mixture of two types of fuel in different ratio were used (sucrose-urea and glycine-glycerol) for the synthesis of $MnFe_2O_4$, $CoFe_2O_4$ and $NiFe_2O_4$.

Structural and morphological characteristics of MFe_2O_4 (Mn, Co, Ni) spinels were studied by powder X-Ray diffraction (XRD) and Scanning electron microscopy (SEM). The results show the formation of single phase spinel ferrites for all samples under investigation. Specific surface areas of samples were determined by low-temperature nitrogen adsorption (BET). The results correlate well with the data of mean crystallite size obtained from X-ray analysis.

Magnetization curves were measured at room temperature (RT) using vibrating sample magnetometer (VSM) in fields up to 6 kOe. They show ferrimagnetic of superparamagnetic behavior depending on the fuel used. The highest saturation magnetization 79emu/g is observed for $MnFe_2O_4$ with fuel glycine:glycerol 0.75:0.25.

Electrochemical performance of nanosized ferrites was studied in a two-electrode cell in a potential range of 0.2–1.2 V in aqueous alkaline electrolyte (6M KOH). Asymmetric supercapacitor cells with $MnFe_2O_4$ as active material were assembled and subjected to electrochemical charge/discharge cycling under galvanostatic conditions at different current loads (30 – 420 mAg^{-1}) using Arbin BT2000 apparatus. Electrochemical tests show that $MnFe_2O_4$ and $CoFe_2O_4$ synthesized with glycerol fuel show better electrochemical performance comparing to ferrites prepared with other fuels or fuel mixtures.

Acknowledgments

The authors are grateful to the program "Young scientist", BAS (Grant DFNP 154/12.05.2016) and National Science Fund of Bulgaria under the contract DFNI E02/18.

Keywords: ferrites, combustion synthesis, asymmetric supercapacitor.

P1 EN12

The problems of electrolyte for sodium-ion batteries

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Despite the ever-growing number of works devoted to the sodium-ion batteries, there is still no generally accepted opinion about the best electrolyte for such batteries. Meanwhile, the strong impact of an electrolyte nature upon behavior of separate electrodes and sodium-ion batteries as whole is undoubted.

The present work is aimed to study electrochemical behavior of positive electrodes based on doped sodium-iron phosphate, and negative electrodes based on sodium titanate in electrolytes differed in both solvent and sodium salt. The following solvents were used: ethylene carbonate (EC) : propylene carbonate (PC) (1:1), EC : dimethylcarbonate (DMC) : PC (1:1:1), EC : DMC : diethylcarbonate (DEC) (1:1:1). $NaPF_6$ and $NaClO_4$ were used as supporting salts.

First of all, an electrochemical stability windows for aluminum current-collectors were estimated in 1 M solutions with using cyclic voltammetry. In all systems studied, current rise at potentials more positive than 4.0 V (Na^+/Na) was registered at the first cycle, that points to electrolytes oxidation. However, at the second and following cycles this current was sharply diminished, and notable oxidation had place only at potentials more positive than 5.5 V. This fact testifies to the formation of stable passive films even at the surface of bare current-collector. EC was shown to be more stable to oxidation, as well as to reduction than PC. At the same time, it is known that PC can provide electrode functioning at low temperatures.

It was found also, that 1M $NaClO_4$ in an EC : PC mixture is more stable than 1 M $NaPF_6$ in the same solvent in the cathodic potential range. In the anodic potential range the reverse situation has place.

The stable passive films revealed the properties of SEI (solid electrolyte interfaces) are formed in all electrolytes studied at both positive and negative electrodes.

Acknowledgements

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P1 GN01

Treatment of reverse osmosis retentate of landfill leachate by electrocoagulation

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Leachate treatment is one of the major environmental issues in the management of landfills. The purification of landfill leachate with membrane technology helps to avoid further contamination of natural water resources. Membrane technologies, including the process of reverse osmosis (RO) are becoming increasingly important in treatment of landfill leachate. Reverse osmosis retentate (concentrate) formed after RO treatment with volume proportion of 30% (70% permeate) is a secondary pollution requires appropriate treatment, because of very high concentrations of organic and inorganic compounds.

This paper represents a case study for the "Ramici" regional landfill in Banja Luka, Bosnia and Herzegovina where the reverse osmosis plant installed. Electrocoagulation (EC) applied for the concentration of the RO retentate was presented in the paper. All the experiments were carried out using iron and aluminium as anode material.

Effects of process parameters such as current density, supporting electrolyte and electrolysis duration are investigated on removal efficiencies of total disolved substances (TDS) and turbidity. Iron anode achieved higher turbidity removal efficiency compared to aluminum anode, 95,76 % and 17,3 % respectively, and higher TDS removal efficiency, 21,64 % and 10,53 % respectively (t=30 min, stirring 400 rpm).

P1 GN02

Catalytical activity of electrodeposited PdNi coatings for the ethanol oxidation in alkaline solution

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Electrodeposition of Pd and PdNi coating samples was achieved galvanostatically from the plating bath containing 0.01 M $PdCl_2$ + 0.6 M $NiCl_2$ + 2 M NH_4Cl. Determination of the alloy coatings composition was performed by the anodic linear sweep voltammetry (ALSV) analysis presented in Fig. 1a, as well as by the energy dispersive X-ray spectroscopy (EDS).The coating samples were tested for ethanol oxidation reaction (EOR) in alkaline solution using cyclic voltammetry (Fig. 1b).

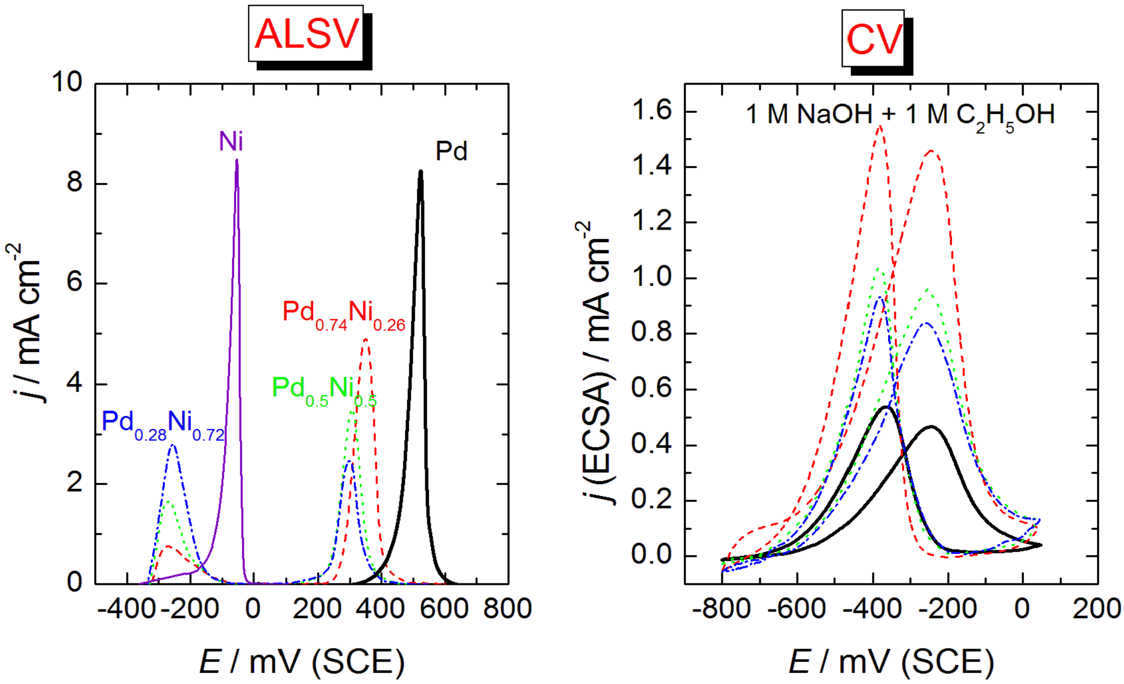

Figure 1: ALSVs of dissolution of pure Pd, pure Ni and their alloys $Pd_{0.74}Ni_{0.26}$, $Pd_{0.5}Ni_{0.5}$ and $Pd_{0.28}Ni_{0.72}$ recorded in the solution containing 1 M NaCl + 0.01 M HCl at RPM = 0 (a); CVs on Pd and PdNi coatings in 1 M NaOH + 1 M C_2H_5OH. Scan rate 50 mV s^{-1}, RPM = 1000 (b).

Among the CVs for the EOR at PdNi coating samples presented in Fig. 1b, the current density increased with the increase of Pd content up to 74 at.%. The most active one was found to be $Pd_{0.74}Ni_{0.26}$. Negatively shifted onset potential for the EOR is also observed for the $Pd_{074}Ni_{0.26}$ pointing out that this coating is more efficient and the more poisoning tolerant than the other investigated coatings.This is a consequence of better utilization of Pd on the surface of $Pd_{0.74}Ni_{0.26}$ coating due to appropriate surface morfology since more active sites are accessible to the EOR. It can be pointed out that improved catalytic activity of investigated binary coatings can be achieved through the optimization of the Ni content and appropriate surface morfology.

P1 GN03

Influence of applied potentials on charge transfer in biofuel cells

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The microbial fuel cells (MFCs) are devices for converting biochemical energy into electrical one by using microorganisms as biocatalysts. Mostly, the mechanisms of extracellular electron transfer (EET) are investigated by cultivation of living cell in the anodic chamber of fuel cell, connected by a salt bridge or proton exchange membrane to the cathodic chamber and an external load interconnecting both electrodes creates the polarization conditions.

In the present study the charge transfer between microorganisms and anode are examined in a half-cell. The influence of various potentials poising the anode was investigated. The response of cells to the poised potential was analyzed by amperometric detection. The secretion of endogenously produced mediator of electron transfer was proved by cyclic voltammetry carried out over time. The increase of the biomass was determined by spectrophometrical methods. It is shown that poising potentials, regulating the activity and growth of microorganisms, reflect on the electrical outputs. The charge transfer processes are characterized by electrochemical impedance spectroscopy and the impact of the applied potentials evaluated. The share of aerobic respiration was determined by measuring the specific cytochrome c oxidase activity of the cellular homogenates.

Acknowledgments

This study is supported by the National Science Fund of the Ministry of Education and Science of Bulgaria through the contract DFNI E02/14/2014.

Keywords: microbial fuel cell, endogenous mediator, charge transfer, cytochrome c oxidase

References:

[1] *M. Mitov, I. Bardarov, P. Mandjukov, Y. Hubenova. Chemometrical assessment of the electrical parameters obtained by long-term operating freshwater sediment microbial fuel cells. Bioelectrochemistry, 106 (2015) 105–114.*

[2] *Y. Hubenova, M. Mitov. Extracellular electron transfer in yeast–based biofuel cells: a review. Bioelectrochemistry, 106 (2015) 177–185.*

[3] *Yolina Hubenova, Eleonora Hubenova, Evelina Slavcheva, Mario Mitov. The glyoxylate pathway contributes to enhanced extracellular electron transfer in yeast-based biofuel cell. Bioelectrochemistry 116 (2017) 10–16.*

P1 GN04

Tensammetry of proteins and polysaccharides on mercury electrode under conditions of catalytic activity

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Proteins and polysaccharides adsorb ubiquitously on the mercury electrodes[1, 2]. Depending on the structure, they produce catalytic hydrogen evolution reaction (CHER) peak in a buffer solution using voltammetric and chronopotentiometric stripping method [3-5]. Here we show that the voltammetric appearance of CHER peak at very negative potentials, ~ -1.8 V in the protein and polysaccharide solution, is accompanied by a capacitive current minimum in alternate current (AC) *out-of-phase* voltammetry. The observed "tensammetric minimum" highly depended on buffer concentration, ionic strength, pH, catalyst concentration and time of accumulation. One of the possible reason for its appearance could be strong adsorption of the positively charged species such as hydrogen ions at the negatively charged mercury electrode. Moreover, tensammetric minimum proved to be sensitive toward catalytically active protein or polysaccharide when present in the mixture with catalytically inactive molecule.

Acknowledgement

Financial support for this work was provided to S.S.K. from the European Union Seventh Framework Programme (FP7 2007-2013) under grant agreement n° 291823 Marie Curie FP7-PEOPLE-2011-COFUND (The new International Fellowship Mobility Programme for Experienced Researchers in Croatia – NEWFELPRO). This work was also supported by Croatian Science Foundation project No. 8607 (AMBIOMERES) and Czech Science Foundation 15-15479S project (to E.P.).

References:

[1] *E. Paleček, in: E. Paleček, F. Scheller, J. Wang (Ed.) Electrochemistry of nucleic acids and proteins. Towards electrochemical sensors for genomics and proteomics, Elsevier, Amsterdam, 2005, pp. 690.*

[2] *M. Plavšić, S. Strmečki, Carbohydrate polymers as constituents of exopolymer substances in seawater, their complexing properties towards copper ions, surface and catalytic activity determined by electrochemical methods, Carbohydate Polymers, 135 (2016) 48-56.*

[3] *S. Strmečki, M. Plavšić, B. Ćosović, V. Ostatna, E. Paleček, Constant current chronopotentiometric stripping of sulphated polysaccharides, Electrochemistry Communications, 11 (2009) 2032-2035.*

[4] *E. Paleček, M. Bartošik, V. Ostatna, M. Trefulka, Electrocatalysis in proteins, nucleic acids and carbohydrates, Chemical Record, 12 (2012) 27-45.*

[5] *E. Paleček, Label-free electrochemical analysis of chitosan and glucosamine-containing oligosaccharides, Electrochimica Acta, 187 (2016) 375-380.*

P1 IF02

Kinetic Monte Carlo investigation into reshaping of the Pt-based nanoparticle catalyst for PEM fuel cells

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Pt-based nanoparticles supported on high surface area carbon (HSAC) have shown to have good properties as catalysts in polymer electrolyte membrane fuel cells (PEMFC), yet the durability of the nanoparticles is sometimes compromised with the cost of having a high catalytic activity. Pt-based nanoparticles after degradation form various shapes which were found out to be dependent of the initial crystal structure. For better understanding of the process kinetic Monte Carlo (KMC)[1,2] was applied to different initial state of the nanoparticles. Results highly resemble images obtained by ADF TEM analysis and consequently they revealed potential route of Pt-based nanoparticles degradation and transformation.

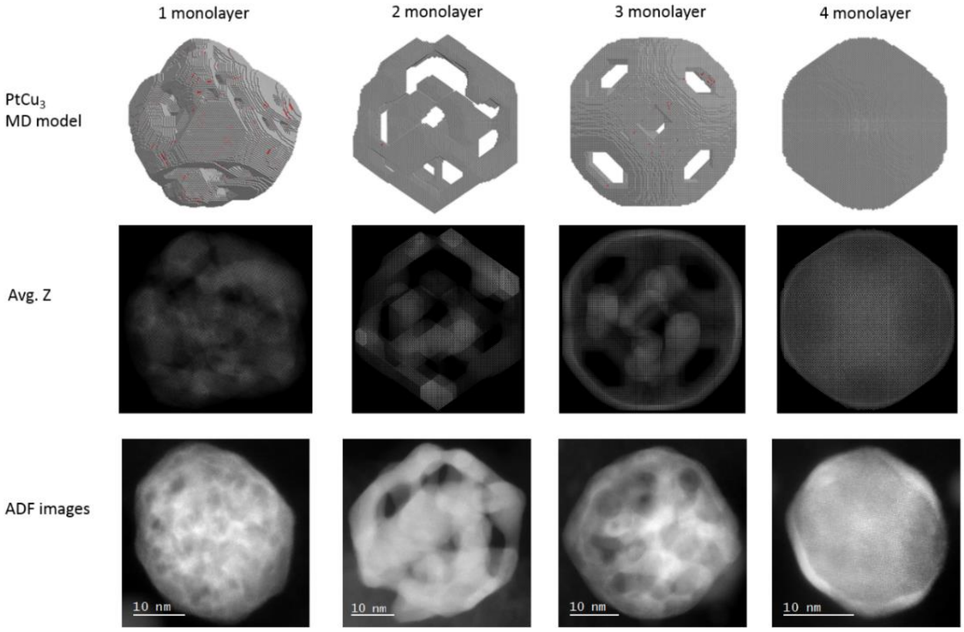

Figure 1: PtCu$_3$ atomic models simulated by KMC after a chemical bath, initially with 1, 2, 3 and 4 monolayers of Pt skin, and the corresponding average Z projections of the models (where Z is the atomic number). In the bottom part different ADF images of PtCu$_3$ and PtCu$_3$:Au nanoparticles cycled after 10K cycles.

References:

[1] *J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, Nature* ***2001****, 410, 450–453.*

[2] *A. Pavlišič, P. Jovanovič, V. S. Šelih, M. Šala, M. Bele, G. Dražić, I. Arčon, S. Hočevar, A. Kokalj, N. Hodnik, et al., ACS Catal.* ***2016****, 6, 5530–5534.*

P2 AN01

Characterization of surface morphology and content of layers of glucose sensor containing glucose oxidase-glutaraldehyde-cysteine on modified gold electrode

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Good biocompatibility of modified gold surface, which enhances the covalent bonded enzyme and consequently glucose oxidation, resulted in already tested stable glucose biosensor with successive attachment of cysteine (Cys), glutaraldehyde (GA) and glucose oxidase (GOx) onto gold electrode (Scheme 1). The surface morphology and content of layers of glucose biosensor were studied by Fourier transformed infra red spectroscopy (FTIR), as well as by the techniques of the atomic force microscopy (AFM) and the optical microscopy (OP). By FTIR it is elucidated that the most prominent bands in the spectrum of biosensor at 1675 and 1160 cm^{-1} originates from the amide I band and enzyme carbohydrate moiety and undoubtedly confirms the attachment of glucose oxidase. Cys was partially adsorbed on Au with an increase of roughness of surface area of about 30 %. The addition of GA on Au-Cys led to formation of agglomerates of 300 nm, uniform in both size and distribution. The small enzyme aggregates (10–20 nm) were observed after the addition of GOx on Au-Cys-GA surface area. The addition of serum causes the strong effect on the appearance of the biosensor without any effect on its electrochemical activity. The serum crystallize in spider`s web-like form completely modifying the surface area of the biosensor. The catalytic activity of the GOx immobilized on Au-Cys-GA for the electrooxidation of glucose in the presence of human serum is presented showing the concentration dependency in a linear range 1.5-7 mM. Biosensor exhibits the low detection limit of 0.94 mM.

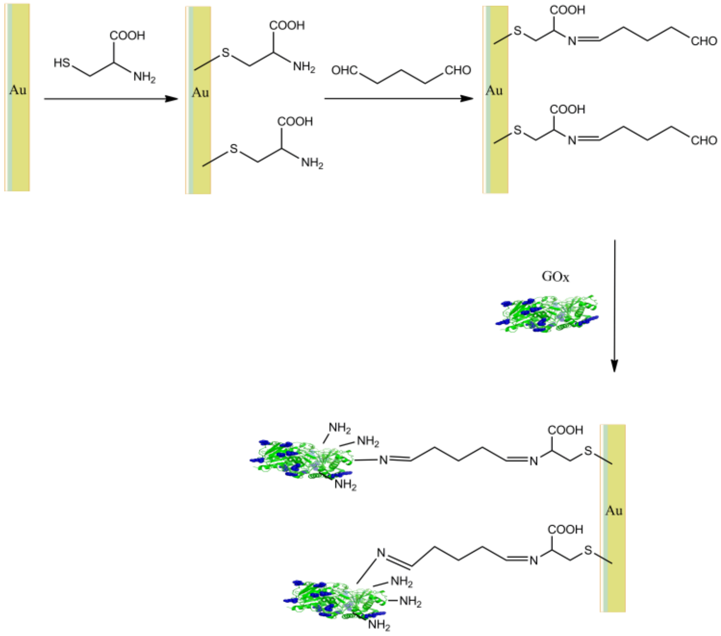

Figure 1: Modification steps of the gold electrode

P2 AN02

Degradation of azithromycin using Ti/RuO_2 anode as catalyst followed by DPV, HPLC-UV and MS analysis

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The electrodegradation of azithromycin was studied by its indirect oxidation using dimensionally stable Ti/RuO_2 anode as catalyst in the electrolyte containing methanol, 0.05 M $NaHCO_3$, sodium chloride and deionized water. The optimal conditions were found to be for NaCl concentration 7 mg cm^{-3}, for the applied current 300 mA and for the azithromycin concentration 0.472 mg cm^{-3}. The differential pulse voltammetry using glassy carbon electrode was performed for the first time in the above mentioned content of electrolyte for the nine concentration of azithromycin (0.075 mg cm^{-3} - 0.675 mg cm^{-3}) giving the limits of azithromycin detection and of quantification as: LOD 0.04 mg cm^{-3} and LOQ 0.09 mg cm^{-3}. The calibration curve was constructed enabling the electrolyte analyzis during its electrodegradation process (Fig. 1) [1]. The electrolyte was analyzed and by high performance liquid chromatography and electro spray ionization time-of-flight mass spectrometry. The electrooxidation products were identified and after 180 min there was no azithromycin in the electrolyte. The proposed degradation scheme is presented [2].

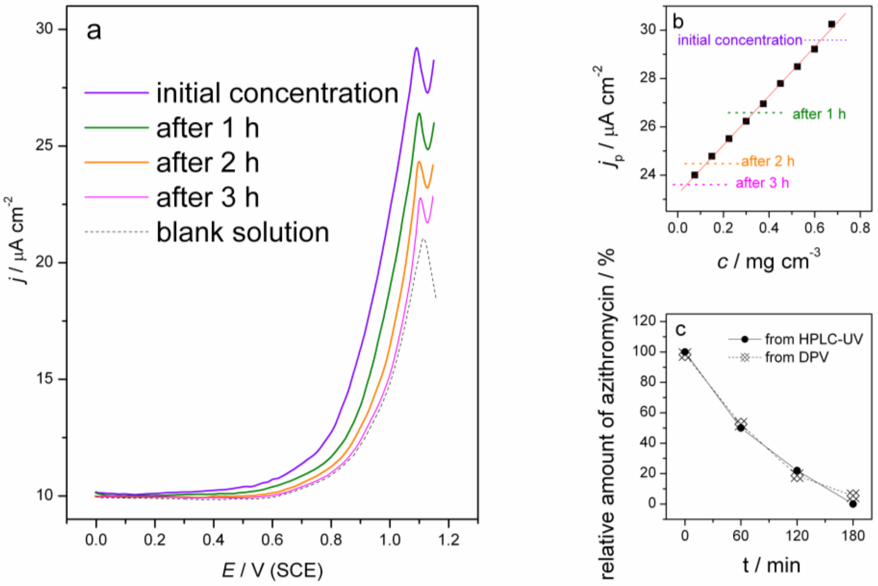

Figure 1: a) DPV at the GC electrode in blank solution (dashed line) and in the presence of the aliquots of electrolyte taken per hour during three hours of the degradation of azithromycin on DSA Ti/RuO_2

References:

[1] *Glavaški OS, Petrović SD, Mijin DZ, Jovanović MB, Dugandžić AM, Zeremski TM, Avramov Ivić ML (2014) Electroanal 26:1877-1880.*

[2] *Kummerer K (2009) Antibiotics in the aquatic environment – A review – Part II. Chemosphere 75:435-441*

P2 AN03

Electrochemical analysis of TiAlV alloy in chloride solution

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Titanium alloys are known in general for their high strength low weight ratio. The excellent mechanical properties and good machinability of TiAlV alloy combined with its high corrosion resistance due to the formation of a tightly adherent oxide film on its surface [1]. These properties make titanium alloys an excellent choice in many applications, including aerospace and chemical industry, marine applications and oil and gas extraction. Due to its excellent biocompatibility when in contact with body tissue or bones the TiAlV alloy has been widely used in different medical applications, including hip replacements and dental implants [2-5].

In this study, a long-term investigation of the corrosion behavior of TiAlV alloy in physiological body fluid (0.9 wt.% NaCl solution) at 37 °C using electrochemical techniques is presented. Chronopotentiometric, electrochemical impedance spectroscopy and potentiodynamic curve measurement analysis of TiAlV alloy in chloride media have been performed in sequence after 1, 3, 5, 7, 10, 15, 24, 36 and 72 h of immersion. A detailed analysis of the fitted impedance data using different equivalent electrical circuit models will shed light into the phenomena occurring on the alloy surface. The susceptibility of the TiAlV alloy towards localized and general corrosion will also be discussed.

Keywords: TiAlV alloy, medical grade materials, electrochemical impedance, chloride solutions

References:

[1] *Revie, R.W. and H.H. Uhlig, Corrosion and corrosion control: an introduction to corrosion science and engineering. 4th ed. 2008, Hoboken, New Yersey: John Wiley & Sons, Inc.*

[2] *Filip, P., et al., TiAlV/Al2O3/TiNi shape memory alloy smart composite biomaterials for orthopedic surgery. Materials Science and Engineering: A, 1999.* ***273–275****: p. 769-774.*

[3] *Joska, L., et al., The effect of a DLC coating adhesion layer on the corrosion behavior of titanium and the Ti6Al4V alloy for dental implants. Surface and Coatings Technology, 2012.* ***206****(23): p. 4899-4906.*

[4] *Gajski, G., et al., Physico-chemical characterization and the in vitro genotoxicity of medical implants metal alloy (TiAlV and CoCrMo) and polyethylene particles in human lymphocytes. Biochimica et Biophysica Acta (BBA) - General Subjects, 2014.* ***1840****(1): p. 565-576.*

[5] *Liu, X., P.K. Chu, and C. Ding, Surface modification of titanium, titanium alloys, and related materials for biomedical applications. Materials Science and Engineering: R: Reports, 2004.* ***47****(3–4): p. 49-121.*

P2 AN04

Electrochemical properties of 5-*O*-caffeoylquinic acid investigated by square-wave voltammetry and differential pulse voltammetry

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Chlorogenic acids (CGAs) are one of the groups of polyphenolic compounds widely distributed in different plant materials. Chemically, CGAs are family of different esters formed between (-)-quinic acid and certain *trans*-cinnamic acids, most commonly caffeic, ferulic and *p*-coumaric acids. In this study the electrochemical properties one of the most abundant CGAs in plants, namely 5-*O*-caffeoylquinic acid (5-CQA) was studied by square-wave voltammetry (SWV) and differential pulse voltammetry (DPV). The electrochemical properties of 5-CQA were compared with the electrochemical properties of caffeic acid (CFA), main structural moiety of 5-CQA. The study reveals that electrochemical properties of 5-CQA strongly depends on its chemical structure and electronic properties, particularly on electron-donating effect of −OH and −CH=CH− groups, and a strong electron-withdrawing effect of ester (−COOR) group in the chemical structure of 5-CQA molecule. SWV and DPV measurements show that electrochemical oxidation/reduction of 5-CQA at a glassy carbon electrode (GCE) is reversible, pH-dependent, two electron-two proton process. The oxidation/reduction processes occurred on the catechol moiety (*ortho*-dihydroxyl groups) in the structure of 5-CQA molecule. The oxidation product(s) relatively strongly adsorb on the GCE surface, especially at higher concentration of 5-CQA. It was observed that the anodic peak current of 5-CQA show maximum in solution of pH 7, due to the maximum concentration of 5-CQA$^-$ anion at this pH value. The electrode reaction proceeded in the solution of 5-CQA is diffusion controlled process. The anodic peak current of 5-CQA show linear relationship with the concentration in the concentration range 5-50 μmol L^{-1}, with low limit of detection (LOD) of $7.7 \cdot 10^{-7}$ mol L^{-1} for SWV and $1.2 \cdot 10^{-6}$ mol L^{-1} for DPV measurements. SWV and DPV of coffee samples have shown that electrochemical properties of water coffee extracts were very similar to that of investigated 5-CQA. Therefore, SWV and DPV can be used as very sensitive and selective methods for determination of CQAs content (and CGAs content) in different coffee samples.

References:

[1] *M. Namazian, H. R. Zare, Electrochim. Acta 50 (2005) 4350–4355.*

[2] *P. J. Eravuchira, R. M. El-Abassy, S. Deshpande, et al., Vib. Spectrosc. 61 (2012) 10-16.*

[3] *S. Mishra, P. Tandon, P. J. Eravuchira, et al., Spectrochim. Acta Part A 104 (2013) 358-367.*

[4] *M. Šeruga, I. Tomac, Int. J. Electrochem. Sci. 9 (2014) 6134-6154.*

[5] *I. Tomac, M. Šeruga, Int. J. Electrochem. Sci. 11 (2016) 2854-2876.*

P2 AN05

Heavy metal ions electroanalysis from waters using chemically modified electrodes based on 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyridine

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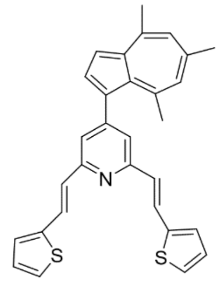
The concentration level of cadmium and lead is a relevant indicator for assessing water pollution, knowing that the presence of these heavy metals constitutes serious threats to human health. Besides the spectral analytical methods used for heavy metals determination in waters, the electroanalysis of these analytes gains more and more ground due to several benefits which they confer, including miniaturization and portability, very good selectivity, sensitivity and low cost. After an extensive investigation of several azulen-derivatives compounds [1, 2], the electrochemical behavior of these substances showed that they possess a special property to form complexing conducting polymers on the surface of carbon disk electrode. These polymeric films proved to be good electrodic materials to achieve chemically modified electrodes (CMEs) suitable to be applied in heavy metal cations electroanalysis.

The present work is devoted to investigation of the ability of a new synthesized azulene compound 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyridine (**L**) (Figure 1) to form complexing polymeric films (Poly**L)** in order to obtain CMEs for Cd(II) and Pb(II) analysis. The poly**L** films were obtained by oxidative electropolymerization of the monomer **L** and the CMEs thus achieved have been investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Chemical preconcentration-anodic stripping technique was employed in order to analyze the mentioned metallic cations.

The application of new polymer-coated electrodes achieved by electropolymerization of monomer **L** in the recognition of Cd(II) and Pb(II) cations led to significant improvement of their detection limits, at the level of 5 x 10^{-6} mol L^{-1} for Cd(II) and 6 x 10^{-8} mol L^{-1} Pb(II). Optimization of the determination conditions for these ions has been carried out regarding to pre-concentration times, polyL film thickness, deposition potential, linearity and limit of detection.

By using CMEs based on 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyridine for Cd(II) and Pb(II) analysis from water samples, similar results to atomic absorption spectrometry have been obtained.



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Acknowledgments

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References:

[1] *P. Szlachcic, K. S. Danel, M. Gryl, K. Stadnicka, Z. Usatenko, N. Nosidlak, G. Lewińska, J. Sanetra, W. Kuźnik, Dyes and Pigments* ***2015****, 114, 184-195.*

[2] *G.-O. Buica, E.-M. Ungureanu, L. Birzan, A.C. Razus, L.-R. Mandoc (Popescu), J. Electroanal. Chem.,* ***2013****, 693, 67–72.*

P2 AN06

Long-time immersion study of medical grade stainless steel in chloride solution using different electroanalytical techniques

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A wide variety of medical-grade materials, including ceramics, titanium alloys and stainless steel has been used in various medical applications, especially in total hip arthroplasty [1, 2]. These materials have to be durable, non-toxic to human body and biocompatible. Several studies have been performed on the development of different coatings on the medical-grade steel (AISI 316LVM) to be used as drug delivery systems in orthopedic applications [3, 4].

In this study, a detailed chronopotentiometric, electrochemical impedance spectroscopy and potentiodynamic curve measurement analysis of medical-grade steel immersed for up to 72 h in 0.9 wt.% NaCl solution at 37 °C, is presented. The influence of immersion time on the corrosion resistance of the medical-grade steel towards general and localized corrosion will be discussed. Different equivalent electrical circuit models are used to fit the impedance data in order to understand the corrosion mechanism of medical-grade steel in chloride solutions after long-time immersion.

Keywords: medical-grade steel, electrochemical impedance spectroscopy, chloride solutions

References:

[1] *Konttinen, Y.T., et al., Metals for joint replacement, in Joint Replacement Technology (Second Edition). 2014, Woodhead Publishing. p. 81-151.*

[2] *Kluess, D., et al., Ceramics for joint replacement, in Joint Replacement Technology (Second Edition). 2014, Woodhead Publishing. p. 152-166.*

[3] *Finsgar, M., et al., Novel chitosan/diclofenac coatings on medical grade stainless steel for hip replacement applications. Scientific Reports, 2016. 6, Article Number: 26653.*

[4] *Horvat, G., et al., Novel ethanol-induced pectin–xanthan aerogel coatings for orthopedic applications. Carbohydrate Polymers, 2017. 166: p. 365-376.*

P2 AN07

Voltammetric analysis of organic surface active substances in the aquatic environment

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Surface active substances (SAS) as constituents of dissolved organic carbon (DOC) as well as particulate organic carbon (POC), were studied in the water samples from different environmental compartments (urban atmosphere, sea- and freshwater systems, soil from agriculture area, and mining water.Investigation was performed byelectrochemical methods - voltammetric techniques, simple, rapid and nondestructive, that were developed by our groupfor rough physicochemical characterization of DOC in the natural waters [1and references therein]. In the biogeochemical processes in aquatic environment, the physicochemical properties of organic matter (OM) are often more important than the amount present. Surface SAS are concentrated by adsorption processes at the natural phase boundaries where they greatly affect transfer of mass and energy.The most analasis techniques are not sensitive to the interface and simply treat the surface as the part of the bulk. Electrochemical method that has been applied since 1970 enables quantification of SAS and offers insight into its spatial distribution and seasonal variations in the water environment while curve shape analysis enables rough characterization of predominant SAS groups.Adsorption effect of SAS from samples was measured at the hanging mercury drop electrode (HMDE) using phase sensitive alternating current voltammetry (PSACV) out-of-phase mode. The permeability of organic film of SAS was tested by the investigation of the influence of the adsorbed layer on the electrode processes of Cd^{2+} ion which is used as electrochemical tool (PSACV in-phase mode). On that way a rough characterization of OM in natural water samples have been performed using different model substances selected as the major types of DOC in the relevant aquatic systems.

Acknowledgements

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References:

[1] *Orlović-Leko, P., Vidović, K., Plavšić, M., Ciglenečki, I., Šimunić, I., Minkina, T.,J. Solid State Electrochem., 2016, 20(11), 3097-3105.*

P2 AN08

Voltammetric determination of β-carotene in fruits and vegetables

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β-Carotene is a red-orange, fat-soluble carotenoid pigment found in fruits, vegetables and green leafy plants. It is one of the most abundant carotenoids found in the human diet and exerts numerous roles in biological systems. One of its major functions in humans is provitamin A activity. In addition, the consumption of a diet rich in β-carotene has been associated with a reduced risk for development of numerous oxidative-stress related diseases, such as cancer, cardiovascular diseases and various age-related degenerative diseases. These protective and therapeutic effects of β-carotene are mainly attributed to its antioxidant properties, i.e. the ability to quench reactive oxygen species and prevent or decrease oxidative damage to biomolecules (DNA, lipids and proteins). Owing to the beneficial health effects of β-carotene, there is an interest in developing a simple, rapid and reliable method for its determination in foods.

β-Carotene is electroactive and can be electrochemically oxidized due to the conjugated double bonds. Depending on the analyte concentration differential pulse voltammetric response of β-carotene on a glassy-carbon electrode in acetone / 0.1 M $NaClO_4$ consists of one or two peaks. At concentrations lower than $3x10^{-5}$ mol/L one main peak P1 was obtained. By increasing the concentration of β-carotene a small peak P2 at more positive potential appears. The oxidation potential of P1 is shifted toward higher values with increasing of β-carotene concentration. The relationship between peak potentials P1 and the logarithm of β-carotene concentration is linear, with the slope of $\Delta E_{P1}/\Delta \log c = 0.067$ V/d.u.

Quantitative analysis of foodstuff was performed under experimental conditions of differential pulse amplitude 50 mV, interval time 0.15 s, pulse time 0.05 s and step potential 2 mV. Under these conditions, linear responses for β-carotene were obtained for concentrations from 4×10^{-6} mol/L to 1.1×10^{-4} mol/L, and calculated LOD and LOQ were 2.5×10^{-6} mol/L and 8.2×10^{-6} mol/L, respectively. The proposed method was applied for the determination of β-carotene in extracts of different fruits (grapefruit, mango) and vegetables (carrot, butternut, sweet potato, spinach, kale and broccoli). Our results demonstrate that differential pulse voltammetry enables fast and simple quantification of β-carotene in a broad range of natural products.

P2 CA01

Electrocatalytic oxygen reduction and oxygen evolution on thin film manganite perovskites

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Heading towards renewable energy systems, conversion and storage, e.g. in chemical bonds, become an important factor. Besides common electrocatalysts like nickel, ruthenium and iridium oxide, there is an increasing interest in the study of manganese oxides. We study epitaxial manganite perovskite thin films such as $Pr_{1-x}Ca_xMnO_3$ (PCMO) and $La_{1-x}Sr_xMnO_3$ (LSMO) to gain an improved fundamental understanding of their stability and activity during electrocatalysis of the oxygen evolution reaction (OER) as well as of the oxygen reduction reaction (ORR).

Up to 200 nm thick (001)-orientated epitaxial films were deposited on 0.5 wt % Nb-doped $SrTiO_3$ substrates via ion beam sputtering. Characterization of crystal structure and layer thickness was done by X-ray diffraction (XRD) and X-ray reflectivity (XRR). Virgin state and post-mortem analysis was performed using atomic force microscopy (AFM) to distinguish modification in the surface morphology. Using a rotating ring disc electrode (RRDE) setup (Figure 1), electrochemical impedance spectroscopy, cyclovoltammetry and ring disc collection measurements were performed in an alkaline electrolyte.

Previous studies on ink-casted particle electrodes used additives such as carbon to provide the electrochemically required conductance to the supporting material. Since carbon is known to degrade during oxygen evolution and the active surface area of nanoparticles can merely be estimated, the study of thin film specimens reduces these experimental uncertainties. Furthermore, experiments with the ferri/ferrocyanide redox couple show a good performance for electron transfer reactions near the thermodynamic redox potential of the OER in an alkaline solution at LSMO [1]. While oxygen vacancies near the surface of PCMO influence the activity of the OER [2], measurements on LSMO imply manganese atoms as the active site for the OER [1,3]. For detailed electrochemical studies, the rotating ring disc setup provides the benefit of separating currents limited by kinetics and mass transport. In comparison to the OER, the Tafel slope of the ORR is much higher, which corresponds to a lower activity. While we did not detect hydrogen peroxide during the OER, hydrogen peroxide was produced during the ORR on LSMO. We have studied the rate constants for both reaction pathways, based on Damjanović's Model [4]. The RRDE studies on well-characterized epitaxial thin film electrodes allow detailed insights in the reaction mechanisms of perovskite oxide surfaces.

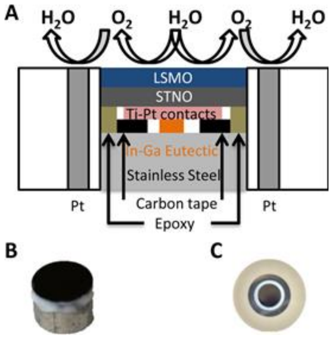

Figure 1: (A) Schematic view of an epitaxial manganite perovskite electrode. Photographs of (B) the assembled electrode and (C) the electrode in an RRDE assembly. For detailed dimensions and the procedure for the electrode assembly, please refer to ref. [1]. Reprinted with permission from ref. [1]. Copyright 2016 American Chemical Society

References:

[1] *Scholz et al., "Rotating Ring–Disk Electrode Study of Oxygen Evolution at a Perovskite Surface: Correlating Activity to Manganese Concentration", J. Phys. Chem. C 2016, 120, 27746–27756*

[2] *Raabe et al., " In Situ Electrochemical Electron Microscopy Study of Oxygen Evolution Activity of Doped Manganite Perovskites", Adv. Funct. Mater. 2012, 22, 3379-3388*

[3] *Scholz et al., "Tailoring the oxygen evolution activity and stability by using means of defect chemistry", submitted*

[4] *Damjanovic et al., "The Role of Hydrogen Peroxide in the Reduction of Oxygen at Platinum Electrodes", J. Phys. Chem., 1966, 70 (11), pp 3761–3762*

P2 CA02

Enhancement of cathodic hydrogen evolution reaction using proton carriers

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The concept of ecologically clean hydrogen still causes significant research interest. Unfortunately, most widely used methods for hydrogen production are based on coal gasification, or hydrocarbons cracking and reforming, having as a result not only hydrogen, but also a huge amount of carbon dioxide. For example, if hydrogen is obtained by steam reforming of methane, for each ton of H_2, an amount of 5.5 tons of CO_2 are released in the atmosphere [1]. Moreover, in coal gasification technology, 11 tons of CO_2 are emitted in environment for 1 ton of H_2 obtained [2].

Although water splitting by electrolysis is a *green* procedure, it is limited by important electric energy consumption and it is applicable particularly in areas where clean, inexpensive electricity is available. The efficiency of the water electrolysis process can be increased by catalytic enhancement of the hydrogen evolution reaction (HER), which can be achieved on one hand by using electroactive materials and modified electrodes for HER, and on the other hand, by introducing additives in the electrolyte solution as proton carriers.

The electrocatalysts in the solution are compounds that are able to increase the concentration of protons in the electric double layer at the interface, by transporting protons from the bulk to the interface, therefore they are called proton carriers. Example of such proton carriers are amines, and their catalytic activity is caused by the lone electron pair of the nitrogen atom.

In our work we have studied the mechanism of catalytic effect of proton carriers on cathodic HER in acid solution and different substrates. Several amines, such as benzylamine, methylamine, *DL*-1-phenylethylamine, aniline, N-methylaniline, 2-biphenylylamine, 3-chloroaniline, 4-chloroaniline have been investigated on copper, gold and platinum electrodes. Also we have tried to achieve correlations between the catalytic effect and the structure and molecular parameters of the investigated amines.

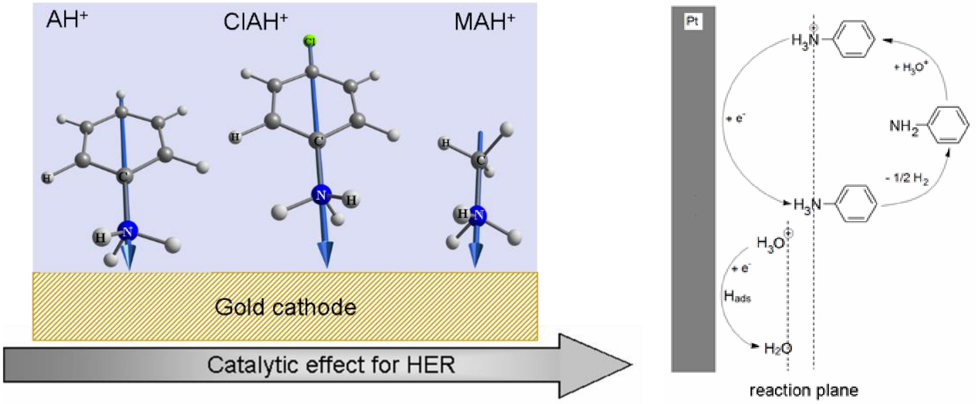

Figure 1: Catalytic effect of aniline, 4-chloro-aniline and methylamine on HER on gold electrode (left) and mechanism of HER in the presence of proton carriers (right)

Generally, the effect of amines is to decrease the charge transfer coefficient 1-α due to adsorption on the electrode-electrolyte interface, but this unfavorable effect is offset by a significant increase of the exchange current density i_0. The catalytic function of amines can be linked to the molecular parameters of protonated amines, from which most important have proved to be the dipole moment and coverage surface.

References:

[1] Press RJ, Santhanam KSV, Massoud JM, Bailey AV, Takacs GA. Introduction to Hydrogen Technology. John Wiley, Hoboken, New Jersey, 2009, p. 196.

[2] Zuttel A, Borgschulte, Schlapbach L. Hydrogen as a Future Energy Carrier. Wiley-VCH Verlag, Weinheim – Germany, 2008, p. 154.

P2 CA03

Tin sulfide films as promising materials for solar assisted catalysis and solar cells: Investigation of electronic structural properties

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Tin sulfide materials belong to groups IV-VI of binary compounds constituted of nontoxic and nature-abundant elements. The narrow band gap of SnS_2 enables the utilization of solar energy and makes it a potential candidate for the low-cost solar energy conversion material and the efficient visible-light-driven photocatalyst.[1-4] The incident photon-to-current efficiency of the single SnS_2 layer can approach about 40%.[2] Also, the sustainable manufacturing of solar devices is feasible if tin sulfide materials are used as cheap, nonstrategic and ubiquitous in nature, leading to the development of environmentally safe devices.[3,4]

A wide application of tin sulfides includes: solar collectors, photodetectors in photovoltaic solar energy devices, photocatalysts in advanced oxidation processes, as well as promising alternative for anode materials to replace commercial carbonaceous electrodes (graphite) in lithium–ion and sodium–ion batteries due to their high capacities.[1-6]

The merits and demerits of the methods proposed for the SnS_2 preparation still inspire a huge researchers' interest to develop simple and economically feasible synthetic route to produce uniform and well adherent thin films. In this work, environment friendly and facile approach has been introduced for synthesis of the passive sulfide films on tin, employing non–toxic and low–cost materials and enabling films formation on versatile shape and surface size. The tin sulfide film, formed by potentiostatic anodic polarization on tin in aqueous electrolyte solution, containing sulfide ions, was investigated using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and diffuse reflectance spectroscopy (DRS).

The electronic structure of the tin sulfide film was discussed on the basis of the band structure model of the surface film, the potential distribution across the film and at the metal|film|electrolyte interfaces as well as the availability of free charge carriers on the electrode|solution interface. The electronic structure of the tin sulfide film influences its susceptibility to the oxidative as well as to the reductive solid–state decomposition. The DRS data enabled the determination of the optical band gap value, E_g using the Kubelka-Munk method. By using the Mott-Schottky analysis, additional semiconducting parameters of the sulfide film: the flat band potential, E_{FB}, and the donor concentration, N_D were determined.

In summary, this work provides a better knowledge of the electronic structure of the tin sulfide film from the viewpoint of semiconductor electrochemistry. The applicability of the mathematical relationships (Mott–Schottky equation), developed for the classical semiconductors, has been successfully extended to this type of materials taking into account the frequency dispersion in the Mott–Schottky tests.[7]

Additionally, the results presented in this work enable a better insight into the electronic structure/semiconducting properties of the tin sulfide film that are essential to predict its suitability for optoelectronic and photovoltaic device applications.

References:

[1] C.H. Lai, M.Y. Lu, L.J. Chen, J. Mater. Chem., **22***, 19 (2012).*

[2] Y. Sun, H. Cheng, S. Gao, Z. Sun, Q. Liu, F. Lei, T. Yao, J. He, S. Wei, Y. Xie, Angew. Chem. Int. Ed. **124***, 8857 (2012).*

[3] Z. Wu, Y. Xue, Y. Zhang, J. Li, T. Chen, RSC Adv., **5***, 24640 (2015).*

[4] L.A. Burton, T.J. Whittles, D. Hesp, W.M. Linhart, J.M. Skelton, B. Hou, R. Webster, G. O'Dowd, C. Reece, D. Cherns, D.J. Fermin, T.D. Veal, V.R. Dhanak, A. Walsh, J. Mater. Chem. A, **4***, 1312 (2016).*

[5] Y. Du, Z. Yin, X. Rui, Z. Zeng, X. Wu, J. Liu, Y. Zhu, J. Zhu, X. Huang, Q. Yan, H. Zhang, Nanoscale, **5***, 1456 (2013).*

[6] L. Liu, F. Xie, J. Lyu, T. Zhao, T. Li, B.G. Choi, J. Power Sources, **321***, 11 (2016).*

[7] J. Katić, M. Metikoš-Huković, I. Šarić, M. Petravić, J. Electrochem. Soc., **163***, C221 (2016).*

P2 FM01

Actual trends in the elaboration of advanced multifunctional protective coating systems for (Al–Cu–Mg) lightweight aircraft alloys

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The present review is an attempt to summarize the basic trends and concepts regarding the elaboration of environmentally friendly multilayered corrosion protective coating systems. It summarizes the recent trends regarding the elaboration of multilayered multifunctional corrosion protective coating systems, including the accepted recent environmental requirements. The paper summarizes the recent trends, related to the development of reliable multilayered corrosion protective coatings, considering the recent environmental restrictions in EU and USA. The function of each layer, composing the multilayered coating system and the respective requirements are described. Special attention is paid to the multifunctionality of these systems (Fig. 1), describing the specific function of each layer, according to recently proposed concepts in the literature.

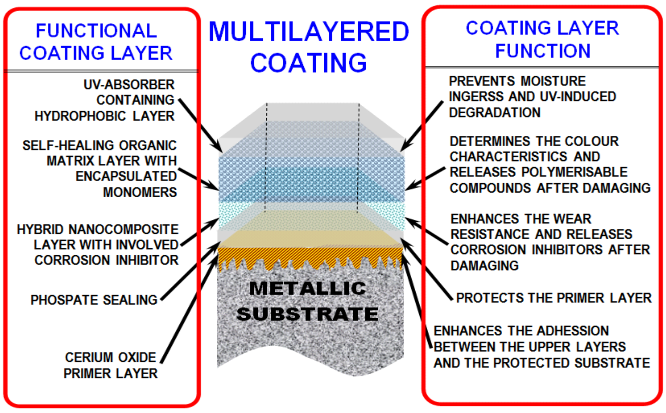

Figure 1: A model of multilayered coating system

The present investigation summarizes the recent trends in the field of advanced protective coating architecture, as well as the concepts for active and passive corrosion protection. Various examples are given for perspective candidates as environmentally friendly coating ingredients.

Since transport is the backbone of modern economics, there is a need for elaboration of lightweight efficient vehicles and transport facilities. In this sense, aluminum and magnesium alloys find continuously increasing application in high-performance aircraft, automobile and marine vehicles. Therefore, various advanced multilayered corrosion protective coating systems have recently been proposed in order to provide reliable long-term corrosion protection combined with various supplemental beneficial properties. The present review is an attempt to summarize the basic trends and concepts regarding the elaboration of environment-friendly multilayered corrosion protective coating systems. This present review summarizes the recent trends in the elaboration of multilayered multifunctional corrosion protective coating systems, according to the recently accepted environmental requirements. Thereafter, a division is done between the concepts for passive and active corrosion protection capabilities.

The basic approaches for the achievement of efficient active corrosion protective properties are described with suitable examples. They include inhibitor incorporation into ceramic or carbon nanoparticles, encapsulation of active self-healing compounds, reinforcing phase involvement and coating finishing by ultraviolet absorbers and hydrophobic compounds. As a main result, an entire conceptual model has been proposed based on the literature research done.

Acknowledgements

The authors are grateful for the funding of this research to the Bulgarian National Scientific Research Fund, under contract DFNI-T02-27.

Keywords: Aircraft alloys, Corrosion protection, Multifunctionality, Self-healing effect, Corrosion inhibitors

P2 FM02

Effect of the thermal treatment of combined (Al/Ce)-oxide films deposited on AA2024-T3 aircraft alloy

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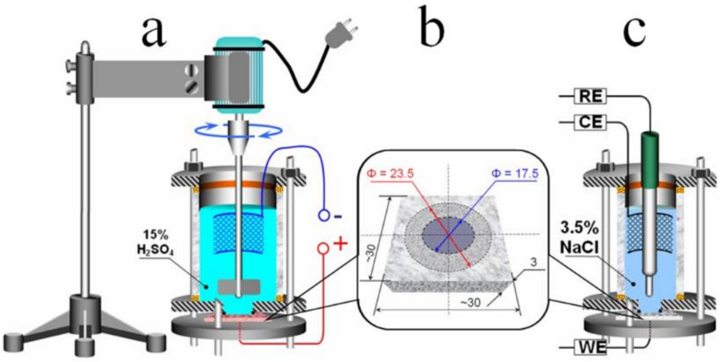
In the present work a brief comparative evaluation of the finishing thermal procedure effects on the combined Aluminum/Cerium oxide layer is performed. AA2024 aircraft alloy samples were submitted subsequently to anodization and Cerium Conversion Coating deposition via dip coating. Afterwards, the already formed (Al/Ce) oxide combined films underwent finishing thermal treatments at two different temperatures. The impact of the thermal treatment was followed by systematic electrochemical and morphological measurement procedures. The electrochemical methods included Electrochemical Impedance Spectroscopy (EIS), combined with Linear Sweep Voltammetry (LSV) during exposure of the specimens to a model corrosive medium.



Anodization setup (a), treated AA2024-T3 samples (b) and measurement electrochemical cell (c), where: RE – reference electrode, CE – counter electrode, WE – working electrode

The anodization and the conversion coating deposition are widely used approaches for efficient corrosion protection of aluminum and its alloys. Both methods provide protective oxide coating primers for improvement of the corrosion protection and the adhesion for possible further treatment.

The alloy thermal treatment is another common method in the industrial practice. It enables primer oxide layer fixation and oxide growth in the pores and defects of the already deposited primers. However, the annealing finishing procedures cause mechanical tensions due to the dilatation/contraction of the metallic substrate.

In the present research a comparative evaluation of the finishing thermal procedure effects on the combined (Al/Ce) oxide layer is performed. The impact of the thermal treatment at two temperatures was followed by systematical electrochemical and morphological measurement procedures. The electrochemical methods include Electrochemical Impedance Spectroscopy (EIS), combined with Linear Sweep Voltammetry (LSV) during exposure of the specimens to a model corrosive medium. The thermally treated combined primer coatings were observed by Scanning Electron Microscopy (SEM) and Energy dispersion X-ray (EDX) analysis. For determination of the chemical compounds (i.e. oxides or hydroxides of Ce(III) and/or Ce(IV)), additional X-ray Photoemission Spectroscopy (XPS) was applied.

The obtained results from all these instrumental analytical techniques enabled to create a conceptual model regarding the finishing thermal treatment impact on the combined (Al/Ce) oxide layer.

Acknowledgements

The authors are grateful for the funding of this research to the Bulgarian National Scientific Research Fund, under contract DFNI T02-27.

Keywords: AA2024-T3 aircraft alloy, Anodized Aluminium Oxide (AAO), Cerium Conversion Coating (CeCC), Electrochemical corrosion tests, Film morphology and composition

P2 FM03

Electroless deposition of palladium nanoparticles on poly(3,4-ethyelenedioxythiophene)

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Conducting polymer (CP) materials offer a specific opportunity to deposit metal particles on CPs by using the intrinsic redox properties of the polymer material ([1-4] and literature cited therein). Reduction of metal ions is coupled to oxidation of pre-reduced conducting polymer layers. The process is self-confined and does not involve additional oxidants in electrolyte solution. For that reason it depends considerably on the structural and electrochemical characteristics of the CP layers. In the present study electroless deposition of Pd is studied on poly(3,4-ethyelenedioxythiophene) (PEDOT) layers obtained in the presence of either polysterenesulfonate (PSS) or dodecylsulfate (SDS) as doping ions. Two types of electrode substrates (glassy carbon – GCE and spectral graphite – SGE) are used for electrochemical polymerization of EDOT. Pre-reduction of the PEDOT-coated electrodes, necessary to drive the electroless deposition process, is carried out by using different pre-conditioning of the CP-coated electrodes corresponding to mild and strong pre-reduction of PEDOT. The electroless metal deposition process is monitored by registering open circuit potential (OCP) transients in the course of the coupled oxidative/reductive reaction. The amount of deposited palladium is determined by anodic voltammetric stripping and the type of metal deposit is imaged by SEM.

It is established that the electrode substrate plays a significant role for the polymerization of PEDOT-PSS with delayed formation of the PEDOT layers observed on GCE in comparison to SGE. Although the ratio of intrinsic redox charge to polymerization charge and thus the doping level of PEDOT remains for both types of electrodes one and the same the electroless palladium deposition proceeds in completely different ways. A steep OCP increase for GCE in contrast to much slower and gradual OCP change for SGE is observed and results in ten times larger amount of metal on PEDOT-PSS/SGE. In the latter case Pd nanoparticles with mean size of about 5 nm are evenly and densely distributed on the PEDOT-PSS surface.

The doping ions used in the course of PEDOT synthesis affect the surface and bulk morphology of the PEDOT layers but also most markedly the way of polymer oxidation in the presence of metal ions. As a result in the case of PEDOT-SDS the OCP remains for a longer time in the high overpotential region for Pd deposition and larger amounts of metal become deposited on the polymer surface. Nevertheless the palladium deposit remains highly dispersed and the mean size of the nanoparticles almost unchanged.

Acknowledgement

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References:

[1] *V. Lyutov, V. Tsakova, J. Solid State Electrochem., 15 (2011) 2553-2562.*
[2] *V. Lyutov, V. Tsakova, J. Electroanal. Chem., 661 (2011) 186-191.*
[3] *M. Ilieva, A. Nakova, V. Tsakova, J. Solid State Electrochem., 20 (2016) 3015-3023.*
[4] *V. Karabozhikova, V. Tsakova, Chemical Papers, 71 (2017) 339-346.*

P2 FM04

One-pot electrochemical synthesis of polypyrrole/graphene oxide composite

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Conductive polymers attract significant attention due to the easy synthesis, low cost, high conductivity and fast redox reactions. Polypyrrole (PPy) is one of the most often used conductive polymers in fields such as sensors, electrochromic devices, corrosion protection, actuators and energy power sources. The properties of Ppy can be significantly improved by controlling the microstructure and morphology of the material. In order to achieve fast redox reaction nanometar-sized and porous structure must be considered. Such porous structure could be obtained when polymerization is carried out in the presence of graphene or graphene-based materials [1,2]. It is expected that Ppy/graphene composite has improved pseudocapacitive properties suitable for supercapacitor application [3].

In this work an electrochemical approach for exfoliation of graphite and synthesis of Ppy/graphene oxide composite was studied. The overall procedure is simple and effective way of graphene synthesis and its intercalation within the polypyrrole layer. The experiments were conducted in two steps. In the first step, graphene oxide was prepared by electrochemical exfoliation of natural graphite flakes. The exfoliation of natural graphite was carried out in sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS) aqueous solutions. Graphite electrode was alternately polarized at positive and negative potentials by using two electrode system. During positive polarization SDS and SDBS intercalate within the structure of graphite, and at the same time oxygen evolution as well as carbon oxidation takes place. By applying negative potential cations intercalate into graphite working electrode and also hydrogen evolution takes place. The overall process resulted in successful exfoliation of graphite electrode. The obtained product, graphene oxide, was characterized by ultraviolet-visible spectrophotometry (UV/Vis), Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM).

In the second step, monomer was dissolved in a solution obtained during exfoliation process and electrochemical synthesis of Ppy/graphene oxide composites was carried out. The obtained nanocomposite was characterized by means of FTIR and scanning electron microscopy (SEM). The electrochemical measurements were performed by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Ion exchange behavior of obtained composite material was also studied by using the electrochemical quartz crystal nanobalance (EQCN).

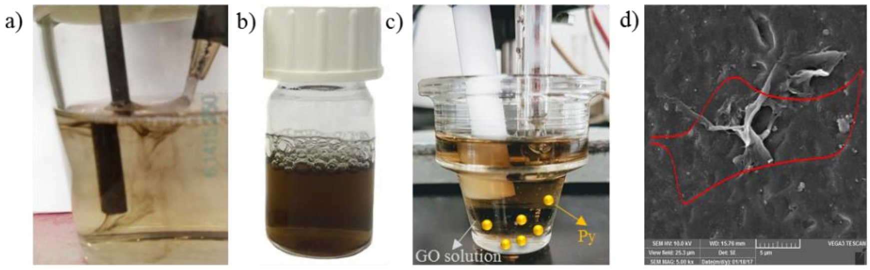

Figure 1: a) Electrochemical exfoliation of graphite rod, b) obtained graphene oxide (GO) solution, c) electrochemical synthesis of Ppy/GO composite, d) SEM image and CV curve of Ppy/GO composite

References:

[1] *D. Sačer, D. Čapeta, I. Š. Rakić, R. Peter, M. Petravić, M. K. Roković, Electrochimica Acta 193 (2016) 311-320.*

[2] *A. Österholm, T. Lindfors, J. Kauppila, P. Damlin, C. Kvarnström, Electrochimica Acta 83 (2012) 463–470.*

[3] *S. Konwer, R. Boruah, S. K. Dolui, Journal of Electronic Materials 40 (2011) 2248–2255.*

P2 FM05

Reduction of graphene oxide by using phenolic compounds from olive leaf extract

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Since its discovery, graphene, the two-dimensional sheet of sp^2 bonded carbon atoms has received significant attention. Based on its excellent electrical, mechanical and thermal properties with a wide range of potential applications there is constant need for its production in bulk quantities. Although developed methods [1, 2] which use standard strong reducing agents bring good results, there is constant need for less hazardous, less toxic and more economic chemicals. There are reports on green routes which use reducing agents such as green tea, ascorbic acid or vitamin C, baker's yeast or amino acids [3].

In this work simple and green chemistry route for the preparation of reduced graphene oxide (rGO) was studied. It was shown that graphene oxide (GO) can be successfully reduced by using phenolic compounds present in olive leaf extract (OLE). The phenolic compounds present in OLE are especially interesting because high amounts of water containing phenolic compounds are generated in olive oil production process. Therefore phenolic compounds could be used as cheap, easy available and green alternative for GO reduction.

In this work graphene oxide reduction process was carried out by using two different methods. The first method was carried out in open air at temperature of 80˚C during five hours and it resulted in black dispersion of rGO. In the second procedure hydrothermal method was used at temperature of 120°C and increased pressure. As a result of increased pressure reduced graphene sheets were assemble into macroscopic aerogel which facilitated isolation of the product as well as its characterisation and electrochemical testing.

The structural properties of the rGO samples were characterized by FT-IR spectroscopy and thermogravimetric analysis (TGA). Structural and morphological studies demonstrate that the part of the oxygen functionalities in GO can be removed effectively by using this process. Capacitive properties of the obtained rGO are determined by using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques.

References:

[1] K. S. Kim, Y.Zhao, H.Jang, S.Y. Lee, J.M. Kim, K. S. Kim, J. H. Ahn, P.Kim, J. Y. Choi, B. H. Hong. Nature 457 (2009) 706

[2] X.Li, X. Wang, L.Zhang, S.Lee, H,Dai, Science 319 (2008) 1229

[3] Zhang J, Yang H, Shen G, Cheng P, Zhang J, Guo S., Chem Commun 46 (2010) 112

P2 FM06

Scan rate dependent electrodeposition of polyaniline nanofibers

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The synthesis method and processing conditions play an important role in tailoring polymer properties, i.e. morphology and as a consequence conductivity, which is one of the main properties of conducting polymers, particularly of polyaniline [1,2].

The morphology obtained by means of electrochemical synthesis is less varied than with chemical oxidation methods due to the ease of controlling synthesis parameters. Some of the factors reported to affect the morphology in electrochemical synthesis are the electrode material [3,4] and scan rate in potentiodynamic deposition [5,6]. Frequently reported morphologies for electrochemical deposited polyaniline are nanofibers or nanofiber networks, as a consequence of the growth mechanism described as a two stages mechanism [4,7].

We have studied the effect of potential scan rate on the morphology and properties of polyaniline films electrochemically deposited on nickel electrode. Polyaniline samples have been obtained by cyclic voltammetry at different scan rates of 10, 25, 50 and 100 mV s^{-1} from a solution of 0.1 mol L^{-1} aniline in 0.5 mol L^{-1} H_2SO_4.

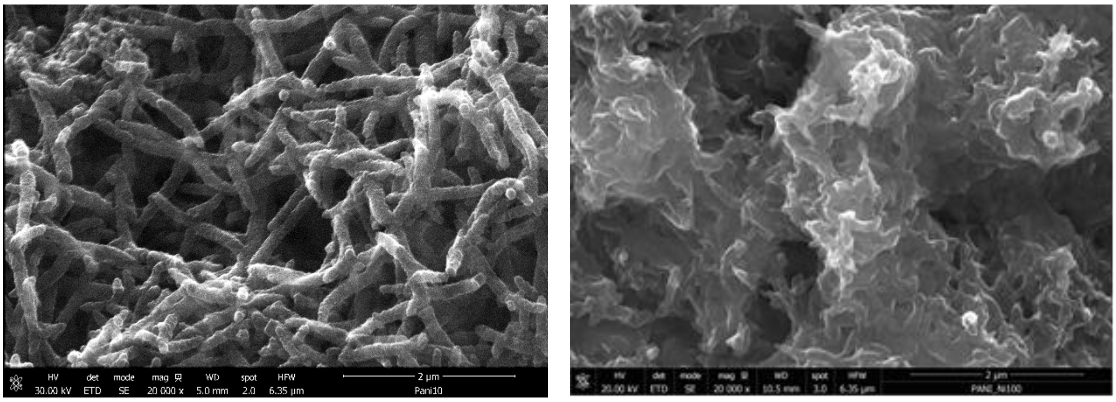

Figure 1: FE-SEM images of polyaniline films grown on nickel at 10 mV s^{-1} (left) and 100 mV s^{-1} (right)

A nanofibrilar network structure has been obtained at low scan rates (10, 25 and 50 mV s^{-1}) whereas at the highest scan rate (100 mV s^{-1}) the structure was more compact, the nanofibers aggregated and their features were not very obvious. Both diameter and length of nanofibers are scan rate dependent, decreasing from 140 to 90 nm and from 1.35 to 0.72 μm when the scan rate is increased from 10 to 50 mV s^{-1}. The nanofiber network tends to be more compact and with less free-volume as the scan rate is increased. Generally, high specific capacitances and low charge transfer resistance values are obtained for all nanofibrilar polyaniline films as compared to the compact structure. Optimum scan rate for deposition was found to be 25 mV s^{-1}, leading to the highest specific capacitance and lowest charge transfer resistance.

References:

[1] *A.G. MacDiarmid, A.J. Epstein, Synth Met 65 (1994) 103-116.*

[2] *S.K. Jeong, J.S. Suh, Oh EJ, Y.W. Park, Kim CY, A.G. MacDiarmid, Synth Met 69 (1995) 171-172.*

[3] *A. Kellenberger, N. Plesu, M. Tara Lunga Mihali, N. Vaszilcsin, Polymer 54 (2013) 3166-3174.*

[4] *N.T. Kemp, J.W. Cochrane, R. Newbury, Synth Met 159 (2009) 435-444.*

[5] *S. Mu, Y. Yang, J Phys Chem B 112 (2008) 11558-11563.*

[6] *A. Cot, S. Lakard, J. Dejeu, P. Rougeot, C. Magnenet, B. Lakard, M. Gauthier, Synth Met 162 (2012) 2370-2378.*

[7] *H. Zhang, J. Wang, Z. Wang, F. Zhang, S. Wang, Synth Met 159 (2009) 277-281.*

P2 FM07

Studies related to the preparation of modified electrodes with azulene derivatives in order to optimize the detection of heavy metal

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Azulene structure with a five-member (electron-rich) cyclic moiety connected to a seven-member (electron-poor) cyclic moiety shows very attractive properties for the synthesis of functional advanced materials like those presenting nonlinear optical and photorefractive properties [1], cathode materials for lithium batteries [2], or light emitting diodes based on organic materials [3].

In order to develop new sensors for heavy metal ions 2,6-bis((E)-2-(furan-2-yl)vinyl)-4-(5-isopropyl-3,8-dimethylazulen-1-yl)pyrylium perchlorate (**L**), has been synthesized and characterized by electrochemical techniques. It was used to prepare poly**L** complexing modified electrodes which can be used to build electrochemical sensors for the detection of heavy metal ions, as shown in our recent works [4]. The preparation conditions of the modified electrodes were varied in order to optimize the detection of heavy metals. The influence of polymerization potential, electrode conditioning and overoxidation conditions has been studied. Poly**L** films have been characterized by electrochemistry and scanning electron microscopy (SEM). The heavy metal ions recognition based on poly**L** has been performed in each case and the conditions which led to the biggest currents have been selected.

Acknowledgments

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References:

[1] *Z. Essaidi et al 2011 Optical Materials **33** 1387*

[2] *T. Osaka et al J. 1987 Electrochem. Soc. **134** 2645*

[3] *P. Szlachcic et al 2015 Dyes and Pigments **114** 184*

[4] *G. Buica et al 2013 J. Electroanal. Chem. **693** 67*

P2 IF01

A new insight into the mathematics behind the extraction of double layer capacitance

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Determination of double layer capacitance (C_{dl}) for a system showing time constant dispersion still keeps its importance in the field of impedance spectroscopy. Here, previously asked question for the system having the equivalent impedance (Z_{eq}) as $Z_{eq}=R_s+[R_p/(1+(i\omega C_{dl}R_p)^{\alpha})]$, "If $Z_{eq}=R_s+[R_p/(1+(i\omega C_{dl}R_p)^{\alpha})]$, then for which value of C_{dl} is $d/d\omega(Z_{Im}/Z_{Re})=0$?[1]" was answered from a different point of view, and former equation for C_{dl} was re-derived (Fig. 1). The equation was applied to numerous experimental data and it has been once again confirmed that it gives correct results for real systems.

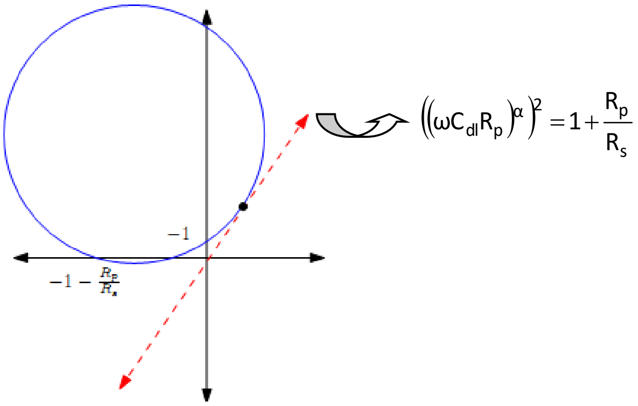

Figure 1: A representative example for the re-derivation steps

References:

[1] M. Özcan , Analyst **140** (2015) 5216-5219.

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