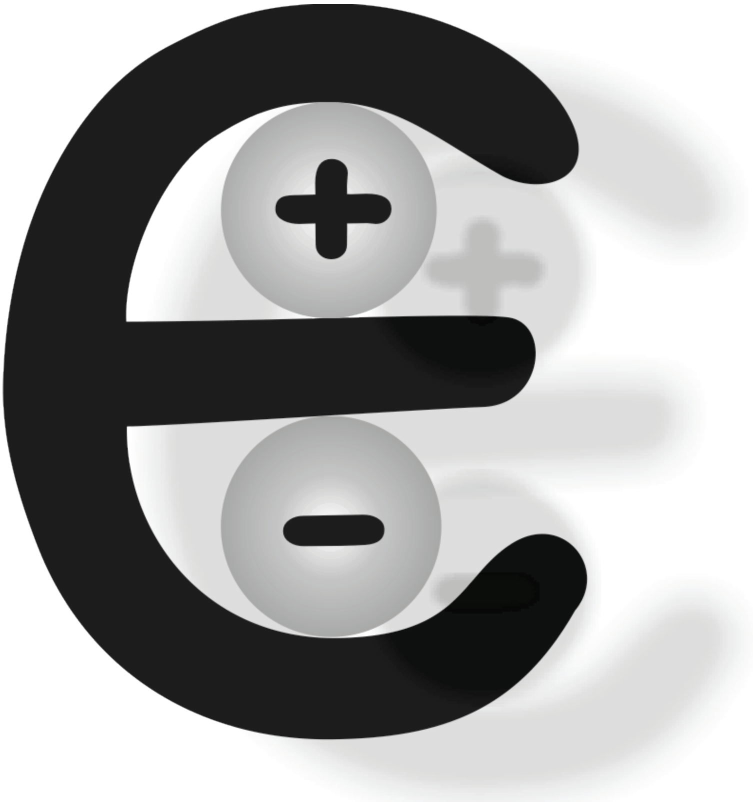
Regional Symposium on Electrochemistry
RSE-SEE
South-East Europe

Second Regional Symposium on Electrochemistry

South-East Europe

Program &

Book of Abstracts



Belgrade, Serbia, June 6-10, 2010.

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Romanian Chemical Society, Electrochemical Division of the **Serbian Chemical Society**,
Slovenian Chemical Society, **Society of Chemists and Technologists of Macedonia**

This book contains short abstracts of
*9 Plenary Lectures (***PL***),*
*18 Key Note Lectures (***KN***), and*
180 contributions accepted
for the presentation at the
Second Regional Symposium on Electrochemistr*y,*
as well as 22 contributions accepted
for the presentation at the
ISE Satellite Student
Regional Symposium
on Electrochemistry.

The Proceedings of the papers (consisting of four pages)
are published on compact-disk (CD),
as an integral part of the Symposium material.
The papers published on the CD are designed in this book by
💿
symbol above the paper title.

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(Sections: **OEH, PEA, SDE, FSP**)[*]

Hall 1b

09.00 – 09.30 **Opening Ceremony**
Addresses by:
Prof. Vesna **Mišković-Stanković**, Chair of the Organizing Committee;
Prof. Ivanka **Popović**, President of the Serbian Chemical Society
Representative of the Ministry of Science and Technological Development of Serbia
Representative of IUPAC, Representative of ISE, Representative of EuCheMs
Ambassador Bratislav **Đorđević**, Head of National Authority for the Implementation of the Chemical Weapons Convention

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Chairperson Fritz **Scholtz**

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Boris M. Grafov
The A.N.Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences, Moscow, Russia
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Constantinos G. Vayenas, *Department of Chemical Engineering, University of Patras, Greece*
Demetrios Tsiplakides, *Chemical Process Engineering Research Institute (CPERI, Thessaloniki, Greece*
Electrochemical promotion of catalysis

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Fritz Scholz *Institut für Biochemie, University of Greifswald, Institute of Biochemistry, Greifswald, Germany*
Electrochemical Studies of the Interaction of Free Oxygen Radicals with Electrode Surfaces and Compounds on Electrode Surfaces

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[*] **PL – Plenary Lecture, KN – Key Note Lecture, O – Oral presentation, P – Poster presentation**
BEH - Bioelectrochemistry and Biomedical Applications, **CPA** - Corrosion, Passivation and Anodic Films,
ESD - Electrochemical and Electronic Sensor Devices, **FSP** - Electrochemistry of Functional Structures and Materials,
SDE - Electrochemical Synthesis, Deposition, Electrolysis and Engineering, **EEH** - Environmental Electrochemistry,
ECS - Energy Conversion and Storage Devices, **ETM** - Experimental and Theoretical Methods in Electrochemistry,
NME - Nanoscale and Molecular Electrochemistry, **PEA** - Physical Electrochemistry and Analytical Electrochemistry,
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M. B. Vukmirovic, S. L. Knupp*, P. Haldar*, R. R. Adzic, *Brookhaven National Laboratory, Upton, New York, USA *University at Albany, State University of New York, Albany, New York, USA,* **Pt Monolayer Electrocatalysts for O_2 Reduction: Pt Monolayer on Carbon-Supported PdIr Nanoparticles**

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G. Topalov, G. Ganske*, E. Slavcheva, U. Schnakenberg*, *Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Sofia, Bulgaria, *Institute of Materials in Electrical Engineering, RWTH Aachen University, Germany,* **Catalytic activity of sputtered Pt and co-sputtered Pt-Ir layers toward oxygen reduction using rotating disc electrode.**

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Chairperson Dimitra **Sazou**

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A. Schwinger, S. R. Stopic, B. K. Friedrich,*IME Process Metallurgy and Metal Recycling, Aachen, Germany,* **Synthesis of $LiFePO_4$ nanoparticles during ultrasonic spray pyrolysis USP**

Chairperson Emil **Paleček**

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Eleonora-Mihaela Ungureanu,
University POLITEHNICA of Bucharest, Romania
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University of Bordeaux I, Bordeaux, France, Tufts University, Boston, U.S.A
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Ivan Ivanov*, Tanja Vidaković-Koch*, Kai Sundmacher*,** **Otto-von-Guericke University, Magdeburg, Germany, **Max-Planck-Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany* **Direct glucose enzymatic fuel cell**

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Chairperson
Svetomir **Hadži-Jordanov**

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Irena Hoskovcová *Institute of Chemical Technology Prague, Czech Republic,* **Electrochemistry of Aminocarbene Complexes of Chromium, Tungsten and Iron**

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Konstantin M. Petrov *Institute of Electrochemistry and Energy Systems at Bulgarian Academy of Sciences, Sofia, Bulgaria,* **Electrochemical methods for cleansing of H_2S in the Black Sea**

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J. Radjenovic, A. Bagastyo, Y. Mu, R. A. Rozendal, K. Rabaey, *Advanced Water Management Centre, The University of Queensland, Australia* **Electrochemical treatment of reverse osmosis concentrate**

Chairperson Jiři **Ludvík**

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E. Paleček, M. Živanović, V. Ostatná, M. Trefulka, *Institute of Biophysics, Czech Academy of Sciences, Brno, Czech Republic,* **Electrochemistry of DNA and non-conjugated proteins. New trends in protein electrocatalysis**

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M. Aleksić, M. Živanović*, V. Ostatná*, T. Doneux**, E. Paleček*, *Institute of Physical Chemistry, Faculty of Pharmacy, University of Belgrade, Serbia, *Institute of Biophysics, Academy of Sciences of the Czech Republic, Brno, Czech Republic, **Faculte des Sciences, Universite Libre de Bruxelles, Belgium*, **Polylysine-catalyzed hydrogen evolution at mercury electrodes**

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M. Tertiş, A. Ilioaia*, **R. Săndulescu,** *Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, *Iuliu Hațieganu University of Medicine and Pharmacy, Faculty of Pharmacy, Cluj-Napoca, Romania,* **Modified electrodes for biosensors used in pharmaceutical and environmental analysis**

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Wednesday, June 9, 2010

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11.40 – 11.55 ESD-O-03	Stelios Polymenis, **Grigoris Grigoriadis,** Giorgos Tsagaris *Department of Materials Science and Engineering, School of Chemical Engineering, National Technical University of Athens, Greece* **Comparative study of the structure and the anomalous electrodeposition of NiCoFe alloys related to pure Ni electrodeposits**
11.55 – 12.10 PEA-O-01	**G.G. Láng**, M. Ujvári, S. Vesztergom, F. Ujhelyi* *Institute of Chemistry, Eötvös Loránd University, Budapest, Hungary, *Department of Atomic Physics, Budapest University of Technology and Economics, Budapest, Hungary* **Measurement of surface stress changes of solid electrodes – effect of film thickness and surface roughness**
12.10 – 12.25 PEA-O-04	**Artjom Maljusch**, Ceylan Senöz*, Michael Rohwerder*, Wolfgang Schuhmann *Analytische Chemie - Elektroanalytik & Sensorik, Ruhr-Universität Bochum, Bochum, Germany, *Department of Interface Chemistry and Surface Engineering, Max-Planck-Institute for Iron Research, Düsseldorf, Germany* **SKP-SECM: System Development and First Applications**
12.25 – 12.40 PEA-O-04	**Aleksandar R. Zeradjanin,** Leonard Stoica, Sabine Seisel, Wolfgang Schuhmann *Analytische Chemie- Elektroanalytik & Sensorik, Ruhr-Universität Bochum, Bochum, Germany* **Scanning electrochemical microscopy as a tool for localized visualization of Cl_2 evolution at dimensionally stable anodes**
12.40 – 13.30	Lunch
13.45 – 22.00	**Excursion**

Thursday, June 10, 2010

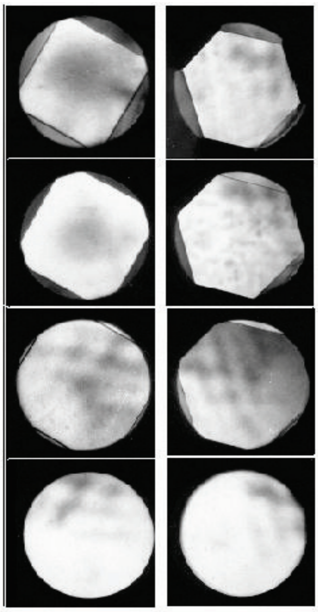
08.30 – 11.30 **Registration** - Sava Centre Main Hall

Hall 1b

	Chairperson Győző **Láng**
09.00 – 09.40 **PL-08**	**Liana Maria Muresan** *Babes-Bolyai University, Department of Physical Chemistry, Cluj-Napoca, Romania* **Zeolite-modified electrodes with analytical applications**
09.40 – 10.05 **KN-16**	**Orce Popovski,** Perica Paunović* and Svetomir Hadži Jordanov* *Military Academy Mihailo Apostolski, *Faculty of Technology and Metallurgy, University Sts. Cyril and Methodius, Skopje, R. Macedonia* **Perfectuation of nano-scaled non-platinum electrocatalysts for HE/O**
10.05 – 10.45 **PL-09**	**Nenad M. Marković** *Material Sciences Division, Argonne National Laboratory, USA* **Electrocatalysis: learning from the past to shape the feature**
10.45 – 11.10 **KN-17**	**Nedeljko V. Krstajić** *Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia* **Evaluation of TiO_2 as catalyst support for the proton exchange fuel cell**
11.10 – 11.30	**Coffee Break – Refreshment**
	Chairperson Nedeljko **Krstajić**
11.30 – 11.45 PEA-O-03	**Mária Ujvári,** G.G. Láng *Institute of Chemistry, Eötvös Loránd University, Budapest, Hungary* **Investigation of the electrochemical reduction of chlorate and perchlorate ions on rhodium**
11.45 – 12.00 PEA-O-07	**Milena Milutinovic*,****, Sébastien Sallard*, Nicolas Mano**, Dragan Manojlovic*, Neso Sojic *University of Bordeaux I, Bordeaux, France, *Department of Chemistry, University of Belgrade, 11000 Belgrade, Serbia, **Centre de Recherche Paul Pascal, Pessac, France* **Electrogenerated Chemiluminescence in an Electrodeposited Redox Polymer**
12.00 – 12.15 GEH-O-03	**Ramadan Ali Bawa**, Afra Mohammed Ehbara, Asma Mustafa Shalfouh *Department of Chemistry, Faculty of Science, University of 7th October, Misurata, Libya* **Electric conductivity study of o-substituted phenoxo iron (III) complexes**
12.15 – 12.40 **KN-18**	**Miran Gaberšček** *National Institute of Chemistry, Ljubljana, Slovenia* **Routes towards high-capacity and high-rate Li ion insertion batteries**
12.40 – 12.55 ECS-O-06	**Alexander M. Skundin,** Tatiana L. Kulova, Daniil M. Itkis*, Dmitrii A.Semenenko*, Eugenii A.Goodilin*, Yurii D. Tretyakov*, *Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow, Russia, *Faculty of Materials Science, Moscow State University, Moscow, Russia* **Lithiated vanadium oxide for positive electrodes of lithium-ion batteries**
12.55 – 13.10 ECS-O-06	**Tatiana L. Kulova**, Alexander M. Skundin, Evgenii I. Terukov*, Oleg I. Kon'kov*, Sergei A. Gurevich*, *Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow, Russia, *Ioffe Physico-Technical Institute, St. Petersburg, Russia* **Amorphous silicon with high cycleability for lithium-ion batteries**
12.10 – 13.25 ECS-O-03	**Klemen Pirnat**, Boštjan Genorio, Robert Dominko, Miran Gaberšček National Institute of Chemistry, Ljubljana, Slovenia **Li-ion baterries based on organic compounds**
13.25 – 13.40 PEA-O-02	**Tsutomu Takamura**, Junji Sizuki*, Kyoichi Sekine** *Harbin Inst. Tech., Harbin, China; *Dpt. Sci., M.N.C.T., Matsue, Japan, **Dpt. Chem. Rikkyo Univ. Tokyo, Japan* **The activity of lithium in bipolar electrode materials during polarization**
13.40 – 14.00	**Closing –** Address by Vesna **Mišković-Stanković**
14.00 – 15.00	Lunch

In Memoriam of Academician Evgeni Budevski (1922-2008)

Zdravko B. Stoynov
Institute of Electrochemistry and Energy Systems- Bulgarian Academy of Sciences, 10 Acad. G. Bonchev, Sofia 1113, Bulgaria



Dislocation free face of Ag single crystal growing in a capillary with a diameter ~200 μm: left-(111) face; right-(100) face [E. Budevski, V. Bostanov, T. Vitanov, Z. Stoynov, A. Kotzeva, *Electrochim. Acta* **11** (1966) 1697].

On October 13, 2008 Academician Evgeni Budevski, the founding father of the Bulgarian Electrochemical School, passed away following a sudden illness.

Acad. Budevski started his research in the field of electrocrystallization in 1949 following his graduation from Sofia University "Sveti Kliment Ohridski" with a degree in Chemistry. He gained scientific recognition with the development of the original capillary method for preparation of dislocation-free faces of Ag single crystals (Figure). He was instrumental in the confirmation of the 2D theory of crystal growth, introduced by Stranski and Kaischew in the 1930s, as well as in the supplementation of Frank's theory with quantitatively validated theoretical calculations related to the growth of polygonized spirals.

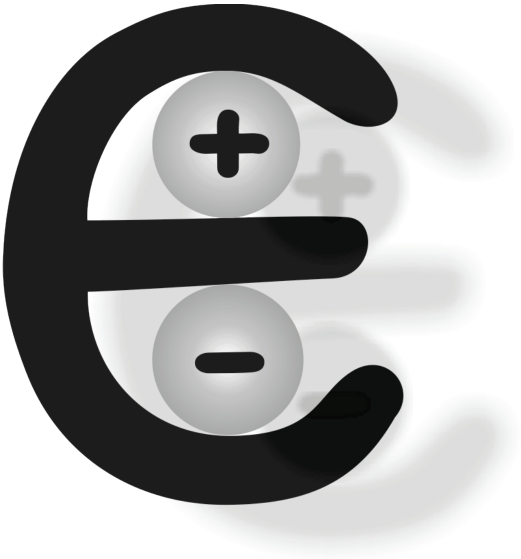
As a founder and the first director of the Central Laboratory of Electrochemical Power Sources, now the Institute of Electrochemistry and Energy Systems, Prof. Budevski was a major driving force behind the research and development of electrochemical power sources. In 1971 CLEPS' electric car driven by primary Zn-air batteries made a world record 220 kilometer run.

In the latter part of his scientific career, which was cut short by his untimely death, Evgeni Budevski tirelessly promoted the Hydrogen economy concept, championed renewable energy, and actively worked on PEMFC. He left more than 150 publications and 40 parents with a high impact on the scientific world.

During his distinguished career Evgeni Budevski received numerous national and international awards: the Dimitrov State Prize (the most prestigious Bulgarian award for that time), the prize of the Electrodeposition Division of The Electrochemical Society, the Marin Drinov Medal of the Bulgarian Academy of Sciences. He was Vice-President of the International Society for Electrochemistry, ISE (1874-1978), Foreign Member of the Saxonian Academy of Sciences – 1974, member of the IUPAC Committee of Electrochemistry (1980-1987), member of the editorial boards of Eletrochimica Acta, J. Applied Electrochemistry and J. Power Sources, member of the Advisory Committee of UNESCO-EPS on Energy Saving and Storage, Member of the Advisory Committee of the President of the Republic of Bulgaria (1997-2001).

Evgeni Budevski will be remembered with the vitality and originality of his scientific and personal philosophy, which did not leave him till his final breath. He loved nature, the outdoors, and the camping lifestyle. A keen skier and yachtsman, he passed on the passion for his hobbies to his co-workers. Together with his loving wife Lily, he enjoyed spending the weekends in their mountain house, where he entertained his numerous friends till his last days.

Plenary Lectures



Belgrade

"The sky above Belgrade is wide and high, unstable but always beautiful; even during winter serenities with their icy splendour; even during summer storms when the whole of it turns into a single gloomy cloud which, driven by the mad wind, carries the rain mixed with the dust of panonian plain; even in spring when it seems that it also blooms, along with the ground; even in autumn when it grows heavy with the autumn stars in swarms. Always beautiful and rich, as a compensation to this strange town for everything that isn't there, and a consolation because of everything that shouldn't be there.

But the greatest splendour of that sky above Belgrade, that are the sunsets. In autumn and in summer, they are broad and bright like desert mirages, and in winter they are smothered by murky clouds and dark red hazes. And in every time of year frequently come the days when the flame of that sun setting in the plain, between the rivers beneath Belgrade, gets reflected way up in the high celestial dome, and it breaks there and pours down over the scattered town. Then, for a moment, the reddish tint of the sun paints even the remotest corners of Belgrade and reflects into the windows, even of those houses it otherwise poorly illuminates."

Written about Belgrade by
***Ivo Andrić**, Serbian Nobel prize laureate*

PL-01

Gibbs fluctuation theory in context of electrochemical equilibrium noise

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Thermal fluctuations play a decisive role in the electrochemical kinetics. The Gibbs fluctuation theory is the general foundation for the elementary act theory. The purpose of this lecture is to discuss the paradox of the Gibbs fluctuation theory. Using Nyquist fluctuation dissipation theorem and Langevin stochastic equation I demonstrate that the thermal fluctuation correlations of high order do not satisfy the Gibbs ergodic idea. In context of nano-electrochemistry the high order correlations may be considered as new factors suitable for the individual characterization of both the electrode process and the electrochemical device. The nonergodicy of Gibbs fluctuation theory suggests that the fluctuation version of the electrochemical charge transfer theory should be developed. The Russian Foundation for Fundamental Investigations is thanked for support (project 08-03-00051-a).

References

1. H.Nyquist, *Phys. Rev*. **32** (1928) 110 No.1
2. W.T.Coffey, Yu.P. Kalmykov, J.T.Waldron, *The Langevin Equation*. World Scientific, NJ, 2005.

PL-02

Electrochemical promotion of catalysis

Costas G. Vayenas and Demetrios Tsiplakides*
LCEP, Dept. of Chemical Engineering, University of Patras, GR-26504 Patras, Greece
**Chemical Process Engineering Research Institute (CPERI), Centre for Research and*
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The effect of electrochemical promotion of Catalysis (EPOC) or non-Faradaic electrochemical activation of Catalysis (NEMCA) allows for the in situ control of the activity and selectivity of catalytic reactions taking place at the electrode-gas interface of solid electrolyte cells[1]. It has been shown by several surface science, catalytic and electrochemical techniques that the EPOC phenomenon (studied already for more than 70 catalytic systems, is due to the electrochemically controlled migration (spillover) of catalytically promoting anionic or cationic species (e.g. $O^{\delta-}$, $Na^{\delta+}$) from the solid electrolyte to the electrode-gas interface[1-4].
A summary of these fundamental studies will be presented, together with recent efforts for the practical utilization of EPOC in automotive exhaust catalysis.

1. C.G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda, D. Tsiplakides, *Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion and Metal-Support Interactions*, Kluwer Academic/Plenum Publishers, New York, 2001.
2. C. Sanchez, E. Leiva, *The NEMCA effect* in Handbook of Fuel Cells: Fundamentals, Technology and Applications, (Eds.: W. Vielstich, A. Lamm, H. Gasteiger), John Wiley & Sons Ltd., New York, 2003, pp. 65-68, 145-149, Vol. 2.
3. C.G. Vayenas, S. Brosda and C. Pliangos, *40th Anniversary issue J. Catal.* **216**, 487 (2003).
4. C.G. Vayenas and C.G. Koutsodontis, *J. Chem. Phys.*, **128**, 182506 (2008).

PL-03

The importance of electrode material in Environmental Electrochemistry

Christos Comninellis
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EPFL-1015 Lausanne, Switzerland, christos.comninellis@epfl.ch

Oxidative electrochemical processes promising versatility, environmental compatibility and cost effectiveness have a continuously growing importance both in selective organic synthesis and in the electrochemical incineration (ECI) of organic pollutants in aqueous media. In case of organic electro-synthesis selectivity is to be enhanced and in the ECI process the aim is the mineralization of the toxic and non-biocompatible pollutants with high current efficiency. Anodic oxidation of organics may proceed by several mechanisms including direct and indirect oxidation. In this work the electrochemical oxidation of organics at DSA® type electrodes based on synthetic boron-doped diamond (BDD) and Iridium oxide anodes in acid medium are presented.

DEMS measurements showed that electrochemical oxidation of organics on BDD does not only involve hydroxyl radicals but also molecular oxygen. The direct evidence for that was found during electrooxidation of acetic acid saturated with isotopically labelled $^{18}O_2$ resulting in evolution of $C^{18}O_2$ and $C^{16}O_2$. The situation is different in case of IrO_2 anodes were the formation of the higher oxide (IrO_3) seems to be the active intermediate in both organics oxidation (main reaction) and oxygen evolution (side reaction).

Furthermore a simplified mechanism involving intermediates of oxygen evolution has been proposed distinguishing between two limiting electrode behaviors:

'Non-active' anodes (typically BDD) on which oxidation take place at high anode potential through physisorbed hydroxyl radicals. 'Active' anodes (IrO_2) on which the reaction takes place at lower potentials involving chemisorbed active oxygen (higher oxide).

Finally a kinetic model of organics oxidation at 'non-active' type anodes is proposed and confirmed by preparative electrolysis.

PL-04

Development and electrochemical characterization of metal matrix nano/micro composite electrodeposits

P. L. Bonora, M. Lekka
Laboratory of Industrial Corrosion Control, University of Trento, Italy

A short description of the proposed mechanisms of particles co-deposition under an electrical field inside a metal matrix is presented followed by a survey of the experimental results obtained by the Research Group of the Industrial Corrosion Control Laboratory of the University of Trento in the production and study of nickel and copper matrix composite deposits containing micro- and nano- particles of SiC with improved abrasion and corrosion resistance properties. The work is divided in three parts. The first two parts concerned the optimization and production, on laboratory scale, of nickel and copper matrix composite deposits, containing silicon carbide micro- and nano-particles. The coatings production was performed by electrodeposition from electrolytic baths containing suspensions of the particles. The deposition was carried out under both direct and pulse current conditions at different applied frequencies. The coating microstructure, microhardness, abrasion resistance and corrosion resistance were studied and compared with pure metallic deposits produced under the same conditions. The corrosion resistance of the coatings towards different corrosive environments was evaluated mainly by means of electrochemical techniques. The codeposition of SiC micro particles increased the coating hardness and the abrasion resistance, while the codeposition of nanoparticles caused microstructural changes producing compact nanostructured coatings. The use of the pulse current had a similar effect on the microstructure and also enriched the amount of codeposited particles inside the metal matrix coatings.

The third part of the work concerned the scaling-up and the industrialization of the process. Actual industrial objects (such as ship propellers both models(1/24) and actual size profiles as well as train axels) were coated with nano-composite nickel matrix deposit and tested under real working conditions while the external side of pasta-extruders were covered with micro-composite copper matrix deposit.

PL-05

Innovative sol-gel and hybrid coatings

Lorenzo Fedrizzi, Luca Paussa, Francesco Andreatta
University of Udine, Department of Chemical Science and Technology, Udine, Italy

Design, development and scale-up of environmentally friendly coatings are very important in order to replace chromate based coatings. Barrier properties, paint adhesion and possibly self-healing ability are relevant aspects for replacement of chromate-based pre-treatments. Sol–gel and hybrid materials are candidates for use in protective coating applications, as it is possible to form highly adherent and chemically inert oxide films or hybrid organic-inorganic layers on metal substrates.

ZrO_2 based pre-treatments were developed by means of sol-gel technology for different substrates including aluminium and magnesium alloys and steel. The deposition of thin pre-treatments was initially carried out by means of dip and spray technology at a laboratory scale. Corrosion inhibitors can be introduced in order to improve the corrosion behaviour of the films. At a later stage, coating deposition was carried out with a robot-controlled air pressure gun in spraying cabins in order to evaluate industrial production of the pre-treatments.

In addition, methacrylate silane-based hybrid films were produced on aluminium alloy AA2024. The hybrid films were doped with cerium nitrate in order to improve corrosion resistance and possibly provide self-healing ability. The work presented has been carried out in the framework of the MULTIPROTECT European project and in particular, with the collaboration of ICV-CSIC (Madrid, Spain).

PL-06

Electrokinetics and deposit nanostructure

P. L. Cavallotti, S. Franz, A. Vicenzo, F. Zhao
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Electrocrystallization must be carefully controlled in order to define the deposit structure at a nano level. A rational approach to the electrodeposition processes in order to control them is presented, taking into consideration and comparing the electrokinetic behavior of the elements and the electrodeposit structure, resulting from the electron exchange reaction at the cathodic surface. Transient electrokinetic parameters are obtained with the secondary current pulse technique, where a square galvanostatic pulse of few ms is overimposed on the cathode while electrodeposition is running; the overvoltage behaviour gives the transient Tafel slope, the adsorption pseudo-capacitance and the diffusive time constant, introduced if the overvoltage does not arrive to a steady state during the short pulse period. These parameters are related to the type of growth of the different structures for different metals and are of particular importance to control nano electrodeposition of magnetic and wear resistant layers.

Contents Index Print EXIT

PL-07

Metallic materials for biomedical applications: laboratory and clinical studies

Ingrid Milošev
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Prolongation of the average age and an active life-style in the senior age are related to the constant increase in the number of joint diseases which eventually require a surgical procedure. The diseased joint is replaced by a joint replacement, the functionality of the joint is recovered and the pain is reduced. In the last decade the number of joint replacement operations has increased several times and is expected to increase further. In order to enable a painless and active life-style of the patients, it is necessary to develop materials with long-term survival *in vivo*. Metallic biomaterials must exhibit high corrosion and wear resistance. *In vitro* research of materials under simulated physiological conditions will be presented. These experiments are complemented by examples from clinical practice performed in collaboration with orthopaedic surgeons. Morphological and chemical changes in the material during the course of *in vivo* performance are related to the processes of wear and corrosion. Local and systemic consequences of these processes in the human body will be presented.

PL-08

Zeolite-modified electrodes with analytical applications

Liana Maria Muresan
„Babes-Bolyai“ University, Dept. of Physical Chemistry, Cluj-Napoca, Romania

During the last two decades, zeolite modified electrodes (ZMEs) have been widely investigated, because of their chemical, physical and structural characteristics (shape, size and charge selectivities, physical and chemical stabilities, high ion-exchange capacity, hydrophilic character etc.) which make them of high interest in the design of electroanalytical systems. Most works in this field have been performed using zeolite-modified carbon paste electrodes, since their surfaces are easily renewed, present low background current and a wide range of working potentials.

In this context, some new ZMEs based on carbon paste, incorporating redox mediators adsorbed on different X-type zeolites, are assessed comparatively and the influence of some experimental parameters on the electrochemical response of these electrodes was investigated. The kinetic parameters for the heterogeneous electron transfer process corresponding to the surface immobilized mediators were determined and all observed differences were used to put on evidence the influence of the mediator structure and of the zeolite nature on the electrochemical activity of the new electrodes and their electrocatalytic properties toward H_2O_2 electro-reduction and NADH or ascorbic acid electro-oxidation.

PL09

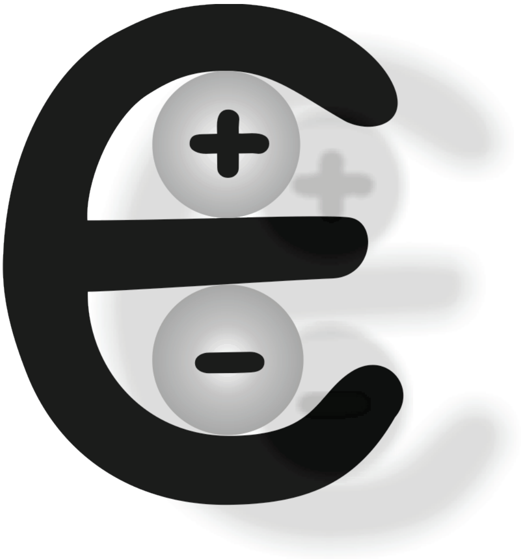
Electrocatalysis: learning from the past to shape the feature

N. M. Marković
Material Sciences Division Argonne National Laboratory, USA

The successful deployment of advanced energy conversion and storage systems depends critically on our understanding of the fundamental bonding interactions at electrochemical interfaces. In aqueous electrolytes, depending on the nature of the reacting species, the supporting electrolyte, and the electrode material, two types of interactions have traditionally been considered: *(i)* direct – covalent - bond formation and *(ii)* relatively weak non-covalent metal-ion forces that may affect the concentration of ions in the vicinity of the electrode but do not involve direct electrode - reactant/intermediate bonding. The range of physical phenomena associated with these two classes of bonds is unusually broad, ranging from charge transfer, release of the ion hydration shell, chemisorption, and catalysis.

In this presentation, we address the importance of both covalent and non-covalent interactions in controlling catalytic activity of electrochemical interfaces. In order to give a brief overview of the field, this presentation will provide a carefully balanced selection of results for the oxygen reduction reaction, the hydrogen oxidation reaction and electrooxidation of small organic molecules first on metal single crystal surfaces and then on corresponding real nanoparticles. By focusing on the mechanism of action, we demonstrate that the ability to make a controlled arrangement of surface atoms presages a new era of advances in our knowledge of the electrochemical reactions.

Key Note Lectures



Gamzigrad (*FELIX ROMULIANA*) - archaeological site, spa resort and UNESCO World Heritage Site

TOP 5 reasons to visit Serbia

Unesco World Heritage Sites

The Monasteries Sopoćani (1979), Studenica (1986) and Dečani (2004) have been put on the official UNESCO list of cultural and natural treasures of the world heritage. In 2006 The World Heritage Committee decided to extend the site of the Dečani Monastery by adding to it three groups of churches, the Patriarchate of Peć, Gračanica Monastery and the Church of the Virgin of Ljeviška. The site is now to be known as Medieval Monuments in Kosovo.

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KN-01

Electrochemical nanogravimetric studies of platinum in acid and neutral media

György Inzelt, Balázs Berkes and Ákos Kriston
Department of Physical Chemistry, Institute of Chemistry, Eötvös Loránd University,
1117 Budapest, Pázmány Péter sétány 1/A, Hungary

Despite the fact that platinum is among the most thoroughly studied electrode materials, there is a renewed interest due to the intense fuel cell studies since Pt is still the mostly used catalyst for both the oxidation of different fuels and also for the oxygen reduction. The understanding of such phenomena as e.g., the dissolution and redeposition of the platinum is a crucial issue. The knowledge accumulated concerning the electrochemically induced surface mass changes in the course of the oxidation and reduction of platinum electrode is summarized. A comparison with the results obtained by using other methods provides a deeper understanding of the processes. Beside the usual characterization of platinum electrode in contact with solutions of mostly used acids and phosphate buffer in the potential range involving the regions of the hydrogen adsorption-desorption and the oxide formation – reduction, the effects of cations, temperature and the behavior in the hydrogen evolution region have been investigated, too. Different and unusal representations have also been used to visualize the effects. The practical consequences have also been emphasized.

KN-02

Electrochemical studies of the interaction of free oxygen radicals with electrode surfaces and compounds on electrode surfaces

F. Scholz
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fscholz@uni-greifswald.de, http://www.chemie.uni-greifswald.de/~analytik/

Free oxygen radicals (FOR's) such as OH$^{\bullet}$, HOO$^{\bullet}$ and O$_2^{-\bullet}$, are highly important in all living systems, partly because they are side products of metabolic reactions, partly because they are deliberately produced in organisms to fight against intruding microorganisms. Free oxygen radicals are also crucial species in environmental atmospheric chemistry. So far, detection and analysis of FOR's is a domain of spectroscopic techniques, and only occasionally electrochemical sensors have been developed for that purpose. Recently, we have started to study the interaction of FOR's with electrode surfaces, and with compounds that are either adsorbed or otherwise deposited on electrode surfaces. We have found that FOR's are highly effective in dissolving the asperities on mechanically polished gold electrodes[1] and this way knock out electrocatalytic centers[2]. It was also possible to chemically dissolve self-assembled monolyers (SAM) of thiols and the progress of layer destruction can be easily monitored with the help of suitable redox systems in solution[3].

Future work will be directed on the elucidation of the reaction mechanisms of free oxygen radicals with electrode surfaces and compounds on electrodes, and aimed at developing analytical sensors for in vivo monitoring of FOR's in tissues and environmental samples.

1. A. M. Nowicka, U. Hasse, M. Hermes, F. Scholz: (a) *Angew. Chem.* **122** (2010) 1079-1081; (b) *Angew. Chem. Int. Ed.* **49** (2010) 1061-1063
2. A. M. Nowicka, U. Hasse, G. Sievers, M. Donten, Z. Stojek, S. Fletcher, F. Scholz: submitted
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KN-03

Interfacial capacitance of the quasi-inert metals in aqueous solutions

T. Pajkossy
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“Classical” electrochemical systems: platinum group metal electrodes in an aqueous solutions are considered. With no Faradaic reactions proceeding, the interfacial impedance is by and large capacitive, due to the charging/discharging of the double layer and to adsorption of some solute species. Accordingly, the voltammograms are usually dominated by peaks due to adsorption processes of various origins, with a “double layer region” in between them.

Impedance spectroscopy yields structural and kinetics information on the double layer through the values of capacitances and resistances. Cyclic voltammetry and impedance measurements on single crystals of platinum group metals will be presented to illustrate that the dynamic behaviour of the double layer of these metals is not due to an electrostatic double layer, but determined mainly by the adsorption-desorption rates of ions.

KN-04

The Role of Surface Structure and Composition in Electrocatalysis

Chao Wang, Dusan Strmcnik, Dusan Tripkovic, Nenad Markovic, Vojislav Stamenkovic
Argonne National Laboratory, Materials Science Division, Argonne, IL, USA

Fuel cells are of significant interest in energy efficiency and renewable energy applications due to their ability to surpass Carnot cycle efficiencies and to be run off of hydrogen derived from renewable resources. Polymer electrolyte fuel cells are particularly attractive for transportation applications.

The primary barrier to commercial fuel cells is the cost, performance and durability of current state of the art Pt-based catalysts. We have reported major catalytic improvements for the oxygen reduction reaction on Pt bi/multi-metallic alloys. The ability to tune surface properties such as surface composition, surface structure, and electronic surface structure are critical aspects toward novel materials with unique catalytic activity and electronic properties[1,2]. An increase in activity of almost two orders of magnitude was found for single crystalline Pt-alloy surfaces[1]. This finding inspired subsequent nanoscale catalyst design in order to synthesize more durable and active catalysts. A synergy between well-defined extended surfaces and novel synthesis of nanoparticles has been established[3] as an extremely promising approach to design functional nanomaterials with advanced properties. This work, supported by US Department of Energy BES and EERE, will be presented along with implications for design of advanced catalysts.

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KN-05

Mechanism of carbon dioxide corrosion inhibitors

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The mechanism of adsorption of surfactant corrosion inhibitors used to control CO_2 corrosion of mild steel in oil field environments can be determined using electrochemical techniques allied with other methods such as atomic force microscopy and molecular modelling software. Corrosion rates from linear polarisation measurements can be fitted to a Temkin adsorption isotherm to determine the equilibrium constant of adsorption, K_{ads}, the free energy of adsorption, ΔG_{ads} and the molecular interaction constant, f. The data, obtained from isotherms at different temperature, can be used in Van't Hoff plots to determine the isosteric enthalpy of adsorption, ΔH_{ads}, and subsequently the entropy of adsorption, ΔS_{ads}. The performance of an inhibitor with temperature is apparent from the Van't Hoff plots as well as evidence of whether the molecules are chemically adsorbed. Molecule properties which best relate to inhibitor performance can be obtained using molecular modelling software. AFM is a complimentary technique that can image the adsorbed, self assembled molecules on surfaces, measure adhesive forces and film thickness.

KN-06

Nanocoatings against corrosion and microbial adhesion

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Nanocoatings on solid surfaces that are important tools in controlling the deteriorating processes, have environmental importance as by the application of mono- and multimolecular layers the pollution of the environment caused by inhibitors can be significantly reduced. In industrial aqueous environment not only the dissolved components, but also the presence of corrosion relevant microorganisms can cause deterioration of metals. In order to enhance the life expectancy and decrease the microbiologically influenced corrosion damages of different structural materials, in our laboratory application of amphiphilic molecules in nano-layers was considered as a strategy for reducing the corrosion and the microbial adhesion on solids.

Our work has aimed to control both processes, i.e. the corrosion and the microbial adhesion with the same mono- and multimolecular films of different amphiphiles prepared by Langmuir-Blodgett (LB) and self assembling (SAM) techniques. At the air-water interface the molecular layers of the carboxylic, phosphonic and hydroxamic acids were analyzed by their isotherms and by Brewster images. LB and SAM layers of different amphiphiles deposited onto iron and copper surfaces were studied in the presence of aggressive dissolved chemicals and of different, corrosion relevant microorganisms. The quality of self assembled as well as of mono- and multimolecular LB layers and the repellent activity of nanocoatings on microbial adhesion and biofilm formation were analyzed by different techniques. The contact angle gave information on the hydrophobicity, the atomic force microscopy on the morphological change caused by the corrosion as well as by the microorganisms; electrochemical measurements informed about the anticorrosion efficiency, fluorescence microscopy on the microbial adhesion. Results got by different methods allowed to draw conclusion about the efficiency of the nanolayers. There were differences in the blocking activity of the amphiphiles applied either in LB or in SAM films. The wettability, the composition of amphiphilic molecules and the layer thickness significantly influence the anticorrosion and the repellent activity. We have found nanocoatings that could reduce the corrosion and the microbial adhesion at the same time.

KN-07

Electrochemical phase speciation of corrosion products on bronze works of art and archeological peaces

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Electrochemical techniques have recently found some interesting applications in the qualitative and quantitative analysis of cultural heritage metal objects. These methods applied to analysis of corrosion products on bronze artwork and archeological objects are complicated by the simultaneous occurence of solution and solid state reactions, electrochemically driven ion insertion and metal redeposition. An electrochemical method of cyclic voltammetry of micro-particles (CVMP) attached to a carbon paste electrode for phase speciation of microsampled corrosion products is demonstrated on two characteristic examples of long-term air and subterranean formed patinas. Patina constituent phases are identified by comparing electrochemical parameters of the patina samples to those of reference compounds. An identification scheme is suggested which may be applied to discern the various corrosion products of bronze based on CVMP electrochemical data. Comparison of CVMP to ATR-FTIR results reveals that the methods are complementary and that their simultaneous application could prove particularly valuable in drawing conclusions about the current state and prospects of conservation and restoration of bronze artefacts.

KN-08

Potential oscillations induced by localized corrosion of passive iron in halide-containing sulphuric acid media

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Potential oscillatory phenomena of different waveforms are induced under current-controlled conditions when the $Fe|H_2SO_4$ interfacial system is perturbed chemically by halide species such as bromides and chlorides. It is shown that the potential oscillatory phenomena are associated with a local breakdown of the iron passive oxide film and pitting corrosion. Potential oscillations do not appear when the perturbation is carried out by chemical species (such as fluorides) that cause only general corrosion of Fe but not pitting corrosion. Diagnostic criteria based on oscillations allow the characterization of the pitting extent and aggressiveness of ions. The oxide growth and its local breakdown are discussed in terms of a point defect model. Halides adsorption into oxygen vacancies inhibits oxide growth and results in an autocatalytic generation of cation vacancies that destabilize the oxide. Formation of ferrous hydroxy-halide species in the outer layer leads to thinning of the oxide and removal from the substrate.

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KN-09

Layer-by-layer deposited metal particles – conducting polymer composite materials for electroanalytic applications

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The Layer-by-layer (LbL) adsorption technique for producing thin composite layers consisting of pre-synthesized metal nanopaticles (NPs) and conducting polymers was recently introduced. There are so far few investigations on the possibility to involve LbL deposited composite layers for electroanalytic purposes.

In the present study two types of LbL deposited composites: Au NPs- polyaniline (PANI) and Pd NPs- PANI are studied with respect to the possibility for electrochemical detemination of dopamine and uric acid (for Au NPs-PANI) and of hydrazine (for Pd NPs-PANI). A comparison of the sensitivity for hydrazine determination is made for Pd-PANI composites obtained by the LbL technique and by electroless deposition of Pd in pre-synthesized PANI.

KN-10

SAXS studies of TiO_2 nanoparticles in polymer electrolytes

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Nanocomposite polymer electrolytes and nanophased metal oxide films are tailored and used as electrodes and electrolytes in galvanic and solar cells of second generation. $(PEO)_8ZnCl_2$ polymer electrolytes and nanocomposites were prepared using TiO_2 nanograins. The influence of added nanosized TiO_2 grains to polymer electrolytes were studied by small-angle X-ray scattering (SAXS) simultaneously recorded with differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) at synchrotron ELETTRA. Infrared (IR) and impedance spectroscopy (IS) were also performed[1,2].

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KN-11

Electrochemical investigation of intramolecular interactions in molecules with two (or more) redox centers

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Many organic, organometallic or coordination compounds have two (or more) redox centers in a molecule. Therefore, they are very attractive and promising electronic systems. The individual redox active parts of the molecule are generally expected to exhibit their characteristic reduction or oxidation properties (potentials, mechanisms). However, a certain combination of substituents connected with special structure can change mutual influence of the original redox centers leading to the formation of a new delocalized electron system with unexpected specific redox properties.

Electrochemical approach is a very suitable tool for experimental investigation of such intramolecular electron interactions. In the contribution, several examples will be mentioned: azines, where the N-N bond prevents the electron interaction of two C=N double bonds, mono-oximes of aromatic 1,2-diketones, where two isomers have different reduction behaviour. Other examples are represented by Fischer aminocarbene complexes, and finally by various mono-and dinuclear transition metal complexes bearing ferrocene as 1) another redox center able to form a new delocalized system, 2) as an electrochemical probe.

KN-12

Polymer films with analytical utility for detection of trace metals

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In the general context of developing new electrochemical receptors for metal ions analysis complexing polymer-coated electrodes have been synthesized by oxidative electropolymerization on glassy carbon (GC) electrode in pyrrole or azulene derivatives milimolar acetonitrile solutions containing tetrabutylammonium perchlorate as supporting electrolyte. These new materials were used for the electrochemical detection of Hg(II), Cu(II), Pb(II) and Cd(II) ions by means of the chemical preconcentration-anodic stripping technique. Competitive complexations of Hg(II) and Cu(II) or Hg(II) and Pb(II) into the modified electrodes were carried out using increasing pre-concentration times and different film thicknesses. Optimization of the conditions for cations ions analysis was done by varying several parameters including pH, deposition potential, accumulation and deposition times, and calibration plots were obtained. In order to improve the ions sensitivity the imprinted films have been tested.

The financial support of this research, received from CNMP 71-067 REMORESE project, is gratefully acknowledged.

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KN-13

Electrochemistry of DNA and non-conjugated proteins. New trends in protein electrocatalysis

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In recent decades electrochemistry focused on a small group of conjugated proteins containing non-protein redox centers. Electrochemistry of a vast majority of proteins important in biomedicine was, however, neglected. Using the constant current chronopotentiometric stripping and Hg electrodes a well-developed electrocatalytic peak H is produced at negative potentials by practically all proteins at nanomolar concentrations. Both bare and chemically modified electrodes are useful for recognition of changes in protein structures induced by denaturing, reducing and oxidizing agents as well as by single amino acid exchange in mutated proteins. Native protein structure can be retained at mercury electrodes but protein surface denaturation can be observed under conditions. Electroactivity of nucleic acids was discovered about fifty years ago. At present electrochemistry of nucleic acids is a mature field, involving a number of applications in biotechnologies. Recently we proposed facile electroactive end-labeling of DNA and PNA with Os complexes. Some of the Os(VI) complexes can also be used as polysaccharide labels.

KN-14

Electrochemistry of aminocarbene complexes of chromium, tungsten and iron

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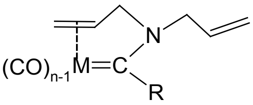
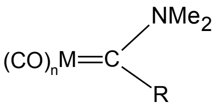
Our study deals with a series of Fischer-type carbene complexes of Cr, W and Fe, with following general formulae: Values of their oxidation and reduction potentials were treated by the Linear Free Energy Relationship (LFER) approach to find the type of structural changes responsible for changes in E_{ox} and E_{red}. We have proved that these molecules have two relatively independent electroactive centres: the oxidation centre is on the electron-rich metal atom, whereas the reduction centre is situated in the carbene carbon region. It follows that E_{red} is sensitive to a ligand substitution, but it is nearly independent of the nature of the central metal atom. On the other hand, E_{ox} cannot be tuned by a ligand substitution, but it is significantly modified by the central atom nature and by the number of π-accepting ligands bonded to the metal. Bonding ability of some ligands strongly depends on the central metal atom: it was found that in pentacoordinated Fe complexes, η^2 bonded allyl group and carbene carbon act as π-acceptors in contrast with their role in hexacoordinated Cr compounds.





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KN-15

Electrochemical methods for cleansing of H_2S in the Black Sea

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Hydrogen sulphide contains in industrial and utility waste waters as well as in some natural lakes and Seas. Unique conditions exists in the Black Sea where 95 % of waters are anaerobic and H_2S reaches concentration of C_{H2S} ~ 10 $mg.l^{-1}$. The paper presents two electrochemical processes for cleaning of H_2S from the Black Sea and industrial waters: (i) electrolysis of H_2S in alkaline solution for production of hydrogen and polysulphides using green energy sources like sun and wind. (ii) simultaneous electro-catalytic reactions of SO_2 and H_2S on spread micro-galvanic elements, based on their chemical affinity, without external power. First process is based on the thermodynamical possibility to produce hydrogen from H_2S with much less energy than from water $-E_{H2O} = 1.23$ V, compared with $E = 0.17$ V for H_2S. Second process combines the reactions of H_2S oxidation and SO_2 reduction in order to create spread micro-galvanic elements on which the two chemicals will react based on the following reaction:

$$2H_2S + SO_2 = 3S + 2H_2O$$

Feasibility study of the proposed processes has been performed. Evaluation of the environmental impact of each process in particular is an essential part of the study.

KN-16

Perfectuation of nano-scaled non-platinum electrocatalysts for HE/O

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Electrode materials for hydrogen evolution/oxidation (HE/O) are of critical importance for achieving the goals of hydrogen economy. Selection of proper electrode materials for industrial electrocatalysis purposes is not at all an easy task. The conflict of technical and economical issues is evident: the best performing electrocatalysts as, e.g. Pt, Pd, and Ru are expensive, while the cheaper (ones that use less noble metal as, e.g. Ni, Co etc.) suffer of corrosion, passivation or similar problems. So far, platinum is the most active and best performing catalytic material. Nonetheless, its commercial application is hindered by its low abundance and high cost. This is why the mainstream task of contemporary electrochemistry is to reduce, or even completely to replace Pt in the electrolysers and/or fuel cells. Approaches aimed at this goal are well known, i.e., *i*) increasing the real surface area and reducing the catalyst load on the electrodes (the physical approach) and *ii*) development of multicomponent catalysts with catalytic activity comparable or even higher than that of Pt (the chemical approach).

In this presentation pathways how to reduce load or even replace Pt in the so called hypo-hyper d-electrocatalysts are shown. Alteration of catalyst's support (Vulcan XC-72, MWCNTs and activated MWCNTs), introduction of TiO_2 as synergetic promoter of intrinsic catalytic activity and non-precious and mixed metallic systems (Co, Ni, Co-Pt, Co-Ru) were studied and their effects analyzed. Co-TiO_2-$MWCNTs_{(a)}$ catalyst has shown the best performances for hydrogen evolution, even better than that of traditional Pt/Vulcan XC-72 electrocatalyst. Addition of 20% Pt in the metallic phase (only 2% in the whole catalyst, CoPt- TiO_2-$MWCNTs_{(a)}$) improved catalytic activity at the level of activity of corresponding catalyst with pure Pt as metallic phase (Pt-TiO_2-$MWCNTs_{(a)}$). Co was found to promote reduction of Pt-particles size. So, the economy in using Pt metal was compensated by considerably higher real surface area of the catalytic phase. In order to achieve this effect, the size of Pt-particles was reduced for 4 times (from 12 nm to 3 nm).

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KN-17

Evaluation of TiO_2 as catalyst support for the proton exchange fuel cell

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The performance and durability of low-temperature fuel cells strongly depend on catalyst support materials. Catalysts supported on high surface area carbons are widely used in polymer electrolyte membrane fuel cell (PEMFCs. However, the corrosion of carbon supports has been recognized as one causes of performance degradation of PEMFC electrodes, in particular under repeated start-stop cycles or high potential conditions.
Due to their high stability in fuel cell environment, ceramic materials (oxides and carbides) have been investigated as carbon-substitute supports for fuel cell catalysts.
This invited lecture presents an overview of ceramic materials tested as a support for fuel cell catalysts, with particular attention addressed to the non-stoichiometric titanium oxides and, Nb doped TiO_2, which have a unique combination of electrical conductivity approaching that of a metal and high corrosion resistance both in acid and in basic solutions.

KN-18

Routes towards high-capacity and high-rate Li ion insertion batteries

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In the first part we will present several new cathode materials for lithium batteries with (much) increased capacity/energy density and discuss their advantages and limitations. In continuation we will show three possible strategies towards increasing the rate capability/power density of modern Li insertion batteries. The first concept involves preparation of a thin conductive film around the active nanoparticles (e.g. carbon nanofilm). The second concept is a sort of inverse picture of the first: it is based on a porous material with thin walls of pores to provide short solid-state diffusion paths. The third, completely new concept involves introduction of nanospacers that slightly separate active nanoparticles. This way, we create micropores exactly in place where most needed - around the active particles. Most of the experimental results will be explained using appropriate mechanistic modeling based on network thermodynamics or similar tools.

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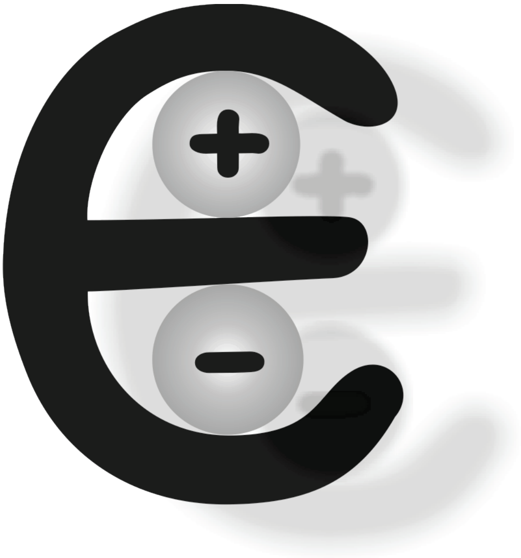
BEH

Bioelectrochemistry and Biomedical Applications



ORAL PRESENTATIONS

Studenica monastery, founded in 1190

Monasteries and Churches

It is difficult to understand Serbian people if you don't know the history of its temples. Some temples are outside of towns, hidden in the forests and placed on top of high inaccessible cliffs. Some are concentrated in high number in small area (Like Ovcar-Kablar canyon, the Ibar valley or Fruska Gora). Turks had damaged the temples and did put them on fire and people did reconstruct them. The oldest date back to the XII century and one church from IX century has been preserved (Peter’s church).

Serbian temples are telling the story of those who constructed them. The most beautiful have been founded by Serbian rulers, and some of those rulers have spent their last years there as monks. Holly places have been founded by aristocracy, monks or ordinary citizens. On the walls of those sanctuaries you can find one of the most beautiful examples of medieval paintings. Some monasteries are under UNESCO world’s cultural and historical protection.

Serbian monasteries are placed on the old Transromanica road that is a part of the Counsel of Europe program: “The major roads of European culture”. Between XI and XII century European art was inspired by Rome and therefore called Romanic art. This artistic style is most visible in the architecture, on religious constructions because the Church was the bearer of the culture in the middle century. At the same time with this artistic style, the Serbian state begins to flourish. The builders were usually from Italy and Adriatic Sea and with them the western influences were brought and were mixed with the Byzantine art thus creating a particular style.

BEH-O-01

Electrochemiluminescence Bead-Based Microarray for Multiplexed Sandwich Immunoassays

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New techniques to realize multiple analyses simultaneously are eagerly needed and being developed. For example, fluorescence is widely used to image sensor microarrays and allows for the detection of a large number of analytes simultaneously[1]. As an alternative, electrochemiluminescence (ECL) is a very sensitive readout mechanism [2] and has already been commercialized[2]. Here we present a new class of sensing microarray that combines ECL detection and the ability to image multiple analytes in a single sample[3].

The biochip consists of encoded beads modified with antibodies, deposited by solvent evaporation in the wells of a microstructured electrode. This electrode is an optical fiber bundle containing 50,000 optical cores that have been etched and then gold- coated. The bead-based platform for performing immunoassays by imaging the ECL enables us to detect multiple analytes simultaneously [3]. For example, using an array with three kinds of beads, each of them modified with different antibodies, we were able to detect samples containing combinations of the corresponding antigens. Some cross reactivity experiments were also run and showed good specificity of the sensors. This work demonstrates for the first time to our knowledge, the possibility of imaging individual sensing microbeads by ECL and to realize multiplexed sandwich immunoassays.

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BEH-O-02

Direct glucose enzymatic fuel cell

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Enzymatic biofuel cells use biocatalysts (enzymes) instead of noble metal catalysts. Enzymes have high catalytic activity and high substrate selectivity under mild conditions but the electrical communication between the enzyme and the electrode is often difficult to achieve and the resulting bioelectrodes suffer from lack of stability.

An enzymatic anode for glucose oxidation that comprises charge transfer complex (CTC) and enzyme glucose oxidase was developed. The influence of structural parameters such as CTC and enzyme loading was tested. Increased CTC loading was found to extend the linear range in the concentration dependence thus improving the anode performance for biofuel cell and biosensor applications.

The bioanode was employed in a specially-designed flow-through biofuel cell enabling kinetic and mass transport investigations of the anode performance under “fuel cell” conditions as well as long-term stability tests. The influence of different cathode architectures and glucose flow rate was investigated. Under optimized experimental conditions the biofuel cell exhibited high open circuit voltage (up to 0.967V) and reasonable power densities (up to 120 μW cm^{-2}).

BEH-O-03

Polylysine-catalyzed hydrogen evolution at mercury electrodes

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It has been shown recently that peptides and proteins at nanomolar concentrations produce chronopotentiometric peak H at mercury electrodes, which is due to catalytic hydrogen evolution. This peak is sensitive to changes in protein structures and represents a new tool in protein research. Here we used for the first time polyamino acids (poly(aa)'s) to obtain information about the role of individual amino acid residues in the catalytic hydrogen evolution reaction and about electrochemical behavior of poly(aa)'s. At pH 6 polylysine (polyLys) and polyarginine, tryptophan (polyArg,Trp) yielded peak H in agreement with their ionization state while polyglutamic acid (polyGlu) produced no response. PolyLys catalyzes hydrogen evolution in its adsorbed state and its responses depend on buffer concentration, accumulation potential and other factors. It appears that even at potentials negative to the potential of zero charge, at moderate ionic strengths, lysine residues can be adsorbed with their hydrocarbon chains close to the Hg surface. PolyLys interactions with DNA can be traced electrochemically.

BEH-O-04

Two-dimensional condensation of nucleic acids components – how it was discovered 45 years ago and contemporary investigations

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In 1965 we have discovered, that purine and pyrimidine derivatives currently occurring in nucleic acids posses an extraordinary high ability of self-association at the electrode surface and can form there by a two-dimensional (2-D) condensation a monomolecular layer (self assembled monolayer – SAM), a compact film. By this high condensation ability nucleic acid bases differ from most of the other purine and pyrimidine derivatives which currently do not occur in nucleic acids. This property was probably significant for the origin of life at the earth. For the time being it is not known why just only a restricted number of purine and/or pyrimidine derivatives show the tendency to self-association. 2D condensation can be observed with certain homopyrimidine oligodeoxynucleotides (ODN) at negatively charged mercury electrode surface as well.

POSTER PRESENTATIONS

BEH-P-01

Conductometric determination of the critical micellar concentration of two oxo derivatives of cholic acid

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Critical micellear concentrations (CMC) were determined for two novel promoters of membrane permeability – 7-monoketocholic acid (7-MKC) and 12-monoketocholic acid (12-MKC), using conductometry. The CMC value is obtained as the point at the curve break in the curve of dependence of the specific conductivity κ on the concentration of bile acids (c_{BA}). Below the CMC bile acid monomers are present, whereas above the CMC the monomer concentration is constant, which is seen as a smaller slope of the curve $\kappa = f(c_{BA})$. This studies suggest the different aggregation abilities of the investigated bile acid derivatives. In an aqueous solution, 7-MKC has a somewhat lower CMC value (43 mM) than 12-MKC (50 mM). Further, it was found that, in addition to the primary micelles, 7-MKC forms also secondary micelles.

Acknowledgement: This study was supported by the Secretariat for Science and Technological Development, AP Vojvodina (Project No. 114-451-00663/2009-02).

BEH-P-02

Bioamperometric system using xanthine oxidase immobilized on controlled-pore glass for antioxidant capacity determination

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WITHDRAWN

Aiming the determination of antioxidant capacity (Aox), xanthine oxidase (XOD) was immobilized in a minireactor filled with controlled-pore glass. The detection of H_2O_2 produced as result of a continuous flow of xanthine (XA) through the bioreactor was achieved by using an amperometric biosensor based on wired horseradish peroxidase (HRP). Os-redox polymer was used to wire HRP to the electrode, and allowed an applied potential of -0.1 V *vs.* Ag/AgCl,Cl^-_{sat}. The bioreactor operating conditions such as pH and concentration of the xanthine solution, the flow rate and sample volume, were optimized in order to keep the signal in the linear dynamic range of the biosensor and to obtain a convenient throughput rate. The repeatability of the whole bioamperometric system, for 50 xanthine injections, was 0.96% (RSD). If stored at 4°C in 15 mM saline phosphate buffer solution (pH 7.4) the bioreactor was used up to 14 days without any significant loss of the XOD activity. Ascorbic acid, as model antioxidant, was injected in the xanthine flow and its Aox is expressed as the concentration (188 ± 34 μM) that causes a 50% decrease of the reduction current.

BEH-P-03

Resistance enhancement to the biodegradation of biocompatible magnesium alloys

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Magnesium and its alloys have some advantageous properties which make them an excellent choice for a number of applications. As the potential biodegradable materials, they show many advantages over current metallic materials and biodegradable plastics and ceramics. Biodegradable magnesium based implants in the human body can be gradually dissolved, absorbed, consumed or excreted, so there is no need for the secondary surgery to remove implants after the surgery regions have healed. Because of the high corrosion rates in physiological environment, protection coatings must be applied to the magnesium based alloys surface to prevent their prematurely degradation.
In this study, the protection efficiency of the self-assemble monolayer of fatty acids (palmitic and stearic) formed on the anodized alloy samples were investigated in a simulated physiological solution (Hank's solution) using voltammetry and electrochemical impedance spectroscopy methods.

BEH-P-04

Cyclic voltammetry study of electrochemically synthesized Ag/PVP nanocomposite

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Hydrogel nanocomposites of silver nanoparticles (AgNPs) and crosslinked poly(*N*-vinyl-2-pyrrolidone) (PVP) were synthesized *in situ* by a novel electrochemical method. PVP hydrogels, crosslinked by γ-irradiation, were swollen in the solution containing 0.1 M KNO_3 and 3.9 mM $AgNO_3$. PVP polymer matrix nanocavities were used as nanoreactors for AgNPs synthesis. The reduction of silver cations was performed using two-Pt-electrode electrochemical cell. The polarity of the electrodes was changed on the half of the implementation time, enabling the Ag^+ ions reduction in the bulk. Cyclic voltammetry (CV) was performed in a three-electrode electrochemical cell, using the saturated calomel electrode (SCE) as a reference. Ag/PVP nanocomposites were scanned by CV immediately after the synthesis and after drying followed by reswelling in 0.1 M KNO_3. Ag/PVP was compared with CVs of the following systems: Pt electrode in 0.1 M KNO_3; Pt/PVP system in 0.1 M KNO_3; Ag/Pt system in 0.1 M KNO_3 + 3.9 mM $AgNO_3$ solution.

BEH-P-05

Electrochemical sensor for the detection of metabolites connected with enzymatic activity of xanthine oxidase.

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Determination of uric acid (UA) levels in body fluids is important for diagnostics and prevention of severe metabolic disorders. Electrochemical determination of the UA relies on an oxidation signal measurable at different carbon-based electrodes. Strong enhancement of the UA oxidation signal can be reached by a simple mechanical grinding of the surfaces of glassy carbon or edge plane-oriented pyrolytic graphite electrodes. Sensitive electrochemical method was developed for simultaneous determination of uric acid (UA), xanthine (XAN), hypoxanthine (HYP) (products of purine catabolism in human), allopurinol (ALO) and oxypurinol (OXY).

BEH-P-06

Electrochemical and SPR studies on the interaction of albumin with bilirubin

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The studies concerning the interaction of human serum albumin (HSA) with bilirubin are important in biological and biophysical science. Among investigated proteins, the human serum albumin paid a special attention being considered as model for the study of ligand protein interactions, but some aspects related to its biochemical functions are not completely described.

The biomolecular interaction of human serum albumin with bilirubin was studied by cyclic voltammetry and Surface Plasmon Resonance (SPR) methods onto a nano-structured gold surface. The both techniques are complementary, but the SPR based analysis has some important features and the advantage is that kinetic and thermodynamic information are obtained from the same experiment. These results in combination with the knowledge of the structure of albumin and bilirubin allows the description of the mechanism of binding and interaction.

BEH-P-07

Detection of unpaired thymine residues in DNA by electrochemical, immunoelectrochemical and acoustic methods

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There is an increased interest in detection of organophosphate pesticides by means of biosensing. Organophosphate pesticides are known to cause a loss of one or more bases in DNA. We used a model system of short oligodeoxynucleotides with varying number of abasic sites representing a biorecognition layer for electrochemical, immuno-electrochemical and thickness shear mode acoustic detection. Electrochemical methods have been shown to recognize even single abasic site within the 19-mer DNA, while the immunoelectrochemical and the thickness shear mode methods required presence of at least 3 lesions in the DNA to give reliable signal change, as compared to intact duplex DNA.

BEH-P-08

A new method for analysis of brucine in crude and detoxified seeds of *Strychnos nux-vomica* by carbon paste electrode modified with multi walled carbon nanotube

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A new, simple, rapid and sensitive electrochemical method for determination of brucine (BR) was developed in Britton-Robinson buffer solution (pH=5) on a carbon paste electrode modified with multi walled carbon nanotube (CNT/CPE). Differential pulse voltammetry (DPV) was used for determination of brucine. The study were carried out using another voltammetry methods such as cyclic voltammetry, chronocuolometry and linear sweep voltammetry. The modified electrode exhibited electrocatalytic properties toward brucine oxidation with a peak potential of 20.0 mV lower than that at the bare carbon paste electrode. The enhanced peak current response is also a clear evidence of the catalytic of the multi walled carbon nanotube modified carbon paste electrode towards oxidation of brucine. Linear calibration curves were obtained in two ranges of 5-30 and 30-355 μM with the detection limit of 0.28 μM for brucine. The electrochemical parameters such as diffusion coefficient (D), electron transfer coefficient (α) and electron transfer rate constant were also determined for the brucine oxidation. The proposed method was successfully applied in determination of brucine in several pharmaceutical formulations. To our knowledge, no paper has been used milk for decrease of brucine and detoxification of *seeds* extract. We report a new method for detoxified of seeds and reduce of brucine.

BEH-P-09

Bioelectrochemical approach to sulfate-rich wastewater treatment

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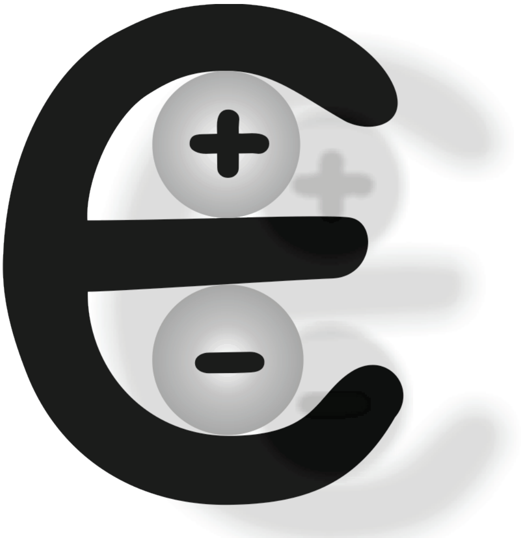
WITHDRAWN

Bioelectrochemical approach for sulfate-rich wastewater treatment, coupling the anaerobic digestion process and electrochemical oxidation of the produced sulfides, has been proposed. In this ab initio study the possibility for sulfide electrooxidation on high surface area carbon felt electrodes was examined. The electrodes were polarized at + 200 mV (vs.Ag/AgCl) in sulfide-containing solutions and the current responce with time was monitored. Immediately after sulfide sample injection anodic currents increasing with the sulfide concentration were recorded, thus improving their origin from the sulfide electrooxidation. In parallel, wastewater collected from manucipality WWTP-Blagoegrad, South western Bulgaria, were kept under anaerobic conditions for over two months and then electrochemically treated at the same manner as the sulfide reference solutions. The anaerobically treated wastewater was also used as an anolyte in a double-chamber fuel cell. The obtained maximum power density of 0.68 mW/cm^2 is comparable with the results reported for other sulfide fuel cells using carbon-based anodes.

CPA

Corrosion, Passivation and Anodic Films



ORAL PRESENTATIONS

Sculpture from Lepenski Vir
Water Fairy

Archaeological sites

Archaeological sites in Serbia date back to the oldest European civilisations and the oldest deciphered writings (Vinca and Lepenski Vir).

Serbian territory is rich with the cultural heritage of Roman Empire. Sixteen Roman Emperors were born in this area. Among them is famous Emperor Constantine, one of the most important individuals of old Roman Empire, who had unfathomable contribution in creating the world as we know it today. Most of the emperors had built their palaces and villas in the places of their birth.

One of the earliest military settlements on the Danube River was Viminacium, near Pozarevac. The Roman troops from this fort were used in war against Dacians. They had built one of the biggest bridges at that time in the canyon of Djerdap. The bridge was almost 1.5 km long and some of the columns were 45m high.

Sirmium is the oldest Roman town in this area, located in the territory of the modern Sremska Mitrovica. Mediana is situated near Niš, Gamzigrad near Zajecar, Justinian I or Empress Town near Leskovac and Singidunum or now Belgrade are places where inestimable busts, mosaics and other constructions were found.

CPA-O-01

Identical-Location Microscopy for the investigation of nanoparticle corrosion

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A newly developed methodology for examining the degradation of nanoparticles is introduced[1,2]. In contrast to the conventional, destructive TEM investigation procedure, this methodology enables the observation of corrosion processes of the same nanoparticles repeatedly. In particular we demonstrate the impact of a potential cycling treatment on a carbon-supported platinum catalyst, and propose a new corrosion mechanism for fuel cell catalyst degradation. Under the applied harsh conditions, whole Pt particles detach from the support and dissolve into the electrolyte without re-deposition. This is supplemented by information from XRD, electrochemical surface area determination, and TF-RDE measurements of the ORR activity. In the end, the outstanding advantages of TEM on identical particle locations will be discussed.

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2. K. J. J. Mayrhofer, S. J. Ashton, J. C. Meier, G. K. H. Wiberg, M. Hanzlik, M. Arenz, *Journal of Power Sources* **185** (2008) 734

CPA-O-02

High Temperature Corrosion of Structural Materials

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A measuring system was built for electrochemical experiments up to 300ºC. The main corrosion properties of the structural materials of the primary circuit of the Paks Nuclear Power Plant (08H18N10T austenitic steal and Zr1%Nb) were determined in simulated working environment (boric acid – potassium hydroxide solution). 08H18N10T steal was compared with two commercial alloys (AISI 304 and AISI 316). All alloys show passive behaviour in wide potential ranges. The cyclic voltammograms and the polarization curves show that 08H18N10T steel remains passive even in the potential range of the hydrogen reduction. The protective property of the oxide layer decreases in the 08H18N10T>AISI316>AISI304 order. Chloride and iodide can induce localized corrosion on Zr1%Nb. The critical concentration decreases with the increasing temperature. Generally pitting corrosion appears only at highly anodic potentials expect in extremely concentrated solution where it ensures at the open circuit potential also. The impedance spectra of stainless steel and Zr1%Nb principally correspond to the oxide layer capacitance. The charge carriers move by coupled migration-recombination mechanism in the thin oxide film and by reaction controlled diffusion in the thick films.

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CPA-O-03

The impact of water quality on the corrosion of water distribution pipes

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The subjects of this study are iron and steel pipes and water that are distributed within Belgrade drinking water distribution system. In order to investigate mutual effects of corrosion and water quality the corrosion deposits on pipes and key water quality parameters such as pH, dissolved oxygen and temperature were analyzed. In that way reasons for better control of pipes corrosion is provided. Depending on the composition of the water next to the pipe surface, corrosion of iron results in the formation of different compounds and solid phases. Fe(II) deposits are formed under reducing conditions, the presence of relatively soluble Fe(II) deposit such as siderite and ferrous hydroxide is confirmed. In the presence of carbonic species, siderite ($FeCO_3$) is prevailing ferrous deposit.

pH values of water have significant influence not only for the stability of corrosion deposit but also to valence of iron ions present in the water. According to measurements which correspond to solubility constant of $Fe(OH)_2$, at pH range 6.0-8.0 the representative and typical ions in water are Fe^{2+}-ions. Changes in temperature of water and DO affect corrosion rate, iron by-product speciation and concentration, and the type of scale formed, but it is observed that the rate of iron release does not give simple relationship to the rate of iron corrosion. Further studies are needed to get deeper knowledge on the mechanism of iron release from corroded pipes and to get better insight on the influence of water quality to corrosion of iron.

CPA-O-04

Corrosion properties of DLC coated stainless steel

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Diamond-like carbon (DLC) coatings have been a subject of extensive investigation in recent years because of their attractive prop**erties for electronic, optical, mechanical and biomedical application. The excellent chemi**cal inertness of DLC films makes them a promising material as wear and corrosion protection coatings in different environments. However, it is difficult to obtain the coatings which exhibit good adhesion on substrate and low porosity.

In this work the DLC coatings on stainless steel substrates (316L) were prepared by two techniques: a-C:H by gridless anode layer source (Veeco Instuments ALS 340L) and a-C:N by sputtering (CemeCon CC800/9). The electrochemical data (classical I-V measurements in combination with electrochemical impedance spectroscopy) were performed in chloride medium at pH 4. Properties such as hardness, adhesion and density were determined for each coating. Measurements related to the surface characterisation such as SEM, AFM and XPS were also performed. The results are discussed and compared to the surface defect density.

WITHDRAWN

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CPA-O-05

Corrosion behaviour of Nitinol (shape memory alloy) modified by organic and inorganic films

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Having in mind a need to extend the quality of life there is an ever-expanding requirement for implantation of metal implants in human body because of their superior properties. Nitinol, nickel-titanium alloy with near-equiatomic composition, derives its attractiveness and widespread use in biochemical engineering from unique mechanical properties known as shape memory effect and superelasticity.

In spite of its good corrosion resistance due to the spontaneous passivation, it is of huge importance to prevent the unwanted release of toxic nickel ions. Hence, Nitinol surface was modified by biocompatible organic self-assembled monolayers and inorganic films (anodically formed passive films) in order to prevent release of nickel.

In vitro characterization of modified and unmodified surfaces of Nitinol was performed in simulated body fluid (Hank's solution) using electrochemical ac and dc methods. Surface films will be characterized by electronic microscopy and spectroscopic methods.

CPA-O-06

Quantum mechanical characterization of possible self-assembled nanostructures of 1H-benzotriazole on copper

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Benzotriazole (BTAH) is among the most efficient corrosion inhibitors for copper. Its performance and mechanism of corrosion inhibition have been intensively studied using experimental techniques. Despite these efforts the exact structure of BTAH on Cu surfaces is still an open issue. For this reason, we examined---by means of extensive density functional theory calculations---structural models that were proposed on the basis of experimental STM (scanning tunneling microscope) images.[1,2] In particular, the proposed two-dimensional adsorbate nanostructures on Cu(111), Cu(100), and Cu(110) were taken as a starting point, from which several different models were constructed within the experimentally determined periodicity. Calculations reveal that some of these models are energetically more stable than the experimentally proposed structures. Moreover, the simulated STM images of a few experimentally proposed structures are not compatible with the experimental images. Namely, instead of atomic structure, the STM gives the information about the structure of electronic states near the Fermi level, hence only a combination of STM experiments and simulations can lead to a proper structure determination.

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CPA-O-07

Electro deposition of Conducting Poly(aniline-co-o-anisidine) films on steel and its corrosion protection performance

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Conducting poly(aniline-co-o-anisidine) coatings were synthesized on low carbon steel by electrochemical polymerization of aniline and 0-nisidine in aqueous oxalic acid by using galvanostatic method. The characterization of these coatings was carried out by using Scanning electron microscopy. The corrosion protection performance of these coatings was evaluated by using Potentiodynamic polarization technique. It was found that uniform and adherent conducting poly (aniline-co-o-anisidine) coating can be obtained on low carbon steel using galvanostatic technique. The potentiodynamic polarization study reveals that the coating offers significant corrosion protection to low carbon steel in acidic medium.

CPA-O-08

Investigation of POD - oil steel corrosion inhibitor as surfactant

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Waste of the caprolactam production that is the POD-oil (Product of Oxidizing and Dehydrogenation) is investigated by electrochemical impedance spectroscopy technique as a corrosion inhibitor of carbon steel in 20% hydrochloric solution. The inhibitor is investigated also as surfactant at the solution – air interface by means of the maximum bubble pressure technique. It is shown that the Langmuir adsorption of inhibitor takes place at solution – air and solution – steel interfaces. Equilibrium adsorption constant and free adsorption energy was estimated for both interfaces. The closeness of the adsorption constant and the agreement of the free adsorption energy values suggest that the inhibitor adsorption on steel is caused basically by the hydrophobic interaction of inhibitor with the solution and less depends on the interaction with steel.

POSTER PRESENTATIONS

CPA-P-01

Corrosion inhibition of bronze by amino acids in aqueous acidic solutions

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The electrochemical behavior of bronze in an aerated solution of 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ (pH=5), in the absence and in the presence of different amino acids was studied by open-circuit potential and electrochemical impedance spectroscopy measurements. The investigated amino acids were: glutamic acid (Glu), arginine (Arg), histidine (His), methionine (Met) and cysteine (Cys). The impedance measurements revealed that all investigated amino acids present inhibition properties on bronze corrosion.

The molecular structure of amino acids significantly influences the magnitude of R_p values and, consequently, their inhibition efficiency. The order of anticorrosive effectiveness of the inhibitors was: Cys > Glu > Met > Arg > His. The variation of the inhibition efficiency with the structure of the amino acids was interpreted taking into consideration the number of adsorption active centres in the molecule, the adsorption mode and the molecular size of the compounds.

In the investigated experimental conditions, the optimum concentration of each amino acid was relatively low (0.1 mM), except for the case of His, when a concentration of 10 mM was necessary to attain its maximum inhibition efficiency.

CPA-P-02

Study of the corrosion resistance of Ni/CeO_2 composite coatings electrodeposited on carbon steel in hydrochloric acid

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Ceramics (SiC, SiO_2, Al_2O_3, TiO_2, ZrO_2, La_2O_3, Y_2O_3 or mixed ceramics of these), polymers (polyethylene, polytetrafluorethylene), metals (Ti, Al) and other materials (hydroxiapatite, diamond, fullerene) have been co-electrodeposited with nickel in order to improve properties, such as hardness, wear resistance, lubrication, corrosion resistance, catalitic, optic and/or electronic properties.

The phase formation of Ni/CeO composites onto carbon steel electrode was investigated using potentiostatic/galvanostatic polarization and chronoamperometric method. In order to obtain the electrodeposited nickel composite coatings, a nickel sulfate bath having the following composition was used for plating Ni matrix: 150 g/L $NiSO_4 \cdot 6H_2O$, 30 g/L H_3BO_3. The addition of micrometer CeO_2 composite with different concentrations was studied. The anticorrosive properties of composite coating in 0.1M HCl solution were studied by Tafel polarization and Electrochemical Impedance Spectroscopy. Incorporation of CeO_2 particles into the Ni matrices was found to improve corrosion resistance of pure Ni coatings. The surface morphologies of composite coating were studied using an Euromex microscope.

WITHDRAWN

CPA-P-03

Optical characterization of discharge events during plasma electrolytic oxidation of aluminum in sodium tungstate

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In this work, we have investigated discharge characteristics during dc plasma electrolytic oxidation (PEO) of aluminum in sodium tungstate using optical emission spectroscopy and real-time imaging. The size of discharges appearing at the oxide-electrolyte interface increases, while spatial density decreases during the PEO process. Several intensive band peaks were observed during PEO caused by electron transitions in W, Na, Al, O, H atoms.

CPA-P-04

Graphical comparison of the marine parameters sensivity of AISI 304 and AISI 316

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AISI 304 and AISI 316 stainless steels are the most widely used of any stainless steels and seawater is the most challenging environment for them. In this research the effects of some influential marine parameters on the corrosion rate of these metals have been assessed via potentiodynamic polarization scan and compared by the use of the graphical curves. Salinity, velocity and temperature are the factors which induce effects. The effect of these factors has been evaluated in synergistic manner. The synergistic effect is normally used to describe the way in which the factors enhance or weaken one another to change the rate of corrosion. In recent years some research has been done on the effects of environmental parameters, which evaluates the individual effect. However the real synergistic effect has not been completely evaluated. The results are obviously necessary and beneficial in marine designs.

WITHDRAWN

CPA-P-05

The study of the iron phosphate coatings porosity in bufered borate solution

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The iron phosphate layers on the low carbon steel surface slows steel corrosion in aggressive environments. The quality of the iron phosphate layer depends on the fraction of the total surface area covered by phosphate coating. Various factors affect this coverage fraction, in particular the composition of the deposition bath, bath temperature and additives used in the electrolyte[1]. In this study phosphating was carried in the phosphate solution (NaOH + H_3PO_4 + $NaNO_2$, pH 3.8) at different temperatures (30-70°C). The porosity of phosphate coatings on low carbon steel was determined using VAD technique[2] in the borate solution. Surface morphology of the steel was studied using SEM and AFM technique.

Anodic polarization showed that phosphate coatings formed on the steel surface resulted in the decrease of the steel dissolution rate. This effect of the phosphate coatings was more pronounced for coatings deposited at higher temperatures of phosphate solution. The decrease in the steel dissolution rate is caused by the decrease of coating porosity. The addition of $NaNO_2$ in the phosphate solution significantly decreased phosphate coating porosity. The lowest porosity of phosphate coating (35.1%), for deposition time of 5 min, was obtained with 1.0 g dm^{-3} $NaNO_2$ in the phosphate solution, at 50°C.

The study of the phosphate coatings morphology showed that coating was evenly dispersed on the whole steel surface. There were two characteristic forms of phosphates present: laminated structure with needle-like forms. The average concentration of specific elements in the phosphate coatings were: oxygen 37.6%, phosphor 3.26% and iron 59.14%.

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CPA-P-06

Analysis of corrosion parameters in conditioned water-steam cycle in the power plants

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One of the primary concerns of all power plants is to ensure that the high-purity water used for power generation is of sufficient quality to maintain plant chemistry parameters. Suppressed ion chromatography (SIC) is a fundamental technique for monitoring water quality with respect to corrosive ions. In this paper, we report a new ion chromatography (IC) method that utilizes the recent advances chromatographic methods for the determination of target ions at sub-to low-µg/L levels in power plant water samples which are causers and indicators of corrosion as well. In this method, the water sample is injected using the large-loop direct injection technique, the analyte ions are separated on an IonPac ion-exchange column using high-purity eluents and detected using the suppressed conductivity detection method. The performance of the new method was evaluated by analyzing water-steam samples from the power plant. It was shown that the SIC technique provides a suitable means for preventing possible corrosion damage to generating equipment in power plants.

Contents Index Print EXIT

CPA-P-07

Study of the cavitation-corrosion and the repassivation kinetics of a highly alloyed austenitic stainless steel in a LiBr heavy brine solution

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The influence of cavitation on the corrosion behaviour of Alloy 31 (UNS N08031), in a LiBr heavy brine solution (992 g/l) has been investigated at 25º C. Cavitation shifted the corrosion potential towards the noble direction, although it increased the passive current density and shifted the value of E_p towards more negative potentials. Repassivation behaviour of Alloy 31 has also been studied as a function of applied potential in 992 g/l LiBr solutions by using potentiostatic tests, obtained after damaging the electrode surface with cavitation. The repassivation rate parameter, *n*, was obtained from the slope of the log i(t) vs. log t representation. The damage generated during the potentiostatic tests has been quantified by means of Confocal Laser Scanning Microscopy. Tt can be concluded that the parameter n increased with decreasing applied potentials. At potentials near the pitting potential (200 mVAg/AgCl), repassivation was not possible.

CPA-P-08

The investigation of structure and composition of 1-hydroxy-benzotriazole and benzotriazole adsorbed films

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Two corrosion inhibitors, 1-hydroxy-benzotriazole (BTAOH) and benzotriazole (BTAH), adsorbed on copper from 3% NaCl aqueous solution, were compared by X-ray photoelectron spectroscopy (XPS). A specific peak attributed to the formation of the Cu(I)BTA surface complex was identified in the XPS induced Auger Cu $L_3M_{4,5}M_{4,5}$ spectra recorded at grazing angles. This peak was used to differentiate between the Cu(I)BTA complex and cuprous oxide. In the case of BTAOH containing solution no such peak was found in the corresponding Auger Cu $L_3M_{4,5}M_{4,5}$ spectrum, indicating the absence of the surface Cu(I)-BTAOH complex. By using angle resolved XPS we showed that the BTAH molecules (either in the Cu(I)BTA complex or uncomplexed) are directed towards the Cu surface through their triazole N atoms. The thickness of the surface films was evaluated using the Tougaard method. The thickness of the BTAH surface layer formed after 1 h of immersion was 1.5 ± 0.3 nm, which was three times thicker than the BTAOH layer formed under the same conditions.

CPA-P-09

The influence of lavender oil on corrosion of Al-3Mg alloy

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Natural oil extracted from *Lavandula angustifolia* L. was investigated as corrosion inhibitor of Al-3Mg alloy in 3% NaCl solution using weight loss measurements and electrochemical polarisation methods. The naturally oil was found to retard the corrosion rate of Al-3Mg alloy in sodium chloride solution. The inhibition efficiency increase with oil content to attain 98% at 4 μL / L oil content, but decreased with increasing temperature. Polarisation measurements show that lavender oil essentially acts as cathodic inhibitors. The inhibiting effect of lavender oil on Al-3Mg surface was attributed to the adsorption on the metal surface, which follows Langmuir's adsorption isotherm. The calculated value of free energy of adsorption was found to be -29,4 kJ/mol, what indicates that lavender oil components might be adsorbed with weak chemical forces on metal surface.

CPA-P-10

Application of Mott-Schottky Technique to Corrosion of Steel in CO_2/H_2S Environments

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The Mott-Schottky electrochemical technique (MS) is used to characterize the electronic properties of semiconductor films in contact with a metal and an electrolyte. It involves the measurement of capacitance at different over-potentials that do not result in significant faradaic current and distruction of the passive film. MS has typically been used to study semiconductors for, rectification, photoelectron and solar energy conversion; however, in recent years it has been applied to investigate corrosion phenomena. The technique particularly lends itself to investigating CO_2 and H_2S corrosion of mild steel in oil and gas production because the films formed in these environments can exhibit semi-conductor behavior and influence localized corrosion of the underlying metal. Apart from other important parameters, it has been found that the donor density of passive films on iron, obtained from Mott-Schottky plots, can be related to the susceptibility to pitting corrosion. A review of MS related to corrosion of iron will be presented in this paper with special significance to localized corrosion in oil field environments.

CPA-P-11

Corrosion behaviour of AISI 204Cu and AISI 304 stainless steels in simulated pore solution

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WITHDRAWN

Conventional steel reinforcements embedded in concrete are passive due to a thin protective oxide layer formed on its surface in high alkaline media such as that contained in the pores of the concrete. However, these reinforcements suffer severe corrosion problems when the reinforced concrete structure is exposed to chloride contaminated environments and/or when the concrete cover is carbonated. There has always been an interest in the possible substitution of the common 300 nickel-bearing steels by the 200 series particularly in times of high nickel prices. It is well established that for 200 series with nickel at 4-5% there is a broad similarity with 304 in standard corrosion tests such as pitting, salt spray testing and long term exposure tests. In contrast, the ultra-low nickel grades have performed markedly poorly compared to 304 in these tests. In this work, corrosion resistance of the new type 204Cu (low Ni, high Mn austenitic stainless steel) and more traditional AISI 304 type is studied when exposed to simulated pore solutions with different levels of contamination (chlorides, carbonation).

CPA-P-12

Effect of surface preparation and temperature treatment on the corrosion resistance of Nitinol

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Nitinol is an alloy with almost equal molar contents of Ni and Ti. It is widely used as a material for coronary stents and in orthopaedic applications. We have studied the effect of surface preparation and surface treatment on the corrosion resistance of Nitinol (superelastic alloy S) in simulated physiological solution at 37°C. Surface preparation comprised grinding, mechanical and chemical polishing, while surface treatment was performed by oxidation in air at temperatures up to 600°C. The effects on the corrosion resistance were investigated by electrochemical methods, i.e. anodic potentiodynamic curves in simulated physiological solution, and surface-analytical methods, XPS and SEM/EDS. Compared to ground samples, polished samples showed a shift of the breakdown potential in a positive direction for several hundreds mV. This result indicates that the surface preparation plays an important role for subsequent electrochemical behaviour. A similar shift of the breakdown potential was observed for samples treated at elevated temperatures. Furthermore, a significant decrease in the corrosion current density was observed. Examination by XPS showed that this is a consequence of TiO_2 formation at the Nitinol surface.

CPA-P-13

Electrochemical characterization of the excitable iron-nitric acid system

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This study addresses the non-linear behavior of the Fe|HNO_3 system at concentrated nitric acid solutions (c_{HNO3}=11-14.4 M). Three distinct states are distinguished, namely active, partially passive and passive, characterized by equilibrium potential values. Different electrochemical processes dependent on the c_{HNO3} and applied potential control the different states. Within the concentration range 11-14.4, the equilibrium open circuit potential, called also as "mixed potential" takes values ranged between ~800-840 mV. This potential regime is located within the passive state of the Fe|HNO_3 system and starts at the Flade potential. It is suggested that the passive state within the range determined between the "mixed potential" and Flade potential is a stable but excitable attractor. When an appropriate cathodic current is applied, a dissolution reaction is initiated locally by breaking the passive oxide film.

CPA-P-14

Adsorption of azole inhibitors on Cu(111)

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Corrosion inhibitors are substances that protect metals against corrosion by decreasing the rate of corrosion processes. Efficient inhibitors are heterocyclic organic compounds consisting of a π-system and O, N, P, or S heteroatoms. Azoles are among the most often used organic inhibitors against copper corrosion. As the adsorption of inhibitor onto the surface is regarded as an important step in the formation of protective film on the surface, we studied the adsorption of azoles – imidazole, triazole, tetrazole and pentazole – on Cu(111) surface by means of atomistic computer simulations based on density-functional theory and plane-wave pseudopotential method. The aim is to determine the role of the number of nitrogen atoms in azole ring on the interaction between inhibitor molecule and copper surface. Our results show that all four molecules adsorb onto the top site of Cu(111) with a single nitrogen atom. Magnitude of adsorption energy decreases linearly with increasing number of nitrogen atoms in azole ring being 0.48, 0.40, 0.26, and 0.16 eV for imidazole, 1,2,3–triazole, tetrazole, and pentazole, respectively. Trend of adsorption energy can be explained with molecular electronegativities.

CPA-P-15

Corrosion of bare and protected copper-nickel alloys under stagnant and flow conditions in seawater

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Copper-based alloys, such as the copper nickels are often used as corrosion resistant materials within the sea environment in manufacturing of tubes, heat exchangers and condensers on ships, desalinization equipments, etc. In spite of their excellent corrosion resistance, these alloys are known to suffer accelerated corrosion when exposed to flowing electrolyte.

The effect of the Ni content in the Cu-Ni alloys (from 10-40 at. %) and the surface Cu-diethyldithiocarbamate films on the corrosion resistance of the materials in synthetic seawater under stagnant and flow conditions were investigated using electrochemical impedance spectroscopy. The results are discussed in terms of segregation of Ni ions in the barrier Cu(I) oxide and the stability of the inhibitor film.

CPA-P-16

Intrinsic coherence resonance in an electrochemical system

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We demonstrate experimentally the existence of intrinsic coherence resonance (ICR) in an electrochemical system in which chlorides induce current oscillations due to localized corrosion of iron in sulfuric acid solutions. ICR is a stochastic resonance-like phenomenon where enhanced regularity in the system dynamics is induced by the system internal noise and not by a finite value of noise imposed externally. At relatively high concentrations of chlorides, two types of oscillatory behavior are induced as a function of the potential representing a passive-active state dissolution (earlier stages of pitting) at lower potentials and an electropolishing state dissolution of iron (late stages of pitting) at higher potentials. The chloride-induced spiking dynamics characteristic at lower potentials was used to quantify the ICR. It is shown that the level of internal noise is regulated by the potential applied at the iron electrode.

CPA-P-17

Influence of $NaHCO_3$ concentration and thermal conditions on iron anode behaviour in hydrocarbonate mediums

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In the present work a comparative analysis of influence of $NaHCO_3$ concentration (in the range of 0.01-0.50 M) and thermal conditions (t = 20 - 80^{o}C) on iron anode behaviour in hydrocarbonate mediums has been carried out using a combination of physicochemical methods. It is demonstrated that in diluted solutions the iron is subject to local activation, which disappears when the content of sodium hydrocarbonate increases, and the metal passes into passive state. The temperature increasing protects the iron from local destructions in the whole concentration range of hydrocarbonate solutions under investigation. The presence of heat transfer from solid to liquid phase in diluted electrolytes destabilizes the system, and has the opposite effect in concentrated mediums.

CPA-P-18

Influence of nitrate ions on the chloride-induced potential oscillations of the iron-sulfuric acid system

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Chloride-induced potential oscillations emerged under current-controlled conditions of the $Fe|H_2SO_4$ interface are used to investigate the inhibitive effect of nitrates on localized corrosion of iron. The galvanodynamic and galvanostatic curves obtained at various concentration ratios of chloride and nitrate ions indicate distinct differences related to the inhibition action of nitrates on pitting corrosion. Upon increasing gradually the nitrate concentration and depending on the current imposed to the system, the number of potential oscillations decreases whereas the oscillatory waveform becomes more characteristic of a more stable passive state. Above a certain critical nitrate concentration, nitrates suppresed completely the oscillations resulting in a stable passive state. A quantitative characterization of the inhibitive action of nitrates is carried out using diagnostic critiria established previously on the basis of chloride-induced potential oscillations. These critiria include the induction time t_{ind} necessary for the onset of oscillations and the oscillation average firing rate $<r>$. The inhibiting effect of nitrates is discussed in terms of a competitive adsorption of chlorides and nitrates on the oxide surface along with nitrate redox reactions.

CPA-P-19

Electrochemical dissolution of molybdenum in deep eutectic solvent

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In our previous work, we reported the electrochemical dissolution of molybdenum Mo in NH_3/NH_4NO_3 non-aqueous system[1]. It is mechanically tough to machine a hard metal like molybdenum; our purpose is to find some suitable solvent that can electrochemically dissolve molybdenum and help in its electrochemical machining. The present work focuses on the electrochemical dissolution of Mo in a deep eutectic solvent (DES) formed between choline chloride and urea in ratio 1:2. This melt possesses physicochemical properties that are comparable to the room temperature ionic liquids (RTILs). Unlike the chloroaluminates and chlorozincates melts, former of which are water sensitive and later are more viscous, choline chloride and urea produce eutectics that are liquid at ambient temperature and have unusual solvent properties[2,3]. The freezing point of this melt is 12^0C. This deep eutectic solvent showed good conductivity and has corrosive ability to great extent. Galvanostatic measurements show the faradic mass loss efficiency up to 17% assuming that the molybdenum dissolves in +5 oxidation state in non-aqueous systems. Cyclic voltammeteric measurements show almost no passivation and on cathodic ramp small reduction of cations is observed. The electrodeposition of Mo was checked on copper, iron, zinc and molybdenum at current density as low as 500uA/cm^2, and no electrodeposition of molybdenum was observed.

CPA-P-20

Influence of temperature and current on hydrogen evolution during cathodic polarisation of Al-Ga alloys

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The yield of hydrogen formed during cathodic polarization of Al-Ga alloys in neutral salt solutions was measured volumetrically as a function of current density, temperature and gallium content in the alloy. The yield of hydrogen was established to be about 2 at all current densities and at low temperatures, while with increasing temperature it approached the value of 4. With the increase of gallium content in the alloy, the yield of hydrogen decreases.

CPA-P-21

Donor-density effect on the stability of titanium oxide films in bromide-containing solutions

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The influence of donor density on the stability of the titanium semiconducting oxide film was investigated in bromide-containing solutions. Titanium oxide films of the same thickness and different donor density were formed at various formation current densities galvanostatically in 0.5 M H_2SO_4. Using the Mott-Schottky analysis the TiO_2 it was found to be an n-type semiconductor whereas the donor density (oxygen vacancies) decreases with increasing formation current density. Passive oxide films of different donor density were used in bromide-containing solutions aiming to trace both the bromide electrochemical oxidation and the breakdown potential of the passive titanium oxide. The peak potential of bromide oxidation remains stable whereas the breakdown potential shifts towards more positive values upon decreasing the donor density. The experimental results are discussed on the basis of the bromide surface adsorption and a point defect model that describes both the oxide growth and its breakdown.

CPA-P-22

N-(2-hydroxybenzilidene) thiosemicarbazide surfactant as an effective corrosion inhibitor of carbon steel in acidic media

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The corrosion inhibition of carbon steel in 0.1 M HCl solution containing 0.15 M NaCl in the presence of N-(2-hydroxybenzilidene) thiosemicarbazide (HBTC) was investigated using electrochemical measurements such as: Tafel polarization, polarization resistance method and electrochemical impedance spectroscopy (EIS). The morphology of carbon steel surface was examined using SEM / EDS technique. The results showed that HBTC acts as an excellent corrosion inhibitor in 0.1 M HCl by suppressing simultaneously the cathodic and anodic processes via chemical adsorption on the carbon steel surface, which followed the Langmuir adsorption isotherm. The inhibition efficiency increased with the increase of HBTC concentration. The values of inhibition efficiency obtained from Tafel polarization, resistance polarization technique and EIS measurements are in good agreement.
A maximum value for inhibition efficiency of 83 % at 2 mM HBTC was obtained. SEM/EDS analysis confirms that HBTC form a thin layer on the carbon steel surface and the significant feature is the adsorption.

WITHDRAWN

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CPA-P-23

Peculiarities of 1,2,3-benzotriazole inhibitive action applying to copper local activation in alkaline-nitrate solutions

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Azoles inhibitive action against copper general corrosion in neutral and acidic mediums was widely presented at modern literature. Significantly little attention was paid to azoles protective function for the most dangerous types of copper local destruction in particularly local activation (LA). The last is widely spread in the heat exchange and water supply systems equipment cooling by carbonate and alkaline waters, containing inorganic and organic activators. At present work it was made the estimation of possibility 1,2,3-benzotriazole (BTAH) action in the concentration range $1\times10^{-7} \div 1\times10^{-3}$ M for inhibition of copper local activation (LA) in alkaline-nitrate solutions under different temperatures 20÷60ºC. It was shown, that BTAH inhibits copper LA according to adsorption-polymerization mechanism at investigated systems, and its efficiency grows under additive concentration and temperature of background solution increase.

CPA-P-24

Anodic oxidation of zirconium in H_3PO_4 solutions

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Subject of interest in this work was formation of anodic oxide films on zirconium in H_3PO_4 solutions at room temperature. The oxides were grown under potentiostatic conditions ($0 < E < 9$ V SCE). Optical constants n and k of both, zirconium substrate and oxides formed at different potentials were determined by means of ellipsometry. Some technique was applied to determine the thickness of the oxide formed spontaneously at in-situ and ex-situ conditions, as well as for the potentiostaticaly formed oxide films on the zirconium surface. Thicknesses of in-situ spontaneously formed film was 1.36 nm, while in ex-situ conditions the corresponding thickness was 4.85 nm. The coefficient of anodization was 2 nm/V.

CPA-P-25

Corrosion prevention by conducting poly (*o*–anisidine) based paint coating on low carbon steel

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Corrosion, being an electrochemical phenomenon, can be tackled through the use of electrochemistry and conducting polymers. Conducting polymer coating on metals or alloys can be obtained using chemical or electrochemical deposition techniques Although, a lot of work has been carried out on electrochemical deposition of conducting polymer on the active metals like iron and steel, it will be difficult to use this approach on massive engineering structures such as ships and bridges. Therefore, chemical synthesis route must be explored and designed towards practical approach. In the present work, hydrochloric acid doped conducting poly (*o*–anisidine) based paint coatings were prepared and subsequently applied on low carbon steel samples. The percentage of conducting poly (*o*–anisidine) powder in paint was varied from 0.1 to 2.5 weight % in order to study the effect of weight content on corrosion performance and to design optimum composition. The coatings were characterized by using UV- visible spectro photo metery, FTIR and SEM. UV- vis spectro photometry confirmed the formation of conducting phase and FTIR revealed the formation of an oxide layer on steel surface. The electrochemical measurements were performed using a potentiostat /galvanostat (Gamry Reference 600, USA). In these measurements, a three electrode geometry consisting of conducting poly (*o*–anisidine) -HCl based paint coated low carbon steel sample as working electrode, platinum as counter electrode and SCE as a reference electrode was used Corrosion performance of the coatings was studied using iron loss, Tafel plots, open circuit potential and impedance measurements. It was found that the coatings exhibited significant corrosion protection in acidic medium. In addition similar experiments were repeated on conducting poly(*o*-aniline) based paint coatings and comparison of these paints based on their corrosion protection performance is included at the end.

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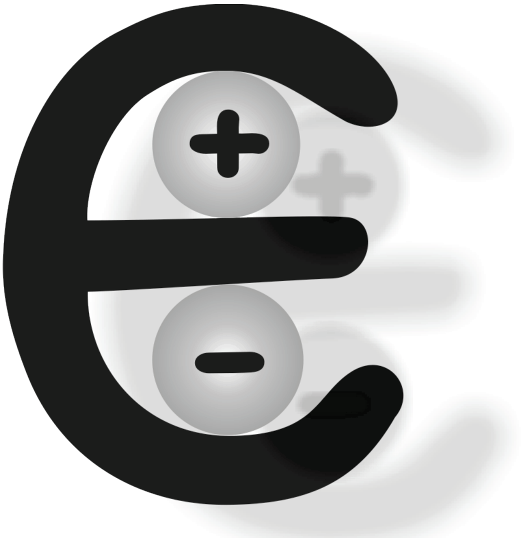
ECS

Energy Conversion and Storage Devices



ORAL PRESENTATIONS

Vršac vineyard

Wine road

Wine road or vine tourism is a specific kind of a holiday combining the wine tasting of a certain area with natural beauties, customs, and cultural and historic monuments of that area. The beginnings of wine growing on the territory of Serbia is connected to a Roman tsar Probe who had allowed that grapevines of high-quality could be grown outside the territory of today's Italy. Tsar Probe on Fruska Gora planted the first high quality grapevine. The first Serbian rulers continued the tradition. There are saved documents testifying that the laws existed for the quality of wine. It not well known that tsar Dusan had built 25 km long wine lines through which the wine from his vineyards had been delivered to capital Prizren. Main grapevine regions in Serbia are in Sumadija and around Velika Morava River, in Timok region, Srem with Fruska Gora, Pocer and Banat.

Bermet Wine

Bermet is an elegant dessert wine, produced on the basis of secret recipes held by a handful of families in the town of Sremski Karlovci in Vojvodina, Serbia. The wine is sweet, usually between 16 and 18% alcohol, with a nice mixture of spices and herbs. Every family has its own different touch, so you won't find two identical kinds. Bermet is usually served as a dessert wine, with coffee and cookies, but can also be served as an aperitif. In the old days, bermet was very popular among the aristocracy of the Austro-Hungarian Empire. It is known that the court in Vienna was buying this wine in large quantities and giving them as gifts. A few varieties of bermet were found on the exclusive Titanic menu on its unfortunate journey.

ECS-O-01

Catalytic activity for hydrogen evolution at conducting polymer(s) modified platinum electrodes in the sulphuric acid solution

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Catalytic activity for hydrogen evolution reaction (HER) at polymer (poly(o-ethoxyaniline and co-polymer of polyaniline and poly(o-ethoxyaniline)) modified Pt electrodes in the sulphuric acid solution is studied using cyclic voltammetry and electrochemical impedance spectroscopy techniques. It is shown that at all polymer modified electrodes HER is proceeding in a way similar to the pure Pt, but with significantly higher contribution of H_2 diffusion. Higher surface activity for HER is observed for the co-polymer (polyaniline + poly(o-ethoxyaniline)) modified electrode than for the pure polymer (poly(o-ethoxyaniline) modified Pt electrode.

ECS-O-02

Polymers and their composites with ruthenium oxide as active electrode materials in electrochemical supercapacitors

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A number of composite electrodes synthesized by casting a suspension of different amounts of ruthenium oxide (RuO_2) in the solutions of poly(vinylidene fluoride) (PVDF) or Nafion® as binders onto glassy carbon (GC) electrodes and covered subsequently by various quantities of deposited polyaniline (PANI) were investigated as the electrodes for applications in electrochemical supercapacitors. The electrochemical properties of the composite electrodes were investigated by cyclic voltammetry and electrochemical impedance spectroscopy techniques. It has been shown that for the composites with lower mass of RuO_2 specific capacitance of about 500 F g^{-1} is achieved with PVDF as a binder and PANI formed in 6 potential cycles. For the same composites, however, better power characteristics could be expected for Nafion® as the binder.

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ECS-O-03

Li-ion baterries based on organic compounds

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Current Li-ion batteries technology is based on the use of inorganic materials. Although electroactive organic materials tend to be rather unstable, they can achieve much higher capacities than inorganic. They are better also from the environmental aspect. One of the main problems is the solubility of organic compounds in electrolytes that are commonly used in Li-ion batteries. This means that these compounds gradually dissolve from the composite electrode material (wired to the current collector) into the electrolyte and the consequence is a decreasing capacity with repeated charging/discharging. Some papers have already introduced the use of electroactive polymers (which are insoluble). We have tried another approach by bonding electroactive organic compounds onto nonsoluble silica nanoparticles and also by bonding them onto modified cellulose molecules. These initial results may show a direction for further development of organic Li-ion batteries.

ECS-O-04

Pt monolayer electrocatalysts for O_2 reduction: Pt monolayer on carbon-supported PdIr nanoparticles

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The kinetics of oxygen reduction reaction (ORR) was investigated in acid solutions on Pt monolayer (Pt_{ML}) deposited on modified carbon supported PdIr/C nanoparticles using rotating disk-electrode technique. The Ir submonolayer is introduced into Pd substrate in order to fine-tune Pt-Pd interaction. The ORR kinetics shows an enhancement at Pt_{ML}PdIr/C nanoparticles in comparison with the reaction on Pt/C and Pt_{ML}Pd/C nanoparticles. The electrochemical measurements suggest that decreased oxidation of Pt_{ML} on PdIr/C compared to Pt/C or Pt_{ML} on Pd/C is the probable cause of enhanced activity. The subsurface Ir causes Pd top layer to contract, so Pt_{ML} is compressed more on PdIr/C then on Pd/C. According to d-band theory, this will produce further weakening of Pt-O interaction which increases ORR activity. The Pt-specific activity for Pt_{ML}PdIr/C is 3 times and 25% higher for the Pt/C and Pt_{ML}Pd/C respectively; the Pt-mass activity of Pt_{ML}PdIr/C is more than 20 times and 25% higher than Pt/C and Pt_{ML}PdIr/C respectively.

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ECS-O-05

Study and performance of carbon xerogels and manganese oxide based electrodes in asymmetric supercapacitors

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Carbon xerogels and manganese oxide materials have been tested in asymmetric supercapacitors with the objective to obtain enhanced capacitive performance. The asymmetric supercapacitor consisted of the carbon-based negative electrode, that exhibited pure capacitive behaviour, and of the metal oxide-based positive electrode, that exibited pseudocapacitive behaviour. Faradaic process occurring on the positive electrode produces an increase of the specific capacitance but also a decrease of the specific power, being the electrochemical reaction a slower process respect to the double layer formation. Materials as metal oxides have been investigated for their utilization in asymmetric supercapacitors and among these manganese oxide occupies a prominent position for its interesting properties.

To obtain high capacitive performance from the device also the negative electrode, that is positioned in series at the positive electrode, must present high specific capacitance. For this reason we have prepared carbon xerogels with high conductivity and surface areas.

The electrochemical tests performed on asymmetric supercapacitors in aqueous electrolyte gave specific capacitance of about 200 F/g.

The basic test procedures were cyclic voltammetry (CV), DC galvanostatic charge and discharge (G-CD) method and electrochemical impedance spectrometry (EIS).

The results indicated that with a carbon xerogel, having surface area of 2360 m^2/g, and manganese oxide it was possible to obtain specific capacitance of about 200 F/g (calculated on unitary weight of material in a single electrode). This results put this supercapacitor at the top level of the more performing devices till now experimented.

ECS-O-06

Lithiated vanadium oxide for positive electrodes of lithium-ion batteries

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Vanadium oxides are known to be promising materials for positive electrode of lithium-ion batteries due to high energy densities, low price and good safety properties, the latter being the most important.

The present work compares commercial LiV_3O_8 (A) and whiskers of lithium-vanadium bronze (B) as an active material of positive electrodes. Whiskers of $Li_xV_8O_{21}$ were synthesized *via* hydrothermal treatment of corresponding xerogel. The electrodes were prepared by spreading of active mass (85% vanadium oxide, 10% acetylene black, 5% PVDF) upon stainless-steel mesh. The electrode were tested in 1 M $LiClO_4$ in a mixture of propylene carbonate and dimethoxyethane. Galvanostatic and cyclic voltammetric curves were registered. The electrodes with material A display initial discharge capacity ca. 380 mAh/g at C/20 and 300 mAh/g at C/5 rate. The electrodes with material B display capacity 500 mAh/g at C/20 and 300 mAh/g at C/5 rate. The capacity fading for material A was higher than that for material B. The advantages of material B are connected with its nanostructure.

ECS-O-07

Amorphous silicon with high cycleability for lithium-ion batteries

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The search of alternative materials to carbon is connected with aspiration for increase of specific capacity (Q_{sp}) of a negative electrode of lithium-ion batteries. The theoretical Q_{sp} of graphite for lithium intercalation is 372 mAh/g whereas many materials are capable to uptake much more amounts of lithium. Thus, the theoretical Q_{sp} of Sn, Al and Si reaches 959, 2235 and 4211 mAh/g, correspondingly. Unfortunately, huge increase of specific volume occurs at lithium insertion into these substances leading to destruction of material (up to pulverizing) and loss of electric contact between particles. This shortcoming can be overcome by using stable nanosize particles. The greatest hopes are set on using of thin-film electrodes based on amorphous silicon or silicon composites. Such electrodes can be manufactured by various methods, including plasma-magnetron sputtering; rf glow discharge from silane gas; or laser sputtering. The present paper compares electrochemical behavior of electrodes made by these very methods.

ECS-O-08

Catalytic activity of sputtered Platinum and co-sputtered Platinum-Iridium layers toward oxygen reduction using rotating disc electrode

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Sputtering is a widely used thin film physical vapour deposition technology that allows homogenous and reproducible coating of large areas of various substrates. In order to reduce the catalyst loading without loss of catalytic activity, recently the magnetron sputtering has been proposed as a method enabling deposition of thin homogeneous films with high catalyst utilization. Through variation of the process parameters like gas pressure, distance between target and substrate, sputtering power, etc. it is possible to deposit reproducible thin films with tailored morphology that can be adapted to specific applications. The method is of particular interest for development and fabrication of gas diffusion electrodes (GDE) for hydrogen energy converters. Our aim is to combine the alloying and sputtering and fabricate thin bimetallic PtIr films by co-sputtering from platinum and iridium targets. The recent work represents a comparison of the electrochemical activity of sputtered low loaded Pt and Pt-Ir loaded GDE during oxygen reduction (ORR) on rotating disc electrode (RDE) in sulphuric acid solution. All samples were deposited on a thin Ti adhesion layer upon hydrophobic carbon paper substrates by magnetron sputtering (Pt-layer) and co-sputtering (PtIr-layer). The sputtering power of the platinum generator was held constant at 100 W, while the iridium power was 30W and 40W. The sputtering pressure for all samples was fixed at 68 mTorr, proved to ensure optimal morphology and high active surface area. The surface structure and morphology were analysed with scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX). The XRD analysis revealed the alloying of the materials and not just a mixing of both elements. The EDX data (Table 1) shows a good correlation between the sputter power and the resulting PtIr-ratio. It was found that at same power the platinum sputtering rate is higher than that of iridium, which is probably due to the higher binding energy of iridium atoms.

POSTER PRESENTATIONS

ECS-P-01

Electrochemical performance of $Li_{1.2}V_3O_8$ in saturated aqueous solution of $LiNO_3$

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The $Li_{1.2}V_3O_8$ was synthesized by modified sol-gel method and treated at several temperatures. Electrochemical performance of $Li_{1.2}V_3O_8$ was investigated by galvanostatic cycling in saturated aqueous solution of $LiNO_3$. The sample treated at 300 °C consisted of uniform rod-shaped particles, 100–150 nm in diameter and 300–800 nm in length. It displayed the best electrochemical performance: the initial discharge capacity amounted to 136.8 $mAhg^{-1}$ and capacity fade upon 50 charging/discharging cycles was only 12 %. This is significant improvement compared to the product obtained by solid state reaction, published by other authors. There is the literature evidence that $Li_{1.2}V_3O_8$ synthesized in similar way displays enhanced electrochemical properties in organic solutions, too.

ECS-P-02

Oxidation of formic acid on bulk and nanosized Pt-Co alloys

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Bulk Pt_3Co and nanosized Pt_3Co and PtCo alloys supported on XC-72 high area carbon were investigated as the electrocatalysts for the oxidation of formic acid. Cyclic voltammetry in 0.1 M $HClO_4$ and stripping voltammetry of CO_{ads} in the same electrolyte show a small difference in the potentials of Pt-oxide formation and reduction and CO_{ads} oxidation. Based on these results, we concluded that electronic modification of Pt by Co atoms, which was theoretically predicted and experimentally proved on solid/gas interface, is exhibited in the electrochemical environment. Promotion of HCOOH oxidation rate on bimetallic Pt-Co surfaces with respect to pure Pt was found to be up to factor of eight in the case of PtCo/XC-72 catalyst. This moderate increase of the reaction rate is ascribed mostly to the ensemble effect, because partial leaching of Co increased Pt:Co ratio at the bimetallic surfaces, diminishing the efficiency of the ensemble effect.

ECS-P-03

Investigation of AB_5-hydrogen storage alloys as anode material for direct borohydride fuel cell

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WITHDRAWN

Three commercial AB_5-type hydrogen storage alloys were examined as anode material for direct borohydride fuel cell (DBFC). Electrodes were prepared by pasting a mixture of fine alloy powder, carbon black Vulcan XC-35 and PTFE emulsion in weight ratio 90:5:5 on nickel foam. A single chamber fuel cell consisting of a metal hydride anode, air gas-diffusion cathode and 5 wt. % $NaBH_4$/6M KOH electrolyte was assembled and tested. Proton exchange membrane (PEM) Nafion® 117, pressed on the catalytic side of the air cathode exposed to the liquid electrolyte, was used in part of experiments. Power density values between 30 and 55 mW/cm^2 were achieved with the different hydrogen storage alloys studied. The use of PEM results in decrease of the power density, but increase of the borohydride fuel utilization. Further investigations on improvement of electrode activity, membrane electrode assembly as well as long-term stability are in a progress.

ECS-P-04

Synthesis of $LiFePO_4$ powder by citrate method

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Lithium iron phosphate has become of great interest as storage cathode for the next generation of rechargeable lithium batteries. Olivine structure $LiFePO_4$/C composite powder was prepared by citrate method. Equimolar amounts of LiOH, $FeSO_4 \cdot 7H_2O$, $(NH_4)_2HPO_4$, were mixed with two different amounts of citric acid in small amount of water. In the first case total cation to citric acid ratio was 1:1, while in the second case the ratio was 1:0.6. Gels were obtained by putting both solutions in oven at 80ºC. Finally, the gels were heated in the mixture of 5% H_2 + Ar at different temperatures. The amount of carbon was determined by TG analysis. Olivine structure was confirmed by XRDP. Electrochemical properties were checked by CV and galvanostatic cycling. The obtained powders show excellent cycleability, with capacity increasing during cycling, but relatively low initial capacity.

ECS-P-05

Novel Pt based nanocatalyst at Nb doped TiO_2 support for oxygen reduction reaction

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The kinetics of oxygen reduction reaction (ORR) has been studied at $NbTiO_2$ supported Pt catalyst in 0.5 mol dm^{-3} $HClO_4$ and 0.5 mol dm^{-3} $HClO_4$ + 0.1 mol dm^{-3} methanol solutions. $NbTiO_2$ support was synthesized by sol-gel procedure. Specific surface area of the support was determined by BET technique. XRD analysis revealed presence of anatase TiO_2 phase in support powder. $NbTiO_2$ supported Pt nanocatalyst was synthesized by borohydride reduction method. The catalyst was characterized by TEM technique and mean particle size of 3.5 nm was found. Kinetics of the ORR was studied by cyclic voltammetry and linear sweep voltammetry techniques at RDE. Catalytic activity, expressed in terms of specific and mass activity, was found to be much higher in comparison with Pt/C catalyst. The catalyst was also more efficient for ORR in methanol-containing electrolyte.

ECS-P-06

Nb-doped TiO_2 as a support of Pt and Pt-Ru anode catalyst for PEMFCs

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TiO_2 doped by 0.5 mass% Nb was synthesized by the acid-catalyzed sol-gel method. BET surface area was determined to be 72 $m^2\ g^{-1}$. XRD measurements showed that TiO_2 has structure of anatase with ~13 nm average crystallite size. Using Nb-TiO_2 as a support, Pt/Nb-TiO_2 and Pt-Ru/Nb-TiO_2 were prepared by borohydride reduction method. TEM imaging of Pt-Ru/Nb-TiO_2 revealed rather uniform distribution of the metallic particles on the support with a mean diameter of 3.8 nm. According to XRD analysis, Pt-Ru particles consist of the solid solution of Ru in Pt (40 at.% Ru) and a small amount of RuO_2.

Cyclic voltammetry of Pt/Nb-TiO_2 and Pt-Ru/Nb-TiO_2 indicated good conductivity of the supporting material. Oxidation of pre-adsorbed CO and methanol on Pt-Ru/Nb-TiO_2 was faster than on Pt/Nb-TiO_2. However, when the activities of Pt/Nb-TiO_2 and Pt-Ru/Nb-TiO_2 for methanol oxidation were compared to those of Pt/XC-72 and Pt-Ru/XC-72, no significant difference was observed. This means that Nb-TiO_2 is a promising replacement for high area carbon supports in PEMFC anodes, but without the influence on the reaction kinetics.

ECS-P-07

Characterization of Co-Ru-TiO_2-MWCNTs electrocatalysts for water electrolysis

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Hyper-hypo d-electrocatalytic materials [1] (hyper d-metal + hypo d-oxide [2]) for water electrolysis were studied with a main goal to reduce the quantity of precious metal in the hyper d-metallic phase [3]. The studied electrocatalysts contain 10% mixed metallic phase Co-Ru (Co:Ru = 1:1 wt., Co:Ru = 4:1 wt.), 18% TiO_2 as a crystalline anatase and the rest was carbon substrate – purified/activated multiwalled carbon nanotubes (MWCNTs) [4]. For comparison corresponding electrocatalysts with pure hiper d-metallic phase (Co and Ru) were prepared.

According to the structural characterization (XRD and TEM), it was shown that the size of hyper d-metallic particles of Co and Ru were near 2 nm, anatase particles near 4 nm. SEM analysis has shown that catalysts components formed agregates with holes between them, that contributes for higher inter-particle porosity. Due to geommetry of carbon nanotubes (empty cillinders) they possess inner holes that increases the trans-particle porosity. FTIR analysis has shown that the level of the hypo-hyper d-interaction between metallic phase and anatase was almost the same in all samples.

Electrocatalytic activity was measured in the alkaline hydrogen electrolyser. The range of the catalytic activity for hydrogen evolution of studied electrocatalysts was the following: Ru > CoRu (1:1 wt.) > CoRu (4:1 wt.) > Co. It is normally Ru, as a precious metal with the highest intrinsic activity, to show the best performances. On the other side, the particle size of metallic phase in all catalysts was the same, thus the effect of the real surface area of active catalytic centres on the catalytic activity was the same.

In our previous study of Co-Pt systems, the efficiency of catalytic activity was different [3]. The activity of mixed Co-Pt catalysts was higher than that of catalyst with pure Pt metallic phase, because Co has been shown as a promoter for reducing Pt particles. The smaller amount of Pt was compensated with considerably higher surface area of the active catalytic centres.

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ECS-P-08

Ion dynamics and different type of charges in the redox reactions of hydrous RuO$_2$

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Electrochemical charging/discharging reaction of hydrous ruthenium oxide was studied by cyclic voltammetry and electrochemical quartz-crystal nanobalance (EQCN) in sulfuric acid as well as in neutral solutions of Na$_2$SO$_4$ and K$_2$SO$_4$. The ruthenium oxide electrode was prepared by attaching the ruthenium oxide particles on gold covered quartz electrode. The results show that the specific capacitance as well as the apparent molar mass of exchanged species depends on the scan rate. The existence of different mechanisms of the redox reaction depending on the potential range was revealed. The results were interpreted with two different charges, one leading to the mass release and another to the mass loss upon oxidation, taking place simultaneously during the oxidation/reduction reaction of ruthenium oxide.

ECS-P-09

Effects of UPD adlayer of foreign metals on the oxidation of ethanol on carbon supported Pt-based catalysts

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Oxidation of ethanol was studied at Sn$_{UPD}$, Ru$_{UPD}$ and Rh$_{UPD}$ modified and unmodified Pt/C, Pt$_3$Sn/C and Pt$_3$Ru$_2$/C catalysts. All unmodified catalysts were characterized by XRD. Potentiodynamic and chronoamperometric measurements were used to establish their catalytic activity for ethanol oxidation. Underpotential deposition of small amount of each one adatoms (~10%) enhanced the activity of Pt/C and Pt$_3$Sn/C catalysts. The onset potential is shifted for ~0.05 V towards lower values and the current densities in the whole potential region studied are up to two times higher regarding to unmodified catalysts. On the other hand, addition of Sn$_{UPD}$ or Rh$_{UPD}$ slightly increases the activity of Pt$_3$Ru$_2$/C, while the presence of Ru$_{ad}$ adlayer decreases its activity for ethanol oxidation. Catalytic action of Sn and Ru adatoms was associated mostly with their ability to adsorb oxygen containing species at lower potentials than Pt, permitting bifunctional mechanism to proceed. Rh adatoms act on the C-C bond breaking activation increasing in this way the activity of modified surfaces for the ethanol oxidation.

Pt$_3$Sn/C modified by ~10% Sn$_{UPD}$ is the best catalyst studied. Its activity enhanced more than two times in respect to Pt$_3$Sn/C catalyst.

ECS-P-10

Influence of continuous cultivation conditions on the yeast biofuel cell performance

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WITHDRAWN

The aim of this study was to elucidate the influence of Candida melibiosica 2491 yeast continuous cultivation on the performance of mediatorless biofuel cell. The yeast strain was cultivated in YP_{fru} medium consisting of yeast extract [illegible]5%, peptone 0.8%, fructose 3%, 67 mM phosphate buffer, pH 7.[illegible], at 28[illegible]. The cultivation was carried out in flask without or in the presence of carbon felt immersed in the suspension. In the latter case the cell suspension was half and totally replaced by fresh medium at a given stage of cultivation. After about 40 hours the open circuit potential dropped to negative values, indicating an initial colonization and biofilm formation on the carbon felt surface. Thus treated carbon felt was applied as anode in double-chamber fuel cell using fresh yeast-free YP_{fru} medium as anolyte and potassium ferricyanide as catholyte. The achieved maximum power density of 84 mW/m^2 exceeds over twice that obtained with pure carbon felt anode and yeast cell suspension as anolyte.

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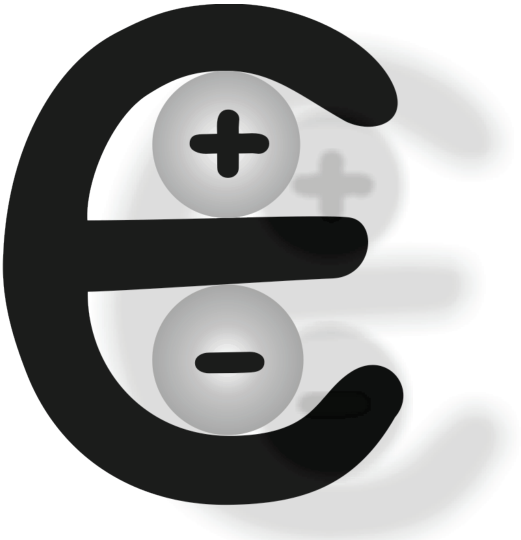
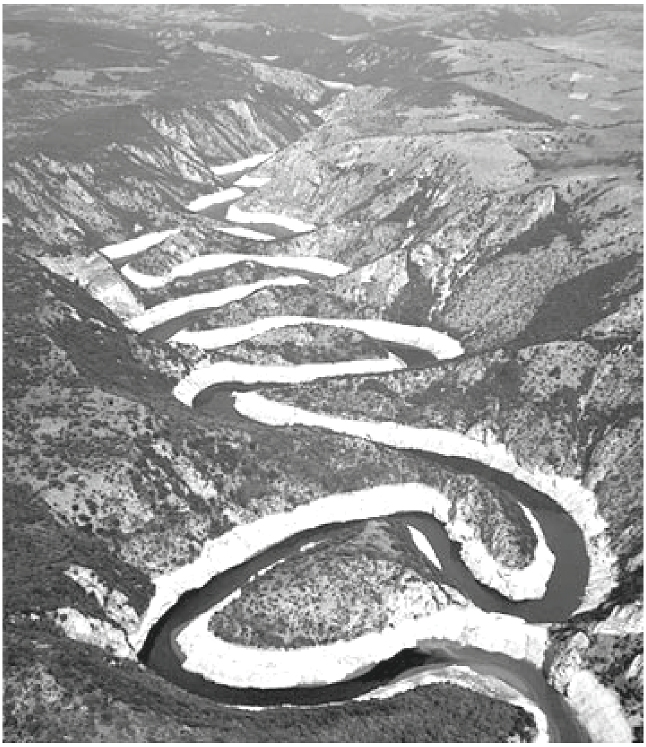
EEH

Environmental Electrochemistry



ORAL PRESENTATIONS



Uvac

Scenic lookouts

Molitva (Prayer)

Molitva is situated in **Uvac** Special Nature Reserve, protected natural asset of great importance. It is situated in south-western Serbia in the region of Stari Vlah-Raška high plateau, wedged between Mt. Zlatar massif in the Southwest and Mt. Javor in the Northeast. Minimum altitude in the reserve is 760 m above sea level, and maximum 1322 m. The surrounding is characterised by karst surface with numerous karst formations. Caves are numerous and vary in size, ranging from rock shelters to Usak Cave System, the largest known cave system in Serbia (6185 м). Caves are very rich in speleothem deposited by the action of dripping water to form stalactites, stalagmites, columns, draperies, transparent needles etc. **Uvac** Special Nature Reserve is distinguished by the presence of 104 bird species. Most important of all is griffon vulture (Gyps fulvus), one of the two vulture species that are still nesting in Serbia. Griffon vultures are, at the same time, the greatest attraction in the reserve. Griffon vulture is a vulture species, of an impressive size with a wingspan of 3m at times, which makes him a powerful flier.

Bilješka stena (Bilješka Rock)

Observation deck Bilješka Rock is situated in National park Tara, 1225 m above the sea level. From there you have a beautiful view of Lake Perućac, river Drina, Bajina Bašta and large part of Bosnia and Herzegovina. Nearby there is a small cottage built during shooting of the film “The birds who never start flying” which can be freely used. Here you can also find Pančić spruce (relict and endemic species of the Balkans).

EEH-O-01

The role of selfprotonation in reduction of substituted hydroxybenzonitriles

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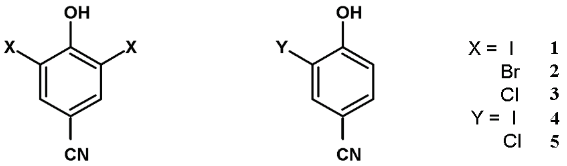
The reduction mechanism of ioxynil **1**, bromoxynil **2**, chloroxynil **3** and their reduction products 3-halogeno-4-hydroxybenzonitriles **4** and **5** was studied in dimethylsulfoxide by electrochemical methods combined with GC/MS identification of products. The reduction is accompanied by the formation of a radical anion and the subsequent fast chemical reactions as the cleavage of a halide. The selfprotonation explains the differences in number of electrons involved in the first redox step in different solvents and in the presence of proton donors.



This work is supported by the Grant Agency of the Czech Republic (203/09/1607 and 203/08/1157) and Ministry of Education (COST OC140).

EEH-O-02

Electrochemical treatment of reverse osmosis concentrate

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In recent years, there has been an increasing interest in the applications of electrochemical treatment for environmental pollution abatement. Some of the advantages of the electrochemical treatment are simplicity and robustness of the process structure and operation, characterized by an efficient control of electron transfer rate and reaction conditions (current density and electrode potential). Also, electricity is used as a clean energy source and it is a chemical-free treatment, at ambient temperature and pressure. This work investigated the efficiency of electrochemical oxidation for the remediation of problematic reverse osmosis concentrate (ROC) stream. The characteristics of the ROC go in favour of the EC treatment: its high salinity ensures an excellent electric conductivity and lowers the energy consumption, and high chloride content can promote indirect bulk oxidation by the generation of hypochlorite. Experiments with stepwise increase in current were conducted using Ru/Ir electrodes as anodes, and stainless steel cathodes. While the colour removal in electrochemical oxidation was excellent (98 %), chemical oxygen demand (COD) and total organic carbon (TOC) removal were observed to be modest at lower current intensity (e.g. 240 mA), 20% and 8 %, respectively. At higher current intensity (e.g. 1 A) the efficiency of removing COD and TOC were greatly increased. Furthermore, removal of 30 trace organic compounds (pharmaceuticals and pesticides) during electrochemical oxidation was investigated by employing advanced liquid chromatography (LC)-quadrupole linear ion trap (QqLIT)-mass spectrometry (MS) for trace analysis of target analytes in ROC. Among the target analytes, several pesticides such as 2,4-dichlorophenoxyacetic acid, triclopyr and N,N-diethyl-meta-toluamide (DEET) showed persistence to electrochemical oxidation at lower current densities, and for their efficient removal higher currents must be used. Nevertheless, outstanding performance of electrochemical oxidation was observed for removing the majority of pollutants analyzed. Electrochemical treatment seems to be a promising alternative for treating problematic waste streams such is ROC.

POSTER PRESENTATIONS

EEH-P-01

WITHDRAWN

EEH-P-02

Temperature effects on bioelectrochemical denitrification of wastewater

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It was recently established that constant electric field stimulates enzyme reduction of nitrate and nitrite either at bacterial culture of *Pseudomonas denitrificans* or cell-free enzyme preparation derived from this strain. In the present study the effect of temperature on the reduction process accomplished by cell-free enzyme preparation with and without application of electric field was studied. Temperatures between 20 and 30^{o}C and cathode potentials between -0.01 and +0.06 V/S.H.E. were tested.

It was found out, that the Arrhenius equation did not fit the case without application of electric field. Practically no energy barrier of enzyme nitrate reduction in the range of the lowest studied temperatures (i.e., 20 – 25 ^{o}C) was observed. Near the optimum temperature the activation energy seems very high. When constant electric field was applied the estimated activation energy was considerably lower, especially for the optimum cathode potential of +0.01 V/S.H.E. Reasonable Arhenius relationship was observed.

The analysis of the obtained results shows that when no electric field was applied the high reaction rate was due to the high entropy factor, whereas in constant electric flied the activation energy was lower although the entropy factor was lower too.

EEH-P-03

Voltammetric determination of Nitrofen and Oxyfluorfen at a carbon paste electrode

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The optimal conditions for the determination of the herbicides Nitrofen and Oxyfluorfen in a mixed supporting electrolyte consisting of Britton-Robinson buffer and methanol were found. Method for the determination of the substances by differential pulse voltammetry on a carbon paste electrode was developed. The calibration dependences are linear and the achieved limits of detection permit trace analysis.

The finnancial support of The Czech Ministry of Youth and Sports (project LC06035, MSM 021620857 and RP14/63) is gratefully acknowledged.

EEH-P-04

Voltammetric Determination of Glyphosate in Soil Samples with Different Content of Organic Matter

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The main aim of this work was improvement and development of procedure for preparation of real soil samples polluted by Glyphosate (Glyp). After derivatization of Glyp, the formed nitrosoglyphosate was determined by differential pulse voltammetry at hanging mercury drop electrode in soil samples with three different contents of organic matter. This method might be suitable for routine analysis of the soil samples during investigation of Glyp effect on the worm populations. At present, this is one of the projects running at FIOCRUZ (Rio de Janeiro, Brazil).

Financial support from Ministry of Education, Youth and Sports of the Czech Republic (LC 06035 and MSM 0021620857), GACR (203/07/1195), Found of Mobility of Charles University in Prague and Brazilian National Research Council is gratefully acknowledged.

EEH-P-05

Synthesis and photoelectrocatalytic activity of TiO_2/WO_3 hybrid structures for pollutant photooxidation under ultraviolet and visible light illumination

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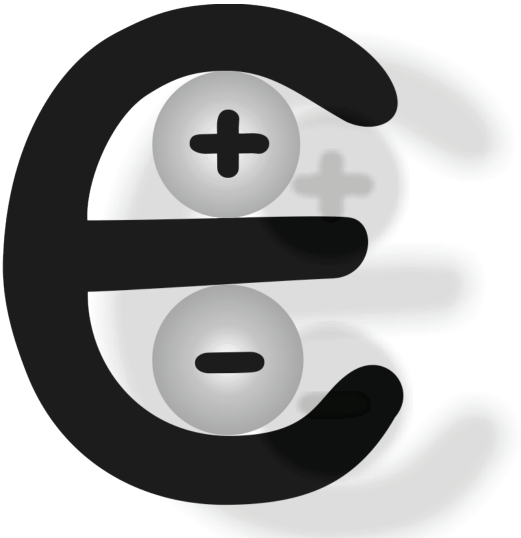
Hybrid strucrures of TiO_2/WO_3 composites were produced on graphite substrates following a three step procedure: i/ electrochemical deposition of WO_3 under potentiostatic conditions, ii/ electrochemical deposition of TiO_2–polyaniline (PANI) composite layers by potentiostatic polymerization of aniline in the presence of TiO_2 nanoparticles, iii/ high temperature (450°C) treatment for decomposition of the PANI structure. Experiments on the photoelectrochemical response of the composite speciments were carried out by cyclic voltammetry and chronoamperommetry in the dark and under illumination by using low power lamps emitting in the visible and UV spectrum ranges. The oxidation of three pollutants – oxalate ions, methanol and malachite green was used to evaluate the photoelectrocatalytic activity of the TiO_2/WO_s structures. The photocurrents registered for the photooxidation of methanol and oxalate were higher than photocurrents measured at hybrid TiO_2/WO_s electrodes obtained in a conventional electrochemical way.

ESD

Electrochemical and Electronic Sensor Devices



ORAL PRESENTATIONS

Devils' Town

Unusual Natural Phenomena

Đavolja Varoš (Devils' Town)

The "Devils' Town" is the natural monument in the south of Serbia.

This natural monument embrace two rare world's phenomena: soil figures as specific relief forms rendering an attractive sight, and two wells of strong acidic waters with high mineralization. The terrain around the figures adds to the attraction of these phenomena rendering rather severe, almost mystical impression, while, on the other hand, the surrounding ambiance is timid and picturesque, with remains of an ancient temple and a few mining pits from medieval times.

The soil figures (202), of different shapes and sizes, from 2 m to 15 m of height, and from 0.5 m to 3 m in width, with their stone caps, have resulted from centuries long specific effects of erosion which has made them grow, change, shorten, disappear and reappear. This geo-morphological phenomenon is a unique occurrence in Serbia and a very rare in the world.

There are similar occurrences in Europe, but Devil's Town towers are much larger and much more stable, which make them one of the most renowned natural monuments of the kind in Europe.

A lot of legends have been created regarding its origin. According to one, the figures represent the petrified wedding guests who, at devil's urging, tried to marry a brother and sister, so the God petrified them to prevent this incest. The other legend says that these are the devils turned into stones by the people who had been forced to carry them on their backs, suffering misfortunes, and who, trying to get rid of them, spent a night at the Devil's Town site.

Within the protected area, there are two mineral water wells of extraordinary properties. The "Devil's Town" well is a cold and extremely acidic spring (pH 1.5) of high mineralization.

The "Red Well" is the second spring located by the hiking track in the centre of the protected area; with waters of pH 3.5. Waters of this kind are very rare in the world. Local population believes in the healing capacity of the "Devil's water" spring, while doctors and geologists still don't recommend these waters, as they have not been thoroughly examined so far.

Deliblatska peščara (Deliblat sand)

Deliblatska peščara (Deliblat sand - the Europian sahara), is a Special Nature Reserve and picnic area.

First planned planting of trees, in order to hold to sand and prevent it from spreading, began in 1818.

Part of this area called ”Labudovo Okno”(15 far from Bela Crkva)
goes down to the Danube and creates the perfect living
conditions for various birds and is one of the largest swapm bird reservations.

The main center in Deliblatska peščara is Devojački bunar.

ESD-O-01

Modified electrodes for biosensors used in pharmaceutical and environmental analysis

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The most important step out of the election of the enzyme and the electrode material (the transducer) is the immobilization strategy. The biocompound immobilization needs to ensure the stability of the enzyme on the electrode surface and to maintain, in most cases, the hydration of the micromedium which ensures the enzyme's biocatalytic activity and prolongs the life of the biosensors. In order to establish the configurations of biosensors that are able to detect nitrates/nitrites in various matrices, was studied the behavior of modified electrodes with an electroconductive polymer film. Polypyrrole films deposition on various electrode materials (Pt, Au, glassy carbon, screen printed electrodes or planar electrodes) was made by several methods. The film permeability was tested in the presence of the redox couple potassium ferrocyanide/ferricyanide. The electroanalytic characterization of the deposited films was performed by using the chronoamperometry method in the presence of an enzyme which was immobilized in the polymeric films. Using graphite based planar electrodes, modified with horseradish peroxydase embedded in polypyrrole films was proved the existence of interactions between the immobilized enzyme and the electroactive species of paracetamol (N-acetyl-p-benzo-quinone imine-NAPQI), generated by enzymatic means in the presence of the hydrogen peroxide. The method used for these determinations was the chrono-amperometry. The electrochemical behavior of nitrates/nitrites in the reduction and oxidation processes on various electrode materials and at different pH's was studied. Better results in the both processes were obtained at low pH values. The influence of different parameters (medium electrolyte, electrode material and pH) on the electrochemical reduction or oxidation of nitrates was studied using cyclic voltammetry in order to establish the optimum working conditions.

These preliminary results will be used to embed the nitrate reductase in electrodeposited polypyrrole films on planar screen printed electrodes, followed by the electrochemical characterization of the new biosensors and their testing in different matrices (drinking water, environmental samples, food and drugs).

ESD-O-02

Screen Printed Carbon Electrode Modified with Lead-Dioxide and Glucose Oxidase as Amperometric Glucose Biosensor

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A new amperometric glucose biosensor was developed based on screen printed carbon electrodes (SPCEs) modified with PbO_2 and glucose oxidase (GOD). In this study, PbO_2 was investigated for its role as a mediator to detect hydrogen peroxide by decreasing its overpotential for its oxidation to oxygen. The carbon ink was bulk-modified with PbO_2 (5% PbO_2) prior to screen-printing. GOD was immobilized on the surface of the SPCE by entrapping it into a permeable membrane of Nafion®. Experimental parameters, such as

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applied working potential, flow rate of the carrier and injection volume were investigated by flow injection analysis using the amperometric biosensor as a detector in a thin-layer flow-through cell. The method was validated with respect to calibration curve, linear dynamic range, detection limit, repeatability and reproducibility. The influence of intereferents, such as ascorbic acid, uric acid, xanthine, hypoxanthine, paracetamol, and gentisic acid, was studied.The applicability to samples (blood, plasma, fruit drinks) will be discussed.

The authors acknowledge the financial support of the Secretariat for Science and Technological Development, Autonomous Province of Vojvodina, R. Serbia (No. 114-451-02011/2007-02) and CEEPUS II (CII-CZ-0212-02-0910).

ESD-O-03

Chemically modified carbon paste as a novel recognition sensor for selective determination of metoclopramide

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Crown ether derivative, 4'-nitrobenzo-15-crown-5 (CED) is used as novel ionophore and potassium tetrakis[3,5-bis(trifluoro-methyl) phenyl]borate (KTFPB) as anionic membrane additive for potentiometric determination of metoclopramide (MCP). Fast Nernstian response for metoclopramide over the concentration range 1×10^{-6} - 1×10^{-2} M at pH 3-7 with lower detection limit of 2×10^{-7} M and calibration slope of 56.2 and 57.4 mV/concentration decade. The proposed sensor reveals by separate solution method (SSM) a good selectivity over different cations. Direct determination of metoclopramide in pharmaceutical formulations and human serum gives results in good agreement with data obtained using standard spectrophotometric method.

POSTER PRESENTATIONS

ESD-P-01

Kinetic approach for evaluation of total antioxidant activity

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Recent attention of clinical chemists is paid to a so-called oxidative stress, recognized as one of the major risk factors in progression of different diseases. This provides an interest to the compounds, which are able to decrease the rate of oxidizing reactions, i.e. antioxidants. We propose a novel approach for assessment of total antioxidant activity by monitoring kinetics of hydrogen peroxide (H_2O_2) scavenging after its injection into liquid sample under study. H_2O_2 is known to be the strongest oxidant, really presented in human body [1]. In addition, kinetic approach, being more informative than the commonly used methods, provides better discrimination of potential antioxidants. Prussian Blue based sensor due to its high sensitivity and operational stability allowed to monitor kinetics of hydrogen peroxide consumption in turbid and colored samples. The pseudo-first order kinetic constants of hydrogen peroxide scavenging in the presence of different food additives correlated with total antioxidant activity of these samples evaluated via standard procedure based on lipid peroxidation.

The authors acknowledge the financial support from Federal Agency of education (grant NK-22P-7).

1. E.E. Karyakina, D.V. Vokhmyanina et all. *Talanta*, **80** (2009) 749.

ESD-P-02

Electrochemical detection of some anions using 4-azulen-1-yl pyranylium salts

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The design of receptors for the anions coordination is an important aspect in order to get a good electrochemical signal. In the present work, the strategy consisting in the detection of the current/potential change of the redox guest activity when the complex is formed has been applied for the anion electrochemical recognition.

The structure of the proposed receptor is based on the 4-azulen-1-yl pyranylium salts. Cyclic voltammetry and differential pulse voltammetry have been used to characterize the new receptors. The obtained results show that some of the studied receptors present electrochemical recognition properties towards HSO_4^- and I^- anions.

The financial support of this research, received from CNMP 71-067 REMORESE project, is gratefully acknowledged.

ESD-P-03

Modified electrode based on Fe-exchanged zeolite incorporated in carbon paste for hydrogen peroxide determination

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Determination of hydrogen peroxide is of great importance for modern medicine, environmental control and various branches of industry. The aim of this work was to explore the possibility of using a Fe-exchanged zeolitic volcanic tuff from Cepari (Bistrita-Nasaud County, Romania) containing 65-68% clinoptilolite, for the preparation of an amperometric sensor for H_2O_2 detection. Thus, the electrochemical reduction of H_2O_2 was investigated using an electrode based on Fe-exchanged Romanian natural zeolite, incorporated in carbon paste conductive matrix (Fe/CV-CPE). The mineralogy and properties of the zeolitic tuff were also determined using chemical analysis, optical microscopy, SEM, X-ray diffraction and BET analysis. The electrochemical behavior of Fe/CV-CPE has been characterized by using cyclic voltammetry and the electrocatalytic activity toward H_2O_2 reduction with chronoamperometry.

ESD-P-04

Simultaneous potentiometric determination of cationic and ethoxylated nonionic surfactants by use of a surfactant sensor

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A sensitive potentiometric surfactant sensor based on 1,3-didecyl-2-methylimidazolium-tetraphenylborate as a sensing ion-pair element served as an end-point detector in ion-pair surfactant potentiometric titrations using sodium tetraphenylborate as titrant. A few mixtures containing a cationic and ethoxylated nonionic surfactant were titrated potentiometrically. Barium ion forms pseudocationic complex with ethoxylated nonionic surfactant that can be titrated simultaneously with cationic surfactant using the same anionic titrant. Due to differences in hydrophobicity of both, nonionic and cationic surfactant investigated, ion associates formed during the titration revealed different stability constants resulting in two, more or less pronounced, analytically usable inflexions in the titration curve. The sensor showed satisfactory analytical performances within a pH range of two through eleven and was tested on several formulated powdered and liquid detergent products of various composition complexity too.

ESD-P-05

High-stable sensor for hydrogen peroxide detection based on mixed nickel-iron hexacyanoferrate electrocatalyst.

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Monitoring of hydrogen peroxide is of great importance for modern medicine, environmental control, and various branches of industry. The present work is the first that proposes a method of synthesis of new sensor materials based on Prussian Blue, stabilized with other transition metal hexacyanoferrates. The developed electrochemical sensor has high analytical characteristics: the sensitivity of analysis is 0,12 A/M·cm^2, low detection limit is $5\cdot10^{-8}$ M, the response is linear in the range from $5\cdot10^{-8}$ M to $1\cdot10^{-4}$ M. In spite of the fact that stabilized sensor demonstrates three times lower sensitivity, the same signal to noise ratio makes it possible to keep intact the linear range.

ESD-P-06

Electrochemical study of conductive polymer based on azulene and 3-thiophene acetic acid

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The obtaining of conducting polymers containing carboxyl-functional group is key point in the immobilization of biological compounds such as proteins, enzymes, antibodies in the polymeric matrix by stable covalent linkages, in order to fabricate biosensors[1-3]. Organic conducting coatings based on azulene and 3-thiophene acetic acid have been prepared by cyclic voltammetry (CV) onto a Pt substrate. The copolymer films were obtained by cycling the potential between -0.6 and 1.8V, using three different supporting electrolytes as tetrabutylamonium hexafluorophosphate ($TBAPF_6$), tetrabutylamonium tetrafluoroborate ($TBABF_4$) and tetrabutylamonium perchlorate (TBAP) in acetonitrile. The electroactive coatings based on polyazulene and poly(3-thiophene acetic acid) exhibited a good p-doping behaviour. The obtained electrochemical sensors shown a liniar resonse to hydrogen peroxide over the range of concentrations from 20 to 200 nM with a sensititity of 0.2 μA/nM. The detection limit was lower than 20 nM.

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ESD-P-07

The reduction of nitroaromatic compaunds on the platinum electrode

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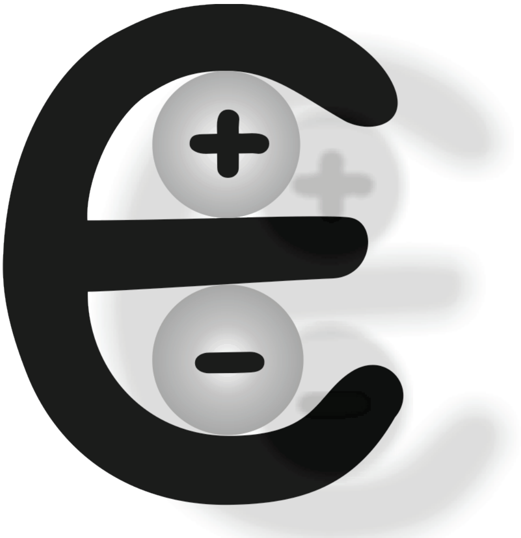
The reduction of 2,4,6-trinitrotoluene (TNT),as an example of nitroaromatic compounds with three nitro groups, was investigated by cyclic voltammetry on a platinum electrode in aqueous sodium chloride solutions with acetonitrile. The obtained cyclic voltammograms showed three well-pronounced reduction peaks in the potential range of –0.43 to –0.8 V (vs. Ag/AgCl reference electrode). The potentials of the peaks were dependant on the potential scan rate as well as on the TNT concentration, indicating the irreversibility of the reduction process. A calibration curve as a linear dependence of the first peak current on the TNT concentration was obtained in the range 4.4 – 638.4 μM L^{-1}.The platinum electrode exhibited an electrochemically stabile behavior for the TNT reduction process. Hence, a Pt electrode could be a suitable material for TNT sensing.

ETM

Experimental and Theoretical Methods in Electrochemistry



ORAL PRESENTATIONS

Šarganska osmica (Šargan's eight)

Šargan is the longest and the most beautiful of the reconstructed narrow-gauge railways that once crossed Europe, and it is typical for Serbia where all possible types of locomotives can be seen. What is it that makes the Šargan Eight so special? The railway was named "eight" due to an unusual figure-eight loop by which the 300 metre altitude between the Mokra Gora Valley and the Šargan, a span of rail 3.5 kilometers long, was connected.

Planning engineers solved the problem in a unique, as well as the only possible way, – an unusual railway loop under the Jatara in a figure 8 form. The "eight" section is 13.5 kilometres long and includes 22 tunnels, ten bridges and viaducts that are alltogether one third of the total railway length. The Jatare Station on this line is probably the only one in the world where nobody has bought a ticket or disembarked from the train in the last quarter century, although the train regularly stopped there. It was almost impossible for any passenger to guess where the "Eight" arrived from and where it was bound. Director Emir Kusturica chose this excellent setting to shoot his movie "Life is a Miracle". He brought a large film crew on location to Mokra Gora, and in addition to the reconstructed railway, he built the Golubići station, which is so skillfully patinated that it appears a century old to the untrained eye. In the same place, he built himself a cottage, and later somebody else built another house, then came the fifth, the twenty fifth, and today there's an entire town there, Drvengrad, or Timber Town, with apartments, church, gallery, national restaurant, cinema, swimming pool, library... all made of wood. The town and the railway station under Šargan are at the disposal of the residents of Mokra Gora..

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ETM-O-01

Investigation of oxygen reduction reaction on Pt by using electrochemical quartz crystal nanobalance and numerical simulation

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The understanding of oxygen reduction reaction (ORR) on platinum surface is a crucial point for the development of fuel cells. Albeit many efforts have been done to discover the reaction schema, no final agreement has been reached A new method has been developed combining mathematical simulations and electrochemical quartz crystal nanobalance measurements to study and explain the surface mass change at different potentials and currents. A widely accepted reaction scheme (Damjanovic et al.) was analyzed by using phase plane analysis such as Poincaré-Bendixson theory. It was shown that bistability may occur in this system at certain parameter values. EQCN with combination of chronopotentiometry was applied detecting the surface mass change with the variation of current and potential, respectively. Different time dependent solutions were simulated and compared with the measured data. A good qualitative agreement was found in the middle current region, but in the low current and in the high current regions the reaction scheme should be modified.

ETM-O-02

Detection and Study of Intermediates and Products of Electrode Reactions at Rotating Ring-Disk Electrodes by Using Dynamic Potential Control

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One of the most convenient and widely used methods of determining the reaction pathway is an electrochemical assay of the reaction products using a rotating ring-disk electrode (RRDE). Despite many advantages, there are some drawbacks and practical inconveniences concerning the application of the method, e.g. the collection efficiency of other devices (array electrodes) is higher, which gives microelectrode systems an advantage in detecting small amounts of generator electrode products. However, by applying appropriate potential programs the sensitivity of the RRDE system can be increased. The aim of the present work was the development and testing of a computer-controlled electrochemical measuring system which allows the application of independent potential programs to the disk and to the ring electrodes. The main components of the system are a Pine AFRDE5 bi-potentiostat and National Instruments data acquisition cards, but the capabilities of the system have been checked by using other potentiostats, *e.g*. Zahner XPots and the AFKEL 409/1 model as well.

ETM-O-03

Non-linear frequency response analysis of the kinetics of electrochemical reactions: a case study – ferrocyanide oxidation kinetics

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In general, electrochemical (EC) systems are non-linear, which means they respond non-linearly to a frequency-dependent periodic input perturbation of high amplitude imposed around a steady-state. In addition, the kinetics of EC reactions are quite complex and different rivalling model presentations can be formulated for certain EC reaction. While standard electrochemical methods (steady-state and electrochemical impedance spectroscopy) showed low sensitivity towards the model discrimination, non-linear frequency response analysis (NLFRA) of EC kinetics can appear advantageous for this purpose. In this work, NLFRA is applied in experimental and theoretical study of ferrocyanide oxidation as a model EC reaction.

ETM-O-04

Frequency response of the electrochemical interface close to dynamic instabilities: Experimental investigation of the oscillatory electrodissolution of copper in trifluoroacetic acid

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The frequency response of neural membranes is known to determine the communication properties of neural networks via band-pass (resonance) or high-pass (integration) filtering of incoming electric signals. In the present work it is shown experimentally that the electrochemical interface is also capable of acting as a band-pass filter, as far as the steady state is a stable focus, and thus mimic neural resonators. In order to realize electrochemical resonance, the electrodissolution of copper in trifluoroacetic acid is explored close to a Hopf bifurcation where the steady state is a stable focus. Electrochemical impedance spectroscopy indicates that the impedance of the system exhibits a characteristic minimum at a specific frequency where the oscillatory current attains maximum amplitude. The existence of resonance is also supported by perturbation experiments of variable frequency in the time domain (impedance amplitude method, ZAP). It is concluded that the electrochemical interface can act as a resonator and thus mimic a primitive information processing ability of neural cells.

ETM-O-05

Comparison of CV scan rates to time constants obtained by EIS in kinetic studies

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Electrochemical kinetic studies are usually done by cyclic voltammetry or electrochemical impedance measurements. However, electrochemists do not tend to mix the two methods leading to fundamental problems when scientists want to compare the results obtained by the two methods.

The problem can be eliminated easily by expressing potential normalized by the thermal voltage (RT/F) – this kind of representation is rather rarely used and sometimes referred to as normalized electrode potential. In this representation sweep rates are expressed in terms of 1/s which permits a direct comparison to time constants. To demonstrate this very simple idea we developed a new CV simulation method based on the algorithms of digital filter design. The correspondence of sweep rates and EIS time constants will be shown for a few basic kinetic models.

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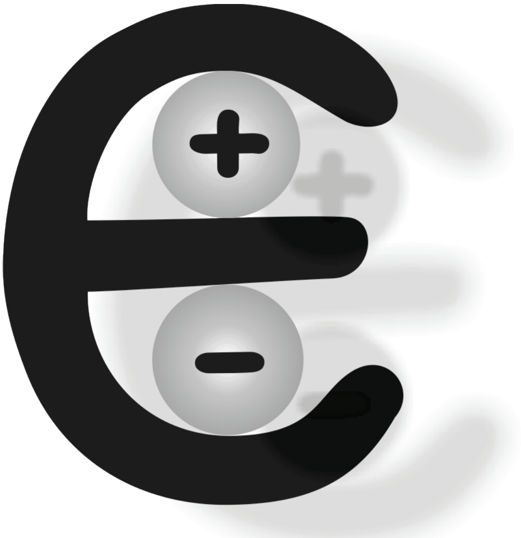
FSP

Electrochemistry of Functional Structures and Materials



POSTER PRESENTATIONS

National park Djerdap

The National Park Djerdap is situated in the north – east of Serbia, along the international border with Romania. The Park stretches along the right bank of Danube, for about 100 km, from Golubac to Karatas near Kladovo, covering a narrow strip of forested hills, which is about 2 – 8 km wide, and ranges 50 – 800 meters in altitude. The National Park Djerdap is one of the most beautiful national parks in Europe, with the oldest geological history. It is also a place where the Danube is its deepest (90 m) and the narrowest (150 m).

Many different civilisations have been present in the area of Djerdap, leaving permanent imprints behind them. As early as Neolithic, about 8000 years ago, on the banks of Danube thrived an impresive culture of prehistoric man, which lasted for a couple of centuries – situated at the site of Lepenski Vir. In Roman times, the area of Djerdap was the bordering area. The outer border was Danube, so that numerous Roman fortifications, settlments and castles were built on the right bank of the river, the remains of which are stil being discovered and researched.

FSP-P-01

Magnetron sputtering as a feasible technique for palladium deposition and its applications for PEM Fuel Cell Systems

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The performance of a membrane device employing thin palladium-based films for hydrogen purification, as fuel for PEM Fuel Cells, is reported in many papers. This technique allows deposition of thin compact film upon a selected substrate material and ensures simplicity of the catalyst or film preparation as well as improved stability, durability and utilization. This work presents a research on the influence of sputtering parameters (dc power, argon pressure), film thickness/metal loading and substrate material on the surface structure and morphology of palladium thin films. The properties of the sputtered films were studied using X-ray diffraction (XRD). It was found that low sputtering power and sputtering pressure lead to deposition of mechanically stable crystalline Pt films. Sputtering parameters was varied between: 0.3÷10 mTorr argon pressure and 100÷1000 W dc power. The sputtered films exhibit a [111] preferred orientation.

FSP-P-02

AC Impedance tracking of glassy carbon activation

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Carbon materials, due to their physical and chemical properties, have found wide application in different electrochemical systems. They are often used as substrates for supercapacitors and different types of electrocatalysts. Upon activation, their electrochemical properties are improved. Glassy carbon can be successfully used as a model for studying the process of carbon activation.

In this work, the activation of glassy carbon by electrochemical oxidation in sulfuric acid was investigated using cyclic voltammetry, electrochemical impedance spectroscopy and atomic force microscopy. Glassy carbon was oxidized during the same time at 5 different potentials. Cyclic voltammetry shows that the higher the potential the larger the increase in double layer capacitance is. Impedance measurements confirmed significant changes in capacitive response of activated glassy carbon in comparison to unoxidized state. AFM examination of treated GC surfaces revealed morphological changes and increase in roughness upon oxidation. If combined, the results of these studies show that the activation of glassy carbon proceeds through three stages: oxidation of active site, growing of graphite oxide layer and mechanical destruction of the surface.

FSP-P-03

TEM analysis of electrodepositied Mo-Ni-O powders

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The Mo-Ni-O powders were electrodeposited from ammonium sulfate containing electrolytes with different Mo/Ni ion concentration ratios. The phase composition of these powders was investigated using TEM, EDS and XRD analysis. The TEM analysis showed that two types of particles were present in the powders: amorphous and crystalline. For crystalline particles it was found that two phases, MoO_3 and $MoNi_4$ prevail in all powders, while the NiO phase was detected in the powder electrodeposited at Mo/Ni = 0.3/1. These findings are in good agreement with our previous results where MoO_3, $MoNi_4$ and $NiMoO_4$ phases were detected in the recrystallized Mo-Ni-O powders. In this work we discovered that the $NiMoO_4$ phase was formed by solid state reaction between NiO and MoO_3 at elevated temperature.

FSP-P-04

Influence of boron incorporation on electrochemical properties of glassy carbon

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The electrochemical properties of glassy carbon (GC) modified by boron were studied by cyclic voltammetry. Boron was introduced into glassy carbon using two methods: by chemical modification achieved by mixing phenol-formaldehyde resin with boric acid and by the irradiation of glassy carbon and its precursor polymer with two types of boron ions, B^{1+} and B^{3+}. Applied fluencies were in the range of 5×10^{15} to 5×10^{16} ions cm $^{-2}$. By chemical modification, a polymer with the uniform distribution of boron in the bulk was obtained while the irradiation method produces samples with boron located in limited narrow region under the surface. Chemically modified glassy carbon exerts higher electrochemical activity for hydrogen evolution compared to pristine glassy carbon. It was noticed that electrochemical activity of boron irradiated samples was influenced by the boron ion charge and type of target.

FSP-P-05

Optical properties of templated CdSe electrodeposits on nanoporous TiO_2

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The advances that have been reported in the last decade on the fabrication of highly ordered TiO_2 nanotube arrays by Ti metal anodization have given rise to a number of novel applications, such as templated electrodeposition. In the field of photoelectrochemistry, the superior charge transfer properties of the anodic TiO_2 arrays establish them as promising alternatives to mesoporous, nanocrystalline TiO_2 structures used in DSSC, while low-bandgap inorganic sensitizers, such as CdSe Q-dots, advantageously fit to substitute organic dyes.
In this work, photoactive CdSe was pulse-plated on a TiO_2 short-nanotube array template, and the electrode was tested in an illuminated cell configuration by voltammetry and photovoltage decay measurements. The enhanced open circuit potential observed with the CdSe/TiO_2 compared to CdSe/Ti electrode could be partly attributed to higher minority charge carrier (hole) lifetime. Both systems were found to follow a linear recombination rate *vs*. hole concentration relation, which differentiates them from the non-linear DSSC system. Annealing at temperatures of 200 to 500 °C improved the electrical characteristics of the cell, but had little effect on the minority carrier lifetime.

FSP-P-06

Polyaniline nanofibers prepared by electrochemical polymerization of aniline on niobium

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In this work a template-free electrochemical method was used to obtain nanostructured polyaniline (Pani) films on niobium. It is believed that the substrate plays a special role in the formation and growth of polyaniline nanofibers. It is expected that during the electrochemical oxidation of niobium „nano-seeds“ of niobium oxide are formed which are the precursor for the formation of Pani nanofibers. The electrochemical polymerization has been carried out in 0.5 mol L^{-1} H_2SO_4 solution under different aniline to acid ratios. The morphology of the Pani films obtained by potential cycling on niobium shows a highly branched structure formed by polyaniline nanofibers, having a mean diameter of 70 nm and about one order magnitude higher length. The electroactive properties of the Pani films were investigated by cyclic voltammetry and electrochemical impedance spectroscopy (EIS) in 0.5 M H_2SO_4 solution. The complex plane plots point out to a typical behavior for conducting polyaniline films, characterized by a pure resistive response at high frequencies and a pure capacitive response at low frequencies.

FSP-P-07

Photovoltaics of sol-gel processed titanium oxide coating

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Titanium oxide is applied as a photocatalyst in organic synthesis and for waste water treatment and outdoor air purification. In this work, photoelectrochemical (PEC) activity of titanium oxide coating on titanium substrate, prepared by the sol–gel procedure from the oxide sol obtained by forced hydrolysis of chloride was investigated. Electrochemical and PEC parameters at photoelectrode change intensively upon UV illumination when organic compounds (alcohols, aldehydes, acids, *etc.*) are present in the electrolyte (H_2SO_4), which proves coating activity for their oxidation. Electrochemical impedance (EIS) characteristics of the coating are found to be sensitive to the photoelectrode potential and UV light. EIS characteristics are discussed on the basis of the values of parameters of equivalent electrical circuit used to fit experimental impedance data.

FSP-P-08

Impedance characterization of LSCF/YDC couple obtained by different technologies

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This work presents conductivity studies of the cathode/electrolyte couple LSCF48/YDC15, which is a buidling block of a new innovative and competitive design of a high temperature fuel cell, operating in the range 600-700°C. It is based on the idea for a junction between a PCFC anode/electrolyte and a SOFC cathode/electrolyte through a mixed H^+ and O^{2-} conducting porous ceramic membrane. Thus, in this concept, hydrogen, oxygen and water are located in three independent chambers, which allows for the avoidance of the gases dilution with water. The applicability of different technologies for electrodes deposition as tape casting, screen printing and plasma spraying is analyzed by electrochemical impedance spectroscopy measurements of electrolyte supported symmetrical half cells $La_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\alpha}/Ce_{0,85}Y_{0,15}O_{2-\alpha}/La_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\alpha}$. The couple LSF48/YDC15 obtained by the three technologies has appropriate microstructure and high conductivity, comparable with data from the literature. The developed materials were applied in the fabrication of the first model cells of the new design.

FSP-P-09

The effect of pozzolanic admixtures on the corrosion of limestone cement mortars stored in combined chloride and sulfate environment at low temperatures

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In this work the effect of natural pozzolana, fly ash, slag and metakaolin on the corrosion of limestone cement mortars is studied. A limestone cement, containing 15% w/w limestone, was used. Mortar specimens were prepared by repalacing a part of cement with the above pozzolanic materials and steel bars were axially embedded into them. After 40 days of curing, the specimens were partially immersed in chloride (Cl^-) and chloride-sulfate (Cl^-/SO_4^{2-}) solution at 5 °C for a period of 10 months. Corrosion potential, corossion rate (Linear Polarization method) and mass loss of the rebars were tested. Pozzolanic materials may inhibit corrosion at the early stages of curing. Fly ash improves corrosion resistance in the Cl^-/SO_4^{2-} solution. Natural pozzolana, slag and metakaolin have a positive effect on corrosion resistance in the Cl^- solution. The use of natural pozzolana, fly ash and metakaolin leads to lower mass loss in the case of the Cl^-/SO_4^{2-} solution. The mass loss of steel rebars was higher in the Cl^-/SO_4^{2-} solution, showing that the presence of SO_4^{2-} favours the corrosion due to chlorides.

FSP-P-10

Characterization of carbon fibrous materials obtained from tree wastes

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Carbon fibres can be obtained in rather wide variety of structures, compositions and properties, depending on the nature of the organic precursor and conditions of the process applied in their preparation. In order to get a high surface area, physical or/and chemical activation processes of material have usually been employed. A challenge in the field of carbon adsorbents is to produce very specific materials with a given pore size distribution from low cost precursors.

In this study we used new type of a precursor for active carbon fibres material –achenes from the Platanus orientalis seeds. We examined the influence of different chemical activating agents on the porous and electrochemical properties of carbon material support. The properties of these fibers were compared with the properties of polysulfone hollow fibers treated on the similar way.

These investigations show that the waste such as fibrous seeds is very promising raw material for active carbon fibers production.

FSP-P-11

Electrochemical Polymerization of Aniline at Moderately High Temperatures

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The aim of this study is to investigate the effect of moderately high temperatures on the electrochemical synthesis and properties of polyaniline (Pani) films. The electrochemical deposition of Pani has been carried out on platinum at three different temperatures (25, 40 and 60°C). Cyclic voltammetry and electrochemical impedance spectroscopy has been applied to study the redox reactions of Pani films deposited on platinum and to evaluate the films pseudocapacitances. The results show that increasing the synthesis temperature leads to an increase of the polyaniline films thickness from 0.4 to 0.9 μm and, respectively, 1.1μm, associated with an increase of the films capacitances from $3x10^{-2}$ F cm^{-2} to $7x10^{-2}$ F cm^{-2} and $10x10^{-2}$ F cm^{-2}. The impedance measurements showed that only Pani-25 and Pani-40 exist in the conductive state over a large potential window, while Pani-60 has an intermediate behavior at low and high electrode potentials.

FSP-P-12

Electrochemical impedance spectroscopy studies with calixarene modified screen printed electrodes

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The screen-printed electrodes (SPE) have been developed for innovative applications of analytical chemistry and they demonstrated a great interest, especially in the development of rapid analytical analysis and biosensor’s fabrication. Moreover, regarding their simplicity, they are simply mass-produced at low costs, having at the same time superior characteristics in comparison with the classical electrodes materials. Two new calixarenes: p-tertbuthylcalix[8]arene ($C_{88}H_{112}O_8$, M = 1297.826) known as C8 and p-tertbuthylcalix[6]arene ($C_{66}H_{84}O_4$, M= 972) known as C6[1] were synthesized and fully spectral and electrochemical characterized. The immobilization of the calixarene at the surface of the SPE was made in two ways: directly, using drops of calixarenes C6 and C8 solutions in $CHCl_3$ deposited directly to the surface of the carbon electrode and by entrapment of calixarene in a polymeric film (polyethylenimine PEI). The advantages of using this linear polymer are a good mechanical stability of the modified electrode, improved film permeability, no need for a supplementary step for electropolimeryzation and water insolubility. EIS (electrochemical impedance spectroscopy) method was applied to analyze the properties of new modified SPE. Parametric equations for Nyquist diagrams applicable in extreme domain of frequencies were used[2, 3]. The equations lead to an analysis of the curves around the frequency of 0.2 Hz. The terms expressing diffusion and charge transfer respectively, as well as the pseudo-admittances involved in computation may be calculated for the proposed equivalent circuits.

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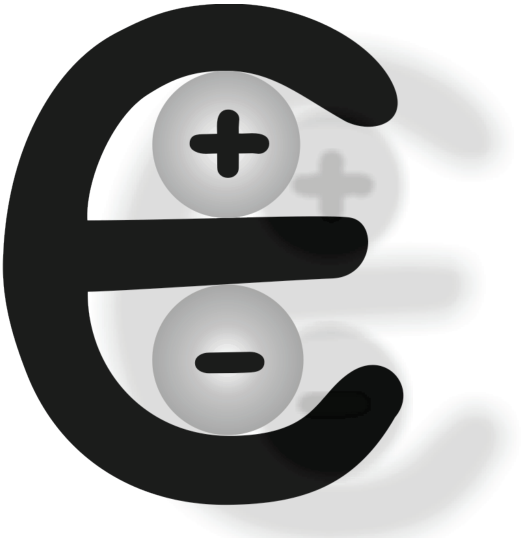
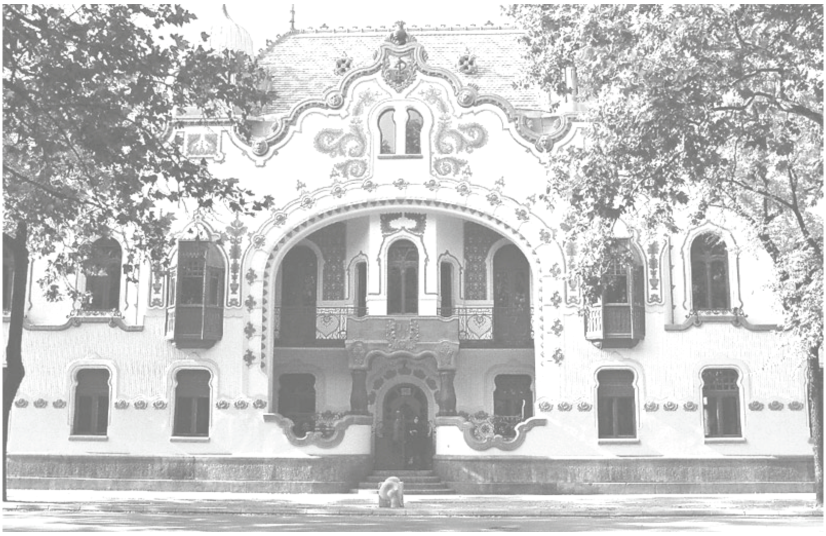
NME

Nanoscale and Molecular Electrochemistry



ORAL PRESENTATIONS


House of Ferenc Rajhl

Subotica

he golden period of Subotica began at the end of the XIX century till the First World War. That was the time when it grew into a modern mideuropean town and when the most significant buildings were built.

The greatest ornament and pride of Subotica is graceful and grandiose City House, with 75 m high tower. It was built in 1910 while the interior decoration took 2 more years to finish. The architects from Budapest – Komor and Jakab – were the creators of this beautiful building. The interior is decorated with expensive marble and ceramics with Transylvanian motives.

They also left their trace in Palic lake. According to the project of these architects, the synagogue in Subotica was also built in 1902. Today, the Synagogue is under the protection of the State. Besides being the architectural treasure of the city, it is also a place where concerts of classical music and plays are held. There is another masterpiece of architecture near the railroad station– a family house of an architect Ferenc Rajhl, known as the palace of Rajhl. It was built in 1904 and was inspired by folk motives of Erdelj.

NME-O-01

Synthesis of $LiFePO_4$ nanoparticles during ultrasonic spray pyrolysis USP

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Nanosized $LiFePO_4$ is a promising approach for a new cathode material. The key benefits for an application of nanosized $LiFePO_4$ are the low costs, the thermal stability and it is non toxic. Now there is a demand for a manufacturing process which produced electrochemically active $LiFePO_4$ at a low cost. The existence of two oxidation degrees of iron in nature (Fe^{2+} and Fe^{2+}) is the major difficulty related to the synthesis of these nanoparticles. To adjust an inert atmosphere we used nitrogen. The reaction temperature in the furnace was 800°C. Previous thermodynamic analysis was performed using FactSage Software in order to predict an existence of different compounds at 800°C. New precursor system was tested in order to investigate a new proposed mechanism for synthesis. The influence of different reaction parameter on particle size was investigated. SEM, EDS, TEM methods were used for the analysis of morphology of prepared nanoparticles. Figure 1 shows TEM-analysis of the nanosized $LiFePO_4$ particles via USP method.

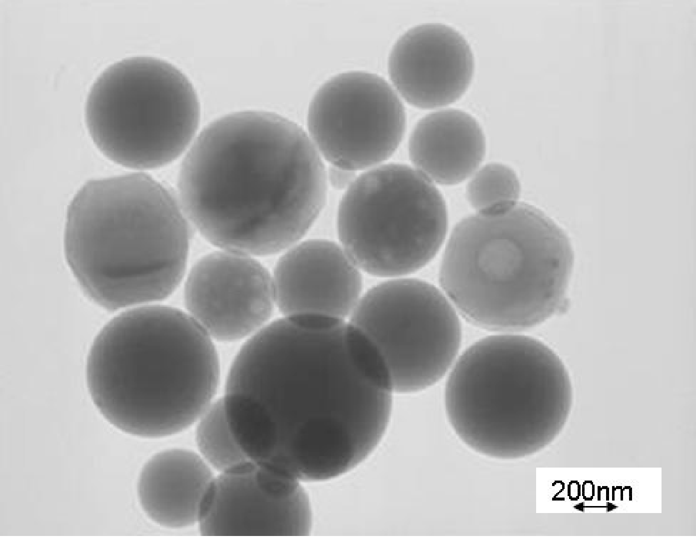

Fig. 1: SEM analysis of nanosized $LiFePO_4$ prepared by USP method

POSTER PRESENTATIONS

NME-P-01

UPD of Cd onto Ag(111) in the presence of sulfate, chloride and iodide anions

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The process of Cd UPD onto Ag(111) has been investigated in the presence of sulfate, chloride and iodide anions by cyclic voltammetry and potentiostatic pulse techniques. It was shown that in all cases Cd UPD commences on the Ag(111) surface covered with adsorbed anions which did not desorb during the Cd UPD but were replaced by Cd ad-atoms and remained adsorbed on top of a Cd layer and/or in between Cd ad-atoms. In the cases of sulfate and chloride anions adsorbed structures which had to be replaced by Cd ad-atoms were randomly distributed, while in the case of iodide anions ordered $(\sqrt{3}x\sqrt{3})R30^{\circ}$ structure of iodide ad-atoms had to be replaced with the same structure of Cd. In all cases Cd UPD started with formation of $(\sqrt{3}x\sqrt{3})R30^{\circ}$ structure, which has been transformed into close packed Cd monolayer. By the PeakFit analysis corresponding voltammograms were transformed into several peaks and all obtained peaks were fitted with the Frumkin adsorption isotherm. The values of the interaction parameter $f \leq -4$ confirmed phase transition process for the formation of both Cd structures.

NME-P-02

Application of TiO_2 nanoparticles in hydroquinone derivative modified carbon paste electrode for determination of epinephrine

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Nanotechnology is expected to be the basis of many of the main technological innovations of the 21st century. Research and development in this field is growing rapidly throughout the world. A carbon paste electrode, modified with 2, 2′-[1,7-hepthandiyl-bis(nitriloethylidyne)]-bis-hydroquinone and TiO_2 nanoparticles, was derived and used for determination of epinephrine. It has been found that oxidation of epinephrine at the surface of such electrode occurs at potentials less positive than at an unmodified carbon paste electrode. The magnitude of the peak current, for modified TiO_2-nanoparticles CPE (MTNCPE), increased sharply in the presence of epinephrine and was proportional to its concentration.

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NME-P-03

Platinum nanoparticles on carbonized PANI nanotubes as electrocatalyst for the oxygen reduction reaction

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The search for abundant and efficient electrocatalytic materials with reduced Pt-content for cathodes in polymer electrolyte membrane fuel cells is currently an active area of research. Efforts are under way to improve the heterogeneous electron-transfer kinetics and the utilization of Pt, by modifying either the carbon support or the platinum deposition techniques, in order to increase the effective catalytic area. In this work carbonized PANI nanotubes containing about 8 wt.% of nitrogen and commercial carbon black (Vulcan XC-72) were compared as catalyst for oxygen reduction reaction. Pt/Pani and Pt/XC-72 catalysts, with different Pt loading, were prepared by a modified polyol synthesis method in an ethylene glycol (EG) solution using H_2PtCl_6 in EG as precursor. X-ray diffraction confirmed the presence of Pt and TGA was used to determine quantitatively the Pt loading. The voltammetry on rotation disc electrode (RDE) was performed in 0.1M NaOH and 0,1M $HClO_4$ solution. Kinetic parameters such as the electron transfer rate and the number of electrons pro reduced oxygen molecule were determined by Koutecky–Levich analysis of the RDE results.

NME-P-04

Morphology of Nano-Scaled Silver Powders Produced by Pulsed Electrolysis

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This study is concerned with formation of nano-scaled silver powders by pulsed electrolysis. The morphology variation was observed depending on the changes of the applied pulsed current density and the duration of the current pulse.

The experiments were performed in nitrate electrolytes: 0.1 M $AgNO_3$ + 10 g dm^{-3} $NaNO_3$, 0.1 M $AgNO_3$ + 100 g dm^{-3} $NaNO_3$. The morphology of the silver powders was observed by means of Scanning Electron Microscopy (SEM), while the size of the particles was determined by means of Transmission Electron Microscopy (TEM).

According to the results, the duration of the cathodic pulse affects the size and uniformity of the silver grains. The smallest and the most uniform grains were produced by applying cathodic pulse with duration of 0.05 s. Nano-scaled silver powder can be produced in conditions far from equilibrium [1,2], i.e. at very high current densities (1-2 A cm^{-2}) [3]. At higher current densities (2 Acm^{-2}) were obtained the smallest silver particles with variety of morphological forms and better uniformity related to the corresponding ones at lower current density (1 A cm^{-2}). It can be summarized that the smallest silver nano particles with 20-60 nm were produced in 0.1 M $AgNO_3$ + 100 g dm^{-3} $NaNO_3$ by applying pulsed cathodic current density of 2 A cm^{-2} for 0.05 s.

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NME-P-05

Correlation of structural characteristics with tribological behavior of Ni and Ni-P / nano-TiO_2 composite coatings

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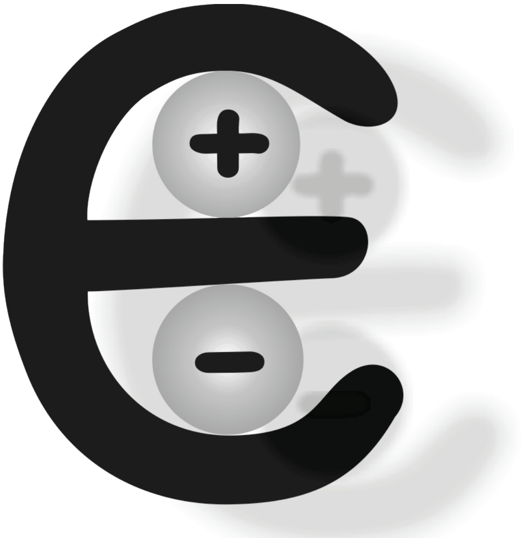
Nanocomposite coatings were obtained by electrochemical codeposition of TiO_2 nanoparticles (mean diameter 21 nm, Degussa P_{25}) with Ni and Ni-P, from an additive-free Watts type bath, under both DC and PC conditions. Pure Ni and Ni-P deposits were produced under the same experimental conditions for comparison. The surface morphology, the crystallographic orientation and the grain size of nickel matrix were investigated, along with the distribution and the percentage of the embedded nanoparticles in nickel based matrices. The aim of the study was to correlate the observed structural characteristics of the coatings with the resulting mechanical properties (microhardness and tribological behavior). The wear behavior of the coatings was investigated by using a Ball-on-Disc tribometer under dry uni-directional sliding conditions, and the results showed that the presence of the reinforcing TiO_2 nanoparticles increased the wear resistance of the composite coatings compared to the pure Ni and Ni-P ones. For the majority of the composites, the sliding wear took place by abrasive and adhesive mechanisms.

OEH

Organic Electrochemistry



POSTER PRESENTATIONS

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Alem Arap mosque

Novi Pazar

Novi Pazar ("New Bazaar") was rebuilt in 1460 by Turkish general Isa-beg Isaković. The Turkish name of the city was Yeni Bazaar. The town was built near Ras – the capital city of medieval Serbia, on the important way that led from Istanbul to Sarajevo and Dubrovnik. Such convenient position has led to its fast expansion, and because of that, in the XVII century, Novi Pazar has become one of the biggest cities on Balkan.

Novi Pazar suffered destruction in XVIII century in Austro-Hungarian war and in XIX century from Serbian rebels. With the relocation of merchant trade roads, the city eventually loses its importance, and therefore today counts only 100.000 habitants.

Novi Pazar has the typical characteristics and looks of an oriental city and the major part of habitants are Muslims. A small fortress from the oldest period of the city is situated in the centre. Well preserved is Amir Aga Han (han means inn) from XVIII century. There is Altum Alem and Alem Arap mosque located in the centre of the town and an old hamam (Turkish bath) right behind it, which is today unfortunately in a poor condition.

OEH-P-01

Electrochemical behaviour of some xanthine alkaloids on graphite based electrodes

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Caffeine (1,3,7-*trimethyl*-3,7-*dihydro*-1*H*-*purine*-2,6-*dione*), aminophylline (1,3-*dimethyl*-7H-*purine*-2,6-*dione* 1,2-*diamine*) and teophylline (1,3-*dimethyl*-7*H*-*purine*-2,6-*dione*) are xanthine alkaloids derivatives that are widely used in drugs industry to obtain many pharmaceutical formulations.

The electrochemical behaviour of the above mentioned compounds was investigated by cyclic voltammetry, on different electrode materials as: glassy carbon in native forms and electrochemically activated, carbon paste electrode unmodified or modified with 1, 4-benzoquinone. The preliminary results obtained with classic electrodes were extended on carbon based screen-printed electrodes, simple and modified with multi-wall carbon nanotubes or Cobalt-phtalocyanine.

The influence of some experimental parameters (pH, scan rate, concentration and electrolytic medium) on electrochemical behaviour of these alkaloids was also investigated. The electrochemical oxidation of these xanthine derivatives is an irreversible and diffusion controlled process, because there is a linear dependence between the peak potentials and the logarithm of scan rates and between the anodic peak current and the square root of scan rate.

OEH-P-02

Process for preparation of conducting polyaniline with low molecular weight used in fabrication of membrane anti-inflammatory

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In order to prepare conducting polyaniline composite and nanocomposite soluble in various organics solvents before and after doping, and we based on these experimentally resultants finding, the present invention relate to a new process for preparing conducting polyaniline with low molecular weight in non acid medium. The present study provide process for preparing polyaniline or another polymer conductors such as (polypirole, polythiophene) or substituted polyaniline (o-anisidine, o-methoxy-aniline, o-toluidine …….), wich comprises dissolving oxidizing agent (solid) slowly in mixture of catalyst and monomer (Mag-H, aniline) after 30 mn at ranging temperature (0ºC to 4ºC) and during 10 mn, after this time we added drop by drop 15 ml to 20 ml of water, the reaction mixture was stirred for 1h 30 mn at the optimal conditions. At the end of polymerization, we obtained the emeraldine salt/clay (PANI-ES/Mag-H). Whereas, the Mag-H it's separate by filtration because it's insoluble in the solvents in which the polymer is soluble. Eventually, the result it's black solution (polymer-solvent), after evaporation result a black powder it's (PANI-ES), washed several times with water and methanol, where dried at 60ºC for 48 h for characterization. The polyaniline base (PANI-EB) was obtained by deal treatment of polyaniline salt (PANI-ES) with a solution of dilute NaOH (0.5M). In a more specific aspect of the present study, the polymer is formed in non acid medium. Another embodiment, the polymer is formed by layered catalyst MMT (Mag-H).

Another embodiment the polymer is formed by oxidizing agent powder (solid) contained alkali metal salt. In another specific aspect, the polymer is formed by intervention of deferent's reactors and water in three steps;

a) between MMT and monomer
b) between mixture of (MMT-monomer) and oxidizing agent
c) between second mixture (MMT-monomer-oxidant) and water

OEH-P-03

Electrochemical and spectral studies on reactivity of selected 2-alkylidene-4-oxothiazolidines in ET reactions

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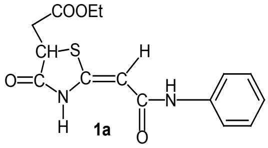
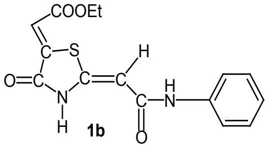
Two stereodefined 2-alkylidene-4-oxothiazolidines **1a** and **1b** possessing the same electron-withdrawing group, CONHPh, but differing in substitution at the C(5)-position of the thiazolidinone ring, were investigated by cyclic voltammetry in DMSO, coupled with UV-VIS and EPR spec-troelectro-chemistry, in presence and absence of added base (TBOH). The electrochemical and spectral studies, corroborated with PM3-semiempirical MO-calculations, led to better under-standing of the reaction sequence and reactivity of the intermediate species, generated in the electron transfer (ET) reactions, either *via* electrochemical reduction of **1b**, or electrochemical oxidation of **1a**.



1a



1b

OEH-P-04

Role of Molecular Weight in the Desorption Behavior of Atactic Poly(vinyl alcohol) (PVA)/Iodine Complex Films

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To precisely identify the effect of molecular weight in the desorption behavior of atactic poly(vinyl alcohol) (a-PVA)/iodine complex film, we prepared two PVAs with similar syndiotactic diad content of [illegible], degrees of saponification of 99.9%, and with different number-average degrees of polymerization (P_n)s of 1700 and 4000, respectively. The desorption behavior of iodine in the a-PVA/iodine complex films was achieved by measuring the weight loss of a-PVA/iodine complex film before and after annealing temperature of 120°C. Through a series of experiments, it was found that desorption of iodine in a-PVA/iodine complex film was decreased with increasing molecular weight of PVA. The amount of iodine desorption of a-PVA/iodine complex film having P_n of 4000 was limited to 3%, whereas that of a-PVA/iodine complex film with P_n of 1700, was almost 10% under same conditions.

WITHDRAWN

OEH-P-05

Electrochemical synthesis of the new substituted piperazines

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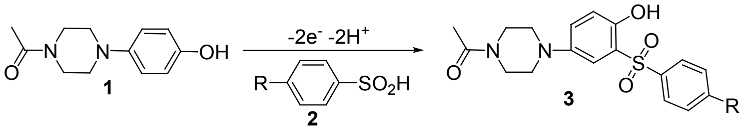
Piperazines are important pharmacores that can be found in biologically active compounds. On the other hand, diaryl sulfones are useful in the practice of medicinal chemistry. In this direction, we thought that synthesis of new organic compounds with both structures of piperazine and diaryl sulfone would be useful from the point of view of pharmaceutical properties. This idea prompted us to investigate the electrochemical oxidation of electrochemical oxidation of 1-(4-(4-hydroxyphenyl) piperazin-1-yl)ethanone (**1**) in the presence of arylsulfinic acids (**2a-c**) as nucleophiles in aqueous solutions. The results indicate that the electrochemically generated quinone-imine participate in Michael type addition reaction with arylsulfinic acids and via an *EC* mechanism convert to the corresponding new piperazine derivatives (**3a-c**). In this work, an efficient and one-pot electrochemical method f is reported.



OEH-P-06

Vitamin C evaluated with crown-ether modified carbon paste electrode

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Vitamin C is essential to a human healthy diet as well as being a highly effective antioxidant, protecting cells against damage by free radicals as reactive by-products of normal cell activity. L-ascorbic acid (AA), the active form of vitamin C, can be determined by using different analytical methods: chromatographic, spectrophotometric, titrimetric, enzymatic and electrochemical ones.

The aim of this work is to investigate the electrochemical oxidation of AA using an electrode based on newly synthesized ether 18-crown-6 derivative, incorporated in carbon paste conductive matrix (CE-CPE). The electrochemical behavior of CE-CPE has been characterized by using cyclic voltammetry (CV). The electrode electrocatalytic activity toward AA oxidation in synthetic samples was investigated, using both CV and amperometric measurements. The results are comparable with those obtained by using the reference method based on titration with 2,6-dichlorophenolindophenol**.**

OEH-P-07

Electrochemical study of a novel series of heterocyclic compounds of pyridine

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We report in this paper the electrochemical study of a novel series of heterocyclic compounds with nitrogen using a simple and efficient synthesis through N-alkylation of 4,4'-bipyridil and 1, 2-bis-(4-pyridil) ethane with reactive halides. The structures of the salts, precursors of fluorescent dyes, were characterized using IR, ^{1}H-NMR, MS and elemental analysis. The use of security documents incorporating fluorescent pigments with different verification and detection responses have been performed. The novel series of heterocyclic compounds tested were embedded during the paper manufacturing by different technologies and interesting results were obtained. The florescence effects depending if the pigments compounds are added in paste mass or in substrate treatment step and have been established the necessary quantities of those.

Acknowledgements: Financial support provided by the PNII no. 71-126/ 2007 is gratefully acknowledged.

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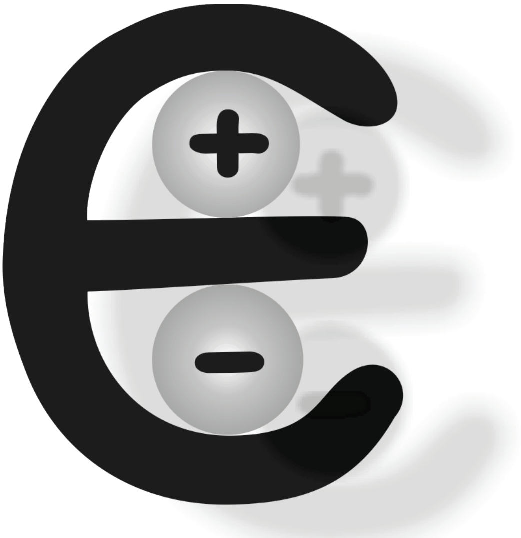
PEA

Physical Electrochemistry and Analytical Electrochemistry



ORAL PRESENTATIONS

Kruševac

Situated in the central part of Serbia, it was once a medieval Serbian capital city. As such, it was built in the period between 1371 and 1377. Duke Lazar was the head of the State. In the mere city, there is an archeological park – the remains of medieval Lazar`s town.

Not much remained of the old town of Krusevac (Kruševac). The most preserved is the church Lazarica and the main tower 18 m high. There is also the monument of duke Lazar, as well as National Museum, inside the complex. The symbol of the town of Krusevac represents the Monument of Kosovo heroes, built at the beginning of the last century. It is at the Square of Kosovo heroes.

The surrounding of Krusevac is rich in medieval monasteries: Naupare, Veluce (Veluće), saint Roman, the church of shroud of Mother of God in Djunis (Đunis). The most famous is a monastery Naupare, famous for its rosettes. It is 12 km from Kruševac.

PEA-O-01

Measurement of surface stress changes of solid electrodes – effect of film thickness and surface roughness

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The changes of the surface stress for a thin metal film on one side of an insulator (e.g. glass) strip (or a metal plate, one side of which is coated with an insulator layer) in contact with an electrolyte solution can be estimated from the changes of the radius of curvature of the strip. If the potential of the electrode changes, electrochemical processes resulting in the change of the surface stress can take place exclusively on the metal side of the sample. The change in the surface stress induces a bending moment and the strip bends. Thus far, to our knowledge, no systematic experimental study has been performed to examine the relationship between the changes in the radius of curvature of the plate (change of the surface stress) during electrochemical polarization and the thickness of the metal layer. In the present work, the results of such an attempt are reported. The effect of surface roughness of the metal layer on the deflection is also discussed.

PEA-O-02

The activity of lithium in bipolar electrode materials during polarization

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By the use of a bipolar cell mass transfer of lithium in metals was investigated in view of diffusion coefficient, amount of lighium transferred in the sample metal depending on the polarization potential. The effect of alloy formation between the matrix metal and lithium was investigated.

PEA-O-03

Investigation of the electrochemical reduction of chlorate and perchlorate ions on rhodium

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The presence of perchlorate and chlorate ions in the environment may represent a potential health hazard for man and animals. Their low-level toxicity is controversial. On the basis of the experimental results a new mechanism for the electrocatalytic reduction of chlorate and perchlorate ions has been proposed. With the use of the kinetic model an expression has been derived for the impedance of the electrode, which adequately fits the experimental data.

PEA-O-04

SKP-SECM: System Development and First Applications

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The addition of Cu and Mg as alloying elements in various aluminium alloys increases their strength due to the formation of highly dispersed Cu-rich intermetallic compounds (IMCs). In order to simultaneously visualize the local work function of Al-based alloys together with their ability to catalytically reduce molecular oxygen we developed an integrated Scanning Kelvin Probe/Scanning Electrochemical Microscopy (SKP-SECM) system. It combines all features necessary for performing SKP, AC-SECM and RC-SECM experiments using the very same electrode as tip. During SKP measurements topographic information of the sample surface is simultaneously obtained and stored in memory. Thus, the topographic insformation can be used later for constant-distance SECM experiments. The development of the SKP-SECM system and its application for the investigation of an Al matrix in which Al_2Cu and Al_2CuMg bulk phases are artificially introduced will be presented and discussed.

PEA-O-05

Determination of acids in fermented foods by HPLC with amperometric detection based on the voltammetric reduction of quinone

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Some organic acids provide a good taste and aroma to foods, so the acid determination is essential for the process and quality assessment of foods. We developed a new method for determining acids by means of the voltammetric reduction of quinone. Based on this method, an HPLC system with electrochemical detection (HPLC-ECD) was fabricated for determining several carboxylic acids, and the method was assessed as an effective means of determining acids in wine and yogurt. The HPLC-ECD was performed using an ion-exclusion column and a glassy carbon working electrode. The method was actually examined for monitoring some carboxyrlic acids during the wine brewing for grape juice with wine yeast, since the acid content can be determined by measuring the current signal of the reduction peak of quinone caused by the eluted acids. The method was also examined for following lactic acid content during the production of yogurt. The method was found to be practically useful for acid assay of various kinds of foods.

PEA-O-06

Scanning electrochemical microscopy as a tool for localized visualization of Cl_2 evolution at dimensionally stable anodes

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Imaging of the electrochemical process at a metal-oxide/electrolyte interface is important for the understanding of Cl_2 evolution on dimensionally stable anodes (DSA).
In order to visualize electrocatalytical activity of Cl_2 evolution on DSA the sample-generation/tip-collection mode of scanning electrochemical microscopy (SECM) as well as the redox-competition mode of SECM were employed. The local distribution of the electrocatalytic activity for Cl^--oxidation of RuO_2-based DSA could be successfully visualized reveiling the local properties of the catalytic layers.
These elucidation of local electrocatalytic properties of surfaces with respect to Cl_2 oxidation allows for the optimization of catalytic properties and the comparison of different materials which may be potentially suitable as catalyst.

Acknowledgement: The authors are grateful to the BMBF (033R018E) for financial support.

PEA-O-07

Electrogenerated chemiluminescence in an electrodeposited redox polymer

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Electrogenerated chemiluminescence (ECL) of $Ru(bpy)_3^{2+}$ is applied in clinical diagnostics, particularly in detecting affinity reactions of immunoreagents and nucleic acids. Derivatives of $Ru(bpy)_3^{2+}$ have been immobilized in polymer and silica sol-gels films, attached to nanoparticles and covalently bound to substrates.
Here we report the electrodeposition of an ECL-exhibiting $Ru^{2+/3+}$ complex-containing hydrogel under physiological conditions. We used for our studies the [poly(4-vinyl-pyridine)-Ru(2,2'-bipyridine)$_2$Cl-ethylamine]. In the presence of tri-n-propylamine (TPrA), the wave of electrocatalytic oxidation of TPrA appeared and light was now emitted simultaneously with the electrooxidation-indicating generation of excited, light-emitting Ru(II)* in the film under physiological conditions. Chloride ligand exchange by protein histidine, lysine or arginine residues is likely to allow the co-electrodeposition of biologically active proteins, such as NAD dehydrogenases, which would produce NADH, a known ECL co-reactant. ECL detection of glucose and other substrates was achieved when the corresponding dehydrogenase is immobilized in the film during the electrodeposition step. Finally, we will present a new photopatterning approach of such redox ECL polymer.

POSTER PRESENTATIONS

PEA-P-01

New type of modified GC electrodes for potentiometric determination of copper

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The analysis of Cu^{2+} by potentiometry using Nafion-modified glassy Carbon electrode incorporated with Cu complex with Methyl 3,5-bis{bis-[(pyridin-2-yl)methyl]amino}methyl)benzoate(1) is described. A significant increase in potentiometric response was achieved at the modified electrode compared to a bare glassy carbon electrode and obstacles for this determination Cu^{2+} was determined in phosphate buffer (pH 7). Parameters and conditions such as the mass of Nafion, the concentration of Cu complex with compound 1 and pH of medium were optimized. Under the optimum conditions, the calibration curve was linear 1×10^{-7} – 5×10^{-5} M. The detection limit was 7×10^{-8} M. A study of interfering substances was also performed. Obstacles of Fe^{3+}, Co^{3+} and Zn^{2+} in concentration of 1×10^{-4} were examined. Also cyclic voltammograms were recorded and voltammetric behavior of modified electrode in copper solution was shown.

PEA-P-02

Ab initio study of hydrogen interaction with (111) FCC transition metal surfaces and monolayer electrocatalysts

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Following the recent tendencies to understand electrochemical processes on the atomic level, computational study of the electronic and geometrical structure of (111) surfaces of FCC transition metal was performed on DFT-GGA level. After the analysis of clean surfaces, the surfaces with adsorbed hydrogen were analyzed. Preferential adsorption sites, equilibrium geometries and hydrogen binding energies ($E_{H\text{-}M}$) were evaluated for the hydrogen coverage ranging from 0.25 to 1 ML. Quantitative agreement with available experimental data was obtained. Obtained results and the data available from the literature regarding hydrogen energetics on the studied metals and its activity for hydrogen evolution reaction (HER) were used to establish the connection between $E_{H\text{-}M}$ and the exchange current densities for HER, giving the well-known volcano-curve, with platinum at the apex. Once this relationship was obtained, models for atomic adsorption were used to predict such modification of surface electronic structure leading to the improvement of its activity toward HER. The results related to hydrogen adsorption on monolayer type palladium and platinum electrocatalysts are presented, and discussed in view of the experimental results existing in literature.

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PEA-P-03

Application of differential pulse voltammetry for determination of Zn-Ni alloy composition

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The various groups of electrochemical methods in the field of metallurgical science are used for investigation of corrosion resistant and identification of deposition and corrosion mechanisms. The principle of all of these methods is based on electrochemical phenomenon polarization and simultaneous trace of resulting current density due to applied potential on the surface of metals. Polarization, in the simplest way is deviations from equilibrium due to the passage of an electrical current through an electrochemical cell causing and changing in the working electrode (WE) potential. Differential-pulse voltammetry is an extremely useful technique for measuring trace levels of organic and inorganic species. The present study is focused on application of differential pulse voltammetry for determination of alloy composition. In this paper determination of alloy composition in Zn-Ni electrodeposited coatings less than 30 μm on copper substrate prepared in alkaline solution in the present of triethanolamin (TEA) as complexing agent is studded and the result of differential pulse voltammetry is compared with atomic absorption spectrophotometry.

PEA-P-04

Comparation of determination of total fatty matter (TFM) in soaps by gravimetric method and potentiometric two –phase titration

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The purpose of this work is to illustrate the difference between the results obtained by two different methods: potentiometric titration and gravimetric method.

Results showed that gravimetric method is non-selective and other components such anionic surfactants, sodium chloride, emolients can be involved in final result.

Solubile soaps (sodium or potassium salts of higher fatty acid) must be titrated with TEGO trant A 100 at pH value higher than 10. In mixture anionic surfactants and soaps are determined as a sum. Complete separation is achieved by acidifying the sample to pH 2.0 when only the anionic surfactants are determined. Intraday precision for potentiometric titration determined from 10 measurements of the same sample, calculated as RSD was 0.9% with upper limit of satisfaction 2.8%, while the systematic error of the method was 0.021 ml with upper limit of satisfaction 0.050 ml. Intraday precision for gravitric method determined from 10 measurements of the same sample, calculated as RSD, was 5.3%.

Appart from being time consuming, gravimetric method does not distinguish between unsaponifibles and unsaponified fat that might be present in the soap and TFM of the soap. Therefore, potentiometric titration is more reliable and more specific method than gravimetric method.

WITHDRAWN

PEA-P-05

Determination of strychnine by electrochemical methods using carbon paste electrode modified with multi walled carbon nanotube in purification and detoxification of *seeds*

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The electrochemical study of strychnine has been investigated by using a bare and modified carbon paste electrode modified with multi-wall carbon nanotube. The study was carried out using voltammetric methods such as cyclic voltammetry, chronocuolometr, linear sweep voltammetry and differential pulse voltammetry. Cyclic voltammetry was used to investigate the redox properties of this modified electrode at various scan rates. The electrochemical parameters such as diffusion coefficient (D), electron transfer coefficient (α) and electron transfer rate constant were also determined for the strychnine oxidation. The diffusion coefficient, $D = 7.6\times10^{-7}$ cm ^{2} s^{-1} for strychnine was determined using electrochemical approaches. Good dynamic ranges and low detection limits were obtained for the compound. Results revealed that the modified electrode shows an electrocatalytic activity toward the anodic oxidation of strychnine by a marked enhancement in the current response in buffered solution at pH 5.0. The peak current increases linearly with the concentration of strychnine in the two ranges of 5-40 and 40-100 μM. The detection limit (S/N >3) for strychnine is 0.43 μM. The method was then successfully applied to determination of strychnine in purification and detoxification of *seeds.* We also surveyed the processing of seeds with milk that earlier papers have not reported.

PEA-P-06

Simultaneous determination of desloratadine and 3-hydroxydesloratadine in human plasma

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The electrochemical behavior of desloratadine (DLOR) and its derivative 3-hydroxy-desloratadine (3OH-DLOR) was investigated by direct current (DCP) polarography, cyclic (CV), differential pulse (DPV) and square–wave (SWV) voltammetry in Britton-Robinson (BR) buffer solutions (pH 4-11). Both compounds are reduced at mercury electrode in irreversible two electron reduction of the C=N bond of the pyridine ring in their molecules.

Deprotonation of the phenolic moiety in 3OH-DLOR molecule at pH>9, causes a significant change in their reduction potentials, enabling simultaneous determination these two molecules in human plasma. The best selectivity was achieved using SWV method at pH 10. Good recovery and sensitivity was obtained for determination in plasma samples, with detection limits of $2.3\cdot10^{-7}$ and $2.1\cdot10^{-6}$M, and determination limits of $7.7\cdot10^{-7}$ and $6.9\cdot10^{-6}$M, for DLOR and 3OH-DLOR respectively.

PEA-P-07

Simultaneous determination of trace Amounts of nickel, cadmium, lead and copper by adsorptive cathodic stripping voltammetry

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A selective and sensitive method for simultaneous determination of nickel, cadmium, lead, and copper by adsorptive differential pulse cathodic stripping voltammetry is presented. The method is based on adsorptive accumulation of the complexes of Ni(II), Cd(II), Pb(II) and Cu(II) ions with 2-aminobenzoic acid onto hanging mercury drop electrode (HMDE), followed by reduction of adsorbed species by differential pulse cathodic stripping voltammetry. Optimal conditions were obtained at pH 7.4, 2-aminobenzoic acid concentration of 4.5×10^{-4} M, accumulation potential of -0.2 V (vs. Ag/AgCl), accumulation time of 65 s, scan rate of 10 mV/s. Under the optimized conditions, a linear calibration curve was established for the concentration of Ni(II), Cd(II), Pb(II) and Cu(II) in the range of 5-250, 10-120, 5-150 and 10-120 ng/mL, respectively, with a detection limit of 1.65 ng/mL Ni(II), 1.78 ng/mL Cd(II), 1.78 ng/mL Pb(II) and 2.05 ng/mL Cu(II). The procedure was successfully applied to the simultaneous determination of both ions in some real samples.

PEA-P-08

The qualitative determination of oseltamivir phosphate in Tamiflu® capsule by cyclic voltammetry with simultaneous HPLC determination

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A gold electrode was applied in the voltammetric determination of oseltamivir phosphate standard in 0.05 M $NaHCO_3$. Oseltamivir phosphate as a standard and as a component of Tamifluâ capsule exhibited the identical cyclic voltammogram. The electrochemical method for the qualitative determination of oseltamivir phosphate in Tamiflu® capsule by cyclic voltammetry was developed.

PEA-P-09

Differential Electrolytic Potentiometric, a detector for FIA Determination of Procainamide in Pharmaceutical Preparations

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Differential electrolytic potentiometry (DEP) was coupled with Flow injection analysis (FIA) technique for the determination of Procainamide in pharmaceutical preparations.

Platinum electrodes were used as an indicating system to follow the oxidation of Procainamide with cerium(IV), and permanganate in an acidic medium. The oxidation reactions of Procainamide with Ce(IV) and/or permanganate are fast enough to permit its determination by flow injection in sulfuric acid media. The univariate method was employed to optimize the variables such as the current density, the flow rate, the oxidant concentration and the concentration of sulfuric acid.

The proposed method was linear in the range 20-100 µgml^{-1}, the DL and R^2 values were 12 µgml^{-1} and 0.995 respectively.

The procedure was applied successfully to the determination of Procainamide in commercial tablets. The results of this study were favorably compared statistically with those obtained with official methods.

PEA-P-10

Bismuth- and antimony-film electrodes in the determination of trace metals by sequential injection analysis/anodic stripping voltammetry

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The possibility of the application of bismuth- and antimony-film modified glassy carbon electrodes was investigated with the objective of determining Pb(II) and Cd(II) by sequential injection analysis combined with anodic stripping voltammetry. The conditions for the film deposition related to the composition of sample/carrier solutions, concentrations of Sb(III) or Bi(III) and HCl, effect of different supporting electrolytes, and plating potentials were optimized. The reproducibility of the analytical signals was characterized by the RSD lower than 3.0%. The procedure developed for both electrodes was tested on a sample of spiked tap water.

Acknowledgement: *Financial support from the Global COE "Science for Future Molecular Systems" MEXT of Japan is greatly acknowledged. Additionally, the Serbian and Czech co-authors acknowledge the support of CEEPUSII (Project No. CII-CZ-0212-02-0910), Secretariat for Science and Technological Development of APV, Republic of Serbia (Project No. 114-451-02011/2007-02), and Ministry of Education, Youth and Sports of the Czech Republic (MSM0021627502).*

PEA-P-11

Comparison of nontraditional carbon film electrode with screen printed electrodes

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In this contribution a nontraditional carbon film electrode is compared with carbon and gold screen printed electrodes (models DRP-110 and DRP-220) (Dropsens). Potential windows and I-E characteristics were measured using DC and cyclic voltammetry at different pH. A test of sensitivity and linear dynamic range of these electrodes was done by DPV determination of 5-aminoquinoline.

Acknowledgement: The financial support from the Ministry of Education, Youth and Sports of the Czech Republic (projects LC 06035, MSM 0021620857 and RP 14/63) and ERASMUS (application 901906) is gratefully acknowledged.

PEA-P-12

Electrochemical behavior of varenicline at mercury, glassy carbon and boron-doped diamond electrodes

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Varenicline is a nicotinic receptor partial agonist, used to treat smoking addiction. It reduces cravings for nicotine and decreases the pleasurable effects of cigarettes and other tobacco products assisting patients in stopping smoking. Acting as an agonist, varenicline binds to the receptor without creating a full nicotine effect on the release of dopamine.

No literature data were found on electrochemical study of varenicline. Its behavior was investigated using mercury electrode by direct current (DC) and differential pulse (DP) polarography, cyclic (CV), differential pulse (DPV) and square–wave (SWV) voltammetry in Britton-Robinson (BR) buffer solutions (pH 2-12). The electrochemical behavior is pH dependent. In acidic medium, pH < 6, two waves are observed. The first one ($E_{1/2}$ ~ -5V) is well developed two electron wave and the second one, poorly developed, occurs at more negative potentials. At pH < 4, the first one is not completely reversible, but at the pH range of 4 to 10 it is presumed to occur in essentially reversible manner. The anodic behavior of varenicline was also investigated on glassy carbon and boron-doped diamond electrodes using different voltammetric techniques.

PEA-P-13

Electrochemical behavior of $YBaCo_4O_7$ in alkaline aqueous solution

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The paper presents the electrochemical investigation of mixed oxide $YBaCo_4O_7$ in alkaline aqueous solution during oxygen insertion/release.
The $YBaCo_4O_7$ compound has been obtained using the solid state reaction method by mixing the precursors Y_2O_3, $BaCO_3$ and $CoO_{4/3}$ according to the stoichiometric cations ratio (Valldor – 2002).
Electrochemical behavior has been studied by cyclic voltammetry and electrochemical impedance spectroscopy. The morphological analysis made using SEM technique revealed that $YBaCo_4O_7$ has a granular structure and also a high porosity. Based on these results the electrochemical reactions occuring at the interface compound – electrolyte solution have been identified and a mechanism for $YBaCo_4O_7$ oxidation/reduction in alkaline aqueous solution has been proposed.

PEA-P-14

Carbon paste electrode for the monitoring of photodegradation of selected insecticides

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The present study is concerned with the differential pulse voltammetric determination of some neonicotinoid insecticides using a tricresyl phosphate-based carbon paste electrode as a working electrode. The developed voltammetric procedure was applied for the monitoring of their photolytic and photocatalytic decomposition in aqueous solution. The applied voltammetric procedure was capable of measuring the concentration changes of the parent compound, both in the presence of degradation products and photocatalyst (in case of photocatalysis). The voltammetric results were compared with those obtained by HPLC method.

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PEA-P-15

Application of tungsten metal electrode for the measurement of high concentrations of OH^--ions

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Tungsten is a metal with a number of various technological applications. Besides that, electrochemical behavior of tungsten has attracted a lot of attention due to its richness and complexity. In the present work electrochemical behavior of tungsten in alkaline solutions ($11<pH<12$) was studied in order to investigate the possibilities of application of metallic tungsten electrode for the measurement of OH^--ion concentration at high pH. Using RDE technique it was demonstrated that anodic dissolution of metallic tungsten is controlled by OH^--ion diffusion. Besides that, the reaction reveals first order kinetics with respect to OH^--ion. Anodic current plateau was reached at potential higher than ~ 1 V vs SCE, while this current was found to be potential-independent in a wide range of anodic potentials. There was found direct linear relationship between the values of anodic current plateau and the concentration of OH^--ions in the solution, which was unaffected by the ionic strength of the solution. These results indicate that metallic tungsten electrode can be used as a fast, robust, calibration-free amperometric sensor for OH^--ions in the solutions with high pH values, where potentiometric measurements using glass electrode lose its high reliability.

PEA-P-16

Trace amounts determination of copper, zinc, lead and cadmium by adsorptive stripping voltammetry in the presence of 2-aminobenzoic acid

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A selective and sensitive method for simultaneous determination of copper, zinc, lead and cadmium by adsorptive differential pulse cathodic stripping voltammetry is presented. The method is based on adsorptive accumulation of the complexes of Cu(II), Zn(II), Pb(II) and Cd(II) ions with 2-aminobenzoic acid (ABA) onto hanging mercury drop electrode (HMDE), followed by reduction of adsorbed species by differential pulse cathodic stripping voltammetry. The effect of experimental parameters such as pH, ABA concentration, accumulation time and potential and scan rate were examined. Under the optimized conditions, linear calibration curves were established for the concentration of Cu, Zn, Pb and Cd in the ranges of 10-120, 5-200, 5-150 and 10-120 ng/mL, respectively. Detection limits of 2.05, 2.76, 1.78 and 2.26 ng/mL for Cu, Zn, Pb and Cd were obtained. An application of the proposed method is reported for the determination of these elements in some real samples such as natural waters and alloys.

PEA-P-17

Electrochemical bromination of peracetylated glycal in polar organic solvents

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Glycals as carbohydrate derivatives with unsaturated double bond recently had been given significant role in organic synthesis of natural products. They are excellent enantiomerically pure starting material for stereoselective transformation and important precursor in synthesis of various natural products and enzyme inhibitors. We are reporting kinetic results for electrochemical bromination of typical peracetilated glycal (tri-O-acetyl-D-glycal). Cyclic voltammetry was used to determine kinetic rate constants of electrochemical bromination in acetonitrile, dichloro methane and dimetil sulphoxide. Bromide in this solvents undergoes oxidation to molecular bromine and subsequently formation of tribromide anion. However in DMSO, evident formation of bromosulphonium cation $DMSOBr^+$ was observed. Rate constant for bromination in MeCN (178 $M^{-1}s^{-1}$) is approximately ten times higher than in DCM (18 $M^{-1}s^{-1}$). This can be easily explained with much higher dielectric constant in MeCN. Since bromination occurs with bromine/tribromide system, stability of charged intermediate is far better in more polar solvent. However, explanation of almost two order of magnitude higher rate constant in DMSO (9883 $M^{-1}s^{-1}$) must lie in different mechanism.. It was shown that choice of solvents may be crucial in glycal derivative synthesis.

PEA-P-18

Quantitation methods in electrochemical stripping analysis

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Due to complexity of the electrode processes and pronounced influence of the sample matrix on the electron transfer at the electroactive surface, the number of quantitation methods in electroanalytical methods is limited. The most frequently applied quantitation methods in electrochemical stripping techniques include calibration curve method and standard addition method. On opposite to chromatographic techniques in which the use of an internal standard is frequent, this relative quantitation method is very rarely applied in electroanalytical techniques. This work gives an overview of the possible absolute and relative methods that can be used for the quantitation purposes in electrochemical stripping techniques. The theoretical background of all methods is elaborated, advantages and disadvantages are discussed with the focus on practical considerations and demystification of the application of the internal standard method in electroanalytical stripping analysis.

PEA-P-19

Nano-composite electrode material for catechol amperometric detection

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WITHDRAWN

In the last few years, new composite electrode materials containing dispersed nanoparticles of noble metals such as: platinum, palladium or ruthenium incorporated into the carbon paste or [illegible] and studied. The metallized carbon might [illegible] supported catalyst”, due to the strong adherence of the metal particles to the substrate.[1]
In this context, a study of Pt-carbon nanoparticles immobilised in a pyyrole or Nafion matrix on a graphite support for the amperometric detection of catechol was carried out. From cyclic voltammetry performed in different experimental conditions, the electrochemical parameters of the bioelectrode were estimated. The electroanalytical parameters corresponding to the phenol detection, using the amperometric sensors based on de nano-composite transducer, were estimated using a classical batch set-up and also, a computer controlled flow injection set-up.

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PEA-P-20

Voltammetric determination of genotoxic 2-nitrofluorene using electrodes based on novel carbon materials

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Electrodes based on novel carbon materials (namely carbon paste electrode based on glassy-carbon microbeads, screen printed carbon paste electrode, and boron-doped diamond film electrode) were used for direct current voltammetric (DCV) and differential pulse voltammetric (DPV) determination of genotoxic 2-nitrofluorene (2-NF). Optimum conditions have been investigated in aqueous-methanolic solutions buffered using Britton-Robinson buffer. Under optimum conditions, limits of quantification were reached in micromolar (for DCV) and submicromolar concentrations (for DPV). Obtained results have been compared with previous determinations of 2-NF at the other types of electrodes.

PEA-P-21

Application of 4-((2-hydroxyphenylimino)benzene-1,2-diol/multi wall carbon nanotubes composite modified glassy carbon electrode for electrocatalytic determination of hydrazine

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Hydrazin is widely used as powerful reducing agents in fuel cells, polymerization catalysts, antioxidants, corrosion inhibitors, photographic developers, oxygen scavengers, and propellants. In this study, a highly efficient hydrazine sensor was fabricated on the basis of 4-((2-hydroxyphenylimino)benzene-1,2-diol (HPIBD) electrodeposited on a multi wall carbon nanotubes (MWCNT) modified glassy carbon electrode (HPIBD-MWCNT-GCE). The results show that the reversibility of HPIBD is significantly improved at a MWCNT-GCE in comparison with GCE alone. The formal potential ($E^{0'}$)of the electrodeposited HPIBD was strongly dependent on the solution pH and two linear segments were found with slope values -56.0 and -28.2 mV/pH. The charge transfer coefficient and the charge transfer rate constant between HPIBD and MWCNT-GCE were calculated in different pHs. It has been found that the oxidation of hydrazine at the surface of HPIBD-MWCNT-GCE occurs at a potentials of about 255 mV and 215 mV less positive than that observed at a HPIBD-GCE and MWCNT-GCE, respectively. The diffusion coefficient of hydrazine was calculated 4.0×10^{-6} cm^2 s^{-1} using chronoamperometric results. Finally, amperometric method exhibits a wide linear range for hydrazine calibration curve.

PEA-P-22

Electrochemical fabrication of a nanostructured well array for surface-enhanced raman scattering

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An ordered array of macroporous optoelectrochemical sensors is presented; this device presents interesting peculiarities combining the electroanalytical properties of the macroporous electrode surface, and the optical characteristics of the coherent fiber bundle used as substrate. This novel array can find application as analytical tool, for example for electrochemiluminescence (ECL) imaging, but can even be used as new substrate for Surface Enhanced Raman Scattering (SERS) [1].

The device was fabricated by chemical etching [2] of a coherent optical fiber bundle to produce an array of microwells. The macroporous surface inside the micrometer pores was obtained by template synthesis using colloidal crystals. The artificial opal is created by solvent evaporation using of a latex beads suspension. Two different methods were used to deposit gold within the self assembled beads. On one hand, we used an electroless deposition method [3], based on the activation of the polystyrene beads surface by deposition of silver nanoparticles, and on the other hand, an electrochemical deposition technique [4] was employed. As far as the latter method is concerned, a preliminary step is necessary to insulate the cladding between the optical fibers, to obtain the electrodeposition only inside the micropores. After removing the particles a macroporous surface is obtained inside the microwells usable for SERS application. Confocal Raman microscopy has been used to detect a benzenethiol monolayer adsorbed on the macroporous gold and to map the spatial distribution of the SERS signal. We demonstrated that such nanostructured wells can enhance the local electromagnetic field and lead to a platform of ordered SERS-active micrometer-sized spots defined by the initial shape of the etched optical fiber bundles.

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PEA-P-23

Electrochemical behavior of $YBACO_4O_7$ in neutral aqueous solution

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Taking into account the possibility to use the mixed oxide $YBaCo_4O_7$ as an oxygen sensor in various environments, the study of electrochemical behavior of compound was extended for neutral aqueous solution. Cyclic voltammetry and electrochemical impedance spectroscopy have showen that the behavior of $YBaCo_4O_7$ is different in neutral solution in comparison with alkaline solution.

Compound porosity has been determined using BET technique (Micromeritics) and the results are in accordance with thermogravimetric studies made in oxygen flow for $YBaCo_4O_7$ compound. Correlating all these results with the voltammetric studies an electrochemical mechanism for $YBaCo_4O_7$ oxidation/reduction in neutral aqueous solution has been proposed.

PEA-P-24

The interface between Au(111) and an ionic liquid

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Cyclic voltammetry and electrochemical impedance spectroscopy measurements were carried out on Au(111) in 1-butyl-3-methyl-imidazolium hexafluorophosphate ionic liquid at potentials of the double-layer charging region of this system. The equivalent circuit of the interface is a capacitance in parallel to a constant phase element (CPE). The high-frequency value of the capacity – that is, the double layer capacitance - is about 6-7 µF/cm2 over the whole potential range under study, whereas the CPE exhibits a peak at a potential coinciding with the potential of zero total charge (pztc), as determined by immersion experiments. This latter element expresses the kinetics of the re-structuring of the interfacial region. In-situ STM measurements reveal marked structural differences positive and negative of the pztc.

PEA-P-25

Formation of multilayered polyaniline – gold nanocomposite coatings by consecutive Layer-by-Layer adsorption for simultaneous detection of uric acid and dopamine

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Polyaniline (PANI) – gold nanoparticles (AuNPs) multilayer structures were built through the layer by layer adsorption technique. The formation of the nanocomposite layers was monitored by cyclic voltammetry and quartz crystal microbalance measurements. Gradual increase in the first anodic peak current of PANI and linear mass increase were observed during the consecutive adsorption steps. It was found that the amount of the AuNPs can be controlled by variation of the nanoparticles adsorption time.

The PANI - Au NPs nanocomposites were studied as electrocatalytic material for simultaneous electroanalytical detection of dopamine (DA) and uric acid (UA). The possibility for simultaneous detection of both analytes without interfering effect was demonstrated by differential pulse volatmmetry. Linear concentration dependences of the anodic peak currents were observed in the concentration intervals 0.007 – 0.148 mM for DA and 0.03 – 0.72 mM for UA.

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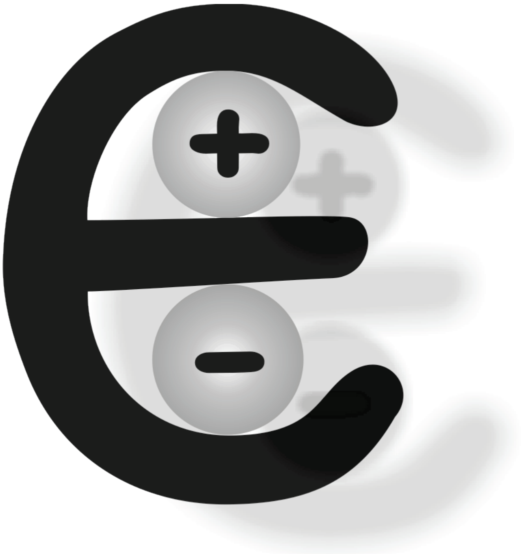
SDE

Electrochemical Synthesis, Deposition, Electrolysis and Engineering



ORAL PRESENTATIONS

Novi Sad

Novi Sad, with 300.000 inhabitants, is the second largest city in Serbia. The oldest areas of the city were made in the middle of the XVIII century. The place, which is always gladly visited by every tourist, is Petrovaradin fortress – one of the largest fortresses in Europe. Novi Sad is also a centre of entertainment. One of the most famous music manifestations EXIT is held every July within the walls of the fortress, then Film Festival, Music Players Festival.

In the centre of the city, at the Square of Liberty, dominates a cathedral built at the end of the XIX century. Many rich citizens of Novi Sad donated money for the building of the cathedral. Opposite the cathedral there is a City Hall built in 1895 and a monument dedicated to Svetozar Miletic, a politician and a mayor of Novi Sad in the second half of the XIX century. The centre of entertainment during hot summer days is Strand, 700 m long beach on the Danube. Around 15 000 people visit this place daily. In 1864 the conflict arouse between Serbs and Hungarian revolutionary government. Bombing the city from the fortress, the Hungarian army destroyed the city and the church also. In this very church, the sons of Mileva and Albert Einstein were christened in 1913. They lived for some time in Novi Sad. On the place where Jewish palaces had stood, in a style of Hungarian secession, one of the biggest synagogues in this part of Europe was built. It happened between 1906 and 1909. It is in the centre of the city, Jevrejska Street 11.

The City Museum is located in the Petrovaradinska fortress, and inside it, there are departments for archeology, ethnology, history and history of art. The museum organizes visits to underground tunnels of the fortress. The network of canals, with its length in total – 16 km, is one of the biggest in Europe.

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SDE-O-01

Water electrolysis on the 3D nickel foam catalyst using solar energy

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The aim of the investigation was to construct and test an alkaline water electrolyser with nickel foam as a new type of electrode material. A 30 W photovoltaic module (PV) was used as a power source. Potential-current characteristics of the electrolyser under natural and force flow circulation as well as the PV module maximum power point trajectory are determined. The hydrogen evolution reaction (HER) was investigated on both foamy and polycrystalline nickel electrodes in a three-electrode reactor using dc and ac electrochemical methods. Improved catalytic activity of 3D nickel foam is attributed to the increased specific area. Mathematical models of the electrolyser and photovoltaic module are given.

SDE-O-02

Chemical/electrochemical metal deposition on hollow fibre

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Hollow fibbers were metalized chemically, making a thin conductive inter-layer, onto which a thicker metal layer was deposited electrochemically.

Hollow fibbers, made from cuprophane and having an outer diameter of 120 μm, were supplied from "Zdravlje" Leskovac, Serbia. The electroless metal deposition was carried out by reduction either silver or copper ions from corresponding conventional baths for chemical plating. Electrochemical deposition onto hollow fibbers covered by a thin layer of chemically deposited metal was carried out from nickel sulphate solution (Watt's bath) as well as from both cyanide and acidic copper baths. The deposition was performed galvanostaticaly at different current densities. After completing the electrochemical metal deposition fibber samples were annealed in order to burn the fibber from inside of formed metal capillary tube around it.

Optical and SEM microscopy were used in studying the surface morphology and cross section of metal coatings of every stage of deposition and thermal treatment.

SDE-O-03

Composition depth profile of electrodeposited Fe-Co-Ni alloys

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Fe-Co-Ni alloys from various baths and with different current densities were produced. The samples were carefully peeled off from the substrate and composition depth profile measurements were performed with secondary neutral mass spectrometry (SNMS) starting from the smooth backside sufrace.

It was revealed that the deposition starts with an Fe-rich zone, in accord with the fact that the deposition of Fe is the most preferred amongst the alloy constituents. The molar fraction of Fe starts to fall from the very beginning of the deposition as a result of the depletion of the electrolyte with respect to the Fe^{2+} ions. The molar fraction of Co first increases then it starts to decrease. The molar fraction of Ni achieves a maximum, while that of Fe and Co decreases to a minimum value in a 90-150 nm thick initial zone.

The composition depth profiles are also suitable to calculate the transport coefficient of Fe^{2+} in the electrolyte. It can be shown that the ionic transport cannot be described as if the diffusion were the only transport phenomenon.

SDE-O-04

Thin-gap electrochemical microreactors for electroorganic synthesis

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Microstructuring represents a novel approach for design of chemical apparatuses with advantage of more intensive, efficient and precise controlled operation. The target of project is to design a new electrochemical microreactor (EMR) providing the high conversion and selectivity of reaction in only a single pass of reaction mixture through the EMR. Model reaction used is oxidation of 4-methylanisole currently used in industry. Microstructured reactor with a thin electrode gap can significantly decrease operational and investment costs arising from the separation and purification of products. First part of contribution deals with the experimental study of gas-liquid flow in thin-gap EMR. The aim of this part was to experimentally describe the behavior of two-phase flow in the wide range of operating conditions (liquid flow rate and current density, pressure, electrode roughness). Second part of contribution deals with testing of two newly designed EMRs with bipolar arrangement. Wide comprehensive set of experiments was conducted to study dependencies of conversion and selectivity on reaction mixture flow rate, applied current density and pressure in apparatus. Results showed very good performance of designed microreactors; nearly total conversion with almost 80 % selectivity was achieved.

SDE-O-05

Comparative study of the structure and the anomalous electrodeposition of NiCoFe alloys related to pure Ni electrodeposits

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The anomalous electrodeposition of NiCoFe alloys was studied in comparison to normal electrodeposition of Ni. The specimens were prepared in corresponding pH and current density conditions on a rotating cathode and their composition was determined via XRF analysis. Specimens' microstructure concerning their fiber axis was carried out using XRD analysis. The optical properties and the microhardness was studied through optical microscopy and reflectance photometry. The current efficiency was also calculated from gravimetric measurements and the use of a current integrator. The Co content of the alloys decreased with the increase of the electrolysis current density, while the Fe content exhibited a local maximum for intermediate current density values. The NiCoFe specimens exhibited higher microhardness and reflectance, but lower current efficiency in comparison to the pure Ni specimens. The latter is considered as a corroborating evidence to the anomalous deposition of the ternary alloy. The fiber axis of pure Ni exhibited a standard sequence for increasing current density, while the NiCoFe specimens were found either amorphous or following the Ni crystal structure only when the Ni content surpassed 50% w/w.

POSTER PRESENTATIONS

SDE-P-01

Corrosion studies of Ni-Mo alloys electrodeposited from citrate aqueous solutions and ionic liquid electrolytes based on choline chloride

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This work presents some results of electrodeposition and corrosion behavior of Ni-Mo alloys deposited from citrate aqueous solutions (2-8Adm^{-2}, 55-70^{o}C, 30-120 min) and from ionic liquids (1-15 A/dm^{2}, 25-80^{o}C, 10-120 min) consisted in choline chloride mixed with urea + citric acid or with ethylene glycol + citric acid. The obtained deposits were characterized from appearance, adherence, layer thickness and cathodic current efficiency. Data regarding the deposit structure, morphology and composition were obtained by XRD, optical microscopy, AFM and SEM microscopy, interferometry and AAS. The corrosion results in 0.5M NaCl aqueous solution were obtained from polarization curves and EIS spectroscopy.

SDE-P-02

Electrochemical study of spent pickling baths for zinc recovery

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The electrochemical behaviour of the main components of the rinsing pickling solutions of the hot dip galvanizing industry, Zn^{2+} and Fe^{2+} in HCl, was studied by cyclic voltammetry. The effect of different variables, such as the solution pH, the inversion potential and the scan rate, on the current-potential curves was studied. The electrochemical reduction of zinc proceeded firstly by an under-potential deposition (UPD) stage and was greatly affected by the HCl concentration. The effect of the scan rate on the UPD peak was studied and showed that the Zn^{2+} reduction was an irreversible process which was not only controlled by diffusion but also charge transfer kinetics. The cyclic voltammetry of Fe^{2+} revealed a peak corresponding to the oxydo-reduction of Fe^{2+} to Fe^{3+} and viceversa. The deposition of metallic iron did not take place and the hydrogen formation was enhanced. For mixtures of iron and zinc in HCl, if the amount of iron was low compared to the zinc concentration, the UPD process of zinc was enhanced and well defined peaks were obtained. However, if the amount of iron was higher, this species promoted hydrogen formation and the peak corresponding to the zinc UPD was overlapped with the hydrogen evolution.

SDE-P-03

A study on Ni electrodeposited from sulphamate bath

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The electrodeposition of Ni on copper substrate was employed to study highly active electrodes as a preliminary step in the electrochemical deposition of Ni nanowire into the porous alumina template. The Ni electrodeposition was study using a sulfamate bath: 1.54 M $Ni(SO_3NH_2)_2 \cdot 4H_2O$, 0.7 M H_3BO_3, SDS 0.2 g L^{-1}. Polycrystalline copper foil was used as cathode, Pt as anode and Ag/AgCl as reference electrode. The electrochemical characterization was performed by different techniques (CA, CV, SVW) to optimised the obtaining of the stable films with different morphologies and thickness, under optimal conditions.

The structure of the nickel layers from sulphamate bath was investigated by scanning electron microscopy (SEM). Vickers hardness of deposit Ni layers was also investigated.

Acknowledgements: This work was financially supported by Project SOP HRD - SIMBAD 6853, 1.5/S/15 - 01.10.2008 (D. E. Rusu (Cosor) and by the project PNII-PCE- ID no 2290.

SDE-P-04

Study of electrode processes during electrodeposition of Cu using choline cloride- ethylene glycol based ionic liquid

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In this paper the use of a special class of ionic liquids named deep eutectic solvent (DES). based on choline chloride and ethylene glycol in electrochemistry is discussed in the context of their use as green solvents. Due to their low toxicity and ready biodegradability, these DES are promising for the electrodeposition of metals. Using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tehniques at 80^0C and with a Pt electrode, we describe the electrolytic deposition of copper from a solution of the metal chloride salt (CuCl or/and $CuCl_2$) dissolved in 1:2 molar mixture of choline chloride /ethylene glycol based DES Voltametric measurements were performed supplementary for determining the electrochemical window for the DES. The effect of scan rate (10-200mV/s) and sample concentration (0.005-0.5M) on anodic/cathodic I_p and E_p was investigated. Cyclic voltammogrames showed redox couples coresponding to cathodic deposition and anodic dissolution of Cu. The process of Cu deposition was also evidence by EIS (Nyquist and Bode diagrams) perfoemed in the same conditions of concentration and temperature.

WITHDRAWN

SDE-P-05

Study of structural and electrochemical characteristics of Cr-containing Pt/ Ebonex catalysts for PEM water electrolysis

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The support of the catalysts used in water electrolysis renders a significant impact on the catalytic efficiency. Recently, the non-stoichiometric Magneli phase titanium oxide (Ti_nO_{2n-1}), known under the registered trade name Ebonex (Atraverda Inc, UK) has been investigated as an alternative of the carbon substrates due to its excellent electronic conductivity and corrosion resistance at high anodic potentials. Moreover, when used as catalytic support for hyper-d-electron metals such as Pt, it is capable to provide strong electronic interactions, resulting in a considerable increase of the catalytic activity. The addition of other hypo-d elements (Co, Mo, etc.) improves the efficiency of the catalyst even further, at the same time reducing the required Pt loading.

The present work investigates the Pt/Cr/Ebonex composite as catalyst toward oxygen evolution reaction in PEM water electrolysis. The substrate used is a commercial Ebonex powder (5 µm) subjected to mechanical treatment in a planetary ball mill to achieve higher surface area. The selected catalytic composition is syntehezed by sol-gel method using acetilacetonate precursors ($M[(C_5H_7O_2)_n]_m$ or M-acac, M=Pt, Cr). The morphology and structure of the synthesized composite catalyst are studied by SEM, XRD and XPS. The electrocatalytic activity is investigated using common electrochemical techniques of cyclovoltametry and steady state polarisation. It is found that Cr component deposited on Ebonex is in amorphous oxidated state, while Pt particles are crystalline and have a size varying in the range 10-12 nm. No alloying between both metals is registered. The electrochemical tests show that Pt/Cr/Ebonex facilitates the oxygen evolution reaction which starts at lower overpotential and proceeds with higher rate compared both to Cr/Ebonex and to Pt/Ebonex catalysts with the same loading. The effect is explained with a realization of hypo-d-hyper-electron effect between both metals and the substrate, proved by XPS analysis.

SDE-P-06

The influence of electrodeposition parameters on composition and appearance of Zn-Mn alloys obtained from chloride bath

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The galvanostatic electrodeposition of Zn–Mn alloys on steel from $MnCl_2$ and $ZnCl_2$ solutions, was studied in an aqueous KCl + H_3BO_3 matrix. The effect of the applied current density (*cd*) and ratio of metal ions in the bath on the current efficiency, coating composition and morphology was investigated, by polarization measurements, atomic absorption spectrometry and scanning electron microscopy. Mn content in the alloy increases with the increase of $[Mn^{2+}]:[Zn^{2+}]$ ratio in the solution. This effect of bath composition is typical for regular type of alloy deposition. The increase of Mn content in the coating is also in clear correlation with increase of applied *cd*. Furthermore, critical deposition *cd*, where rapid increase of Mn content occurs, can be observed. Depending on ions ratio in the solution, the critical *cd* is between 6 and 9 A dm^{-2}.

The alloy films deposited at *cds* up to 12 A dm^{-2} have a morphology displaying hexagonal pyramids, or grains with polyhedral edges, and they appear to be compact. At higher *cds*, non homogeneous deposits are obtained. Coatings with the best appearance are obtained for $[Mn^{2+}]:[Zn^{2+}] = 2:1$.

SDE-P-07

Electrochemical synthesis and characterization of the composite pPy/AC on INOX steel nets

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The composite polypyrrole (pPy) / activated carbon (AC) was obtained by electrochemical codeposition of pPy (0.1M in acetonitrile solution) and dispersed particles of A (10-50 gl^{-1}) with high surface area (~860 m^2g^{-1}) previously activated by chemical treatment in HNO_3.
The obtained pPy/AC-composites on INOX steel nets as a substrate were investigated by cyclic voltammetry, impedance spectroscopy and charging/discharging (constant current) procedure. Thus, a composite material with considerably higher electrochemical activity (~60%) in respect to the pPy-itself, mainly due to the presence of AC in the film (increased quantity) has been obtained.
These composites are with improved electronic conductivity even at potentials where pPy-films are in reduced (insulating) state.
Electrochemical and impedance features of the obtained material indicate a superior characteristic as far as application in rechargeable batteries or supercapacitors are concerned.

SDE-P-08

Magnesium deposition on vitreous carbon from nitrate melt

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For the first time in accessible literature magnesium has been deposited on vitreous carbon electrodes from magnesium nitrate and magnesium nitrate-amoniumnitrate melts at temperatures ranging from 85°C to 200°C. Electrochemical techniques used were cyclic voltammetry and potential step. Deposits were studied by electron microscopy, EDS and XRD. The electrodeposition of magnesium was performed from the melts made with magnesium hexahydrate and anhydrous magnesium nitrate. Different current densities and conditions of deposition from two kinds of melts, leading to different morphology of the deposits obtained, have been attributed to the different immediate surrounding of Mg^{2+} ion. In magnesium hexahydrate melts magnesium cations include six strongly bonded water molecules. A new method for the synthesis of water free magnesium nitrate was designed to avoid the influence of strongly bonded water onto magnesium deposition process. It was found that two reduction processes precede magnesium deposition: more anodic reduction from nitrate to nitrite, and less anodic reduction of nitrite to oxygen and nitrogen. It was established that the surface of the magnesium deposited has been very quickly transformed into magnesium oxide by the evolved oxygen in both kinds of melts.

SDE-P-09

Study of electrode processes during electrodeposition of Cu using choline cloride- ethylene glycol based ionic liquid

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WITHDRAWN

In this paper the use of a special class of ionic liquids named deep eutectic solvent (DES). based on choline chloride and ethylene glycol in electrochemistry is discussed in the context of their use as green solvents. Due to their low toxicity and ready biodegradability, these DES are promising for the electrodeposition of metals. Using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tehniques at 80^0C and with a Pt electrode, we describe the electrolytic deposition of copper from a solution of the metal chloride salt (CuCl or/and $CuCl_2$) dissolved in 1:2 molar mixture of choline chloride /ethylene glycol based DES Voltametric measurements were performed supplementary for determining the electrochemical window for the DES. The effect of scan rate (10-200mV/s) and sample concentration (0.005-0.5M) on anodic/cathodic I_p and E_p was investigated. Cyclic voltammogrames showed redox couples coresponding to cathodic deposition and anodic dissolution of Cu. The process of Cu deposition was also evidence by EIS (Nyquist and Bode diagrams) perfoemed in the same conditions of concentration and temperature.

SDE-P-10

Copper electrodeposition on printed circuits.
III. electrochemical behavior and effect of leveling agents in acid solutions

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To ensure the quality requirements imposed to the copper deposition on printed board circuits the influence of added leveling agents in acid galvanic baths has been studied. As leveling agents nitrogen aromatic derivatives such as benzylamine, N-methylaniline, N,N-dimethylaniline, N-ethylaniline and N,N-diethylaniline have been tested. The electrochemical behavior of these organic additives was studied by cyclic voltammetry and electrochemical impedance spectroscopy. Furthermore, a correlation between the electronic structure of molecules of leveling agents, the double layer capacity of the interface copper-electrolyte solution and the leveling ability has been made. Molecular modeling was performed using the program Hyperchem 8.03, the main characteristics determined being dipole moment, molecular volume and surface area. Also, the most relevant aspects of the electrochemical behavior of copper in acid solutions have been highlighted by cyclic voltammetry. Morphology of copper deposits has been studied by scanning electron microscopy.

SDE-P-11

Preparation and characterization of electrodeposited HAP/Lig coatings with different lignin concentration

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The purpose of this work was to obtain and characterize electrodeposited biocomposite hydroxyapatite/lignin coatings. Nanocrystalline hydroxyapatite (HAP) powder was prepared by a modified chemical precipitation method. Lignin (Lig) is an amorphous polyphenolic natural polymer and its specific chemical structure is highly dependent on its plant origin. Alcell lignin was extracted from a mixture of hardwoods by an organosolv process using aqueous ethanol and it has been used for formation of the novel HAP/Lig coatings. A two-electrode cell arrangement was used for cathodic electrodeposition technique to prepare HAP/Lig coatings on titanium substrate placed as working electrode and two Pt panels as counter electrodes. The electrolyte was ethanol suspension of 1.0 g HAP and lignin powder of different concentration – 0.5, 1, 3 and 10 wt. %, at pH 2.0 adjusted by HCl. The HAP/Lig coatings were obtained at constant voltage of 60 V and deposition time for 45 s. The HAP/Lig coatings were investigated by SEM, XRD, ATR-FTIR and TGA.

SDE-P-12

Electrochemical synthesis of thin-film 3D-microbattery materials

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One of the approaches to the achievement of increased capacity and power capability of thin-film microbatteries is to replace a continuous by a perforated substrate with high-aspect-ratio through microchannels, thereby utilizing the dead volume of the substrate. Each microchannel comprises thin-film, sandwich-like 3D-concentric microbattery (3D-CMB) unit. This work describes progress in the development of 3D-nanosize V_2O_5, FeO_xS_{2-x} and CuS cathodes, composite membrane and anode materials for 3D microbattery applications. The experimental results of ESEM, XRD, XPS and HRTEM characterization of the modified materials and electrochemical tests of the batteries will be presented.

SDE-P-13

Mg-Au alloy formation by Mg deposition from nitrate melts on Au

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For the first time in accessible literature magnesium has been deposited on gold electrodes from magnesium nitrate and magnesium nitrate-amoniumnitrate melts at temperatures ranging from 85^{o}C to 200^{o}C. Electrochemical techniques used were cyclic voltammetry and potential step. Deposits were studied by electron microscopy, EDS and XRD. The electrodeposition of magnesium was performed from the melts made with magnesium hexahydrate and anhydrous magnesium nitrate. In magnesium hexahydrate melts magnesium cations include six strongly bonded water molecules. A new method for the synthesis of water free magnesium nitrate was designed to avoid the influence of strongly bonded water onto magnesium deposition process. The deposition of magnesium in underpotential and overpotential regions results in Au_3Mg alloy formation. More anodic reduction from nitrate to nitrite and less anodic reduction of nitrite to oxygen and nitrogen precede the magnesium deposition. It was established also that the surface of the bulk magnesium deposited has been very quickly transformed into magnesium oxide by the evolved oxygen in both kinds of melts.

SDE-P-14

Stoichiometric $CuInSe_2$ electrodeposited films

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Low cost, wet methods of forming Cu-In-Se thin films of controllable composition, in particular the chalcopyrite $CuInSe_2$ phase, are highly desirable for solar energy conversion devices. The electrochemical synthesis offers a convenient way to prepare such films over large electrode surface areas with good deposition rates. Aqueous cathodic electrodeposition typically from acidic solutions of complexed precursors has been advantageously used to serve as a preparation step in producing mixtures of binary (e.g., Cu_9In_4, Cu_2Se) and ternary ($CuInSe_2$) compounds in the system Cu-In-Se. By all means, a relatively pure polycrystalline phase of the target material $CuInSe_2$ could be obtained only after annealing at moderate treating temperatures (300 – 400 °C). In this work, Cu-In-Se alloys were electrodeposited by a potentiodynamic (pulsed potential) method from aqueous acidic Cu(II), In(III), and Se(IV), citrate solutions on metallic substrates, with the objective to form ternary chalcopyrite by a single step process. The dependence of thin film microstructure on electrical parameters is illustrated in terms of XRD structure, SEM morphology and EDAX composition. Pulse plating conditions were found leading to the direct formation of $CuInSe_2$ crystallites of an unprecedented purity with respect to accompanying elemental and binary phases.

SDE-P-15

Joint titanium and boron electroreduction in chloride-fluoride melts

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WITHDRAWN

It has been shown, that addition to the KCl-NaCl-NaF-KBF_4 melt of titanium trichloride in concentration close to half of potassium tetrafluoroborate results in sharp current increase at potentials 0.25 V more positive than titanium complexes reduction potential. This brings about a wave characterised by steeper slope than waves for the discharge of titanium and boron complex ions. This wave is displayed on voltammograms over broad ranges of polarisation rates and $TiCl_3$ and MBF_4 concentrations. If the ratio $[Ti^{3+}]:[B^{3+}] = 1:2$ does not hold, then electroreduction of TiB_2 is followed (before discharge of alkali metal) by discharge of excess (with respect to this ratio) of a component (titanium or boron).

SDE-P-16

W_2C and ZrB_2 galvanic coatings deposition from ionic melts

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WITHDRAWN

Taking into account peculiarities of electrodeposition of tungsten, zirconium, carbon, and boron from melts, thermodynamic data on decomposition potentials of corresponding compounds, and technological characteristics of deposition of tungsten carbide coatings, we have chosen halide-oxide melt NaCl-LiF-Na_2WO_4-Na_2CO_3. Halide melt NaCl-KCl-NaF-K_2ZrF_6-KBF_4 was chosen for deposition of zirconium diboride coatings. Experiments at 1173 K have shown that tungsten carbide coatings can be deposited from melt containing 5 wt % Na_2WO_4. Parallel discharge of combined complexes of zirconium and boron can be achieved by maintaining molar ratio at level $[Zr(IV) + B(III)] : [F^-] > 1 : 4$ (at ratio $[Zr(IV) : [B(III)] = 1 : 2$) in the KCl-NaCl melt. In this case, uniform phase of zirconium diboride is formed in wide current density range. Temperature interval of 1073-1173 K is optimal at cathodic current density of 5-20 A dm^{-2}. Tungsten carbide and zirconium diboride electroplates deposition can be recommended for increase in surface hardness, as well as wear, abrasive, and corrosion resistance of steel materials.

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SDE-P-17

Effect of surfactants on the stability of TiO_2 suspensions used in Zn-TiO_2 nanocomposites electrodeposition

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TiO_2 particles co-deposition with Zn used in order to improve corrosion and wear resistance of coatings, usually takes place in a classical zinc electroplating bath containing suspended TiO_2 particles. One of the problems encountered during electrodeposition is the low stability of suspensions, resulting in formation agglomerates. In this context, the present work aims to investigate the possibility of enhancing the stability of TiO_2 suspensions by using surfactants. For this purpose, the zeta potential, the size of TiO_2 nanoparticles, the rate of sedimentation and the turbidity of suspensions were evaluated in the absence and in the presence of two surfactants: a polyacrylate salt (Coadis BR 3) or a polyether carboxylate salt (Coadis BR 85). Electrochemical corrosion measurements of Zn-TiO_2 coatings obtained in the presence of BR 85 were performed in $(NH_4)_2SO_4$ solutions, and the results were corroborated with the suspensions properties.

SDE-P-18

Zn-Ni alloy coatings from alkaline bath containing triethanolamine. Influence of additives

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Zn-Ni alloys replace successfully cadmium coatings in the automotive industry and provide superior sacrificial protection to steel than pure zinc. Basic alkaline baths usually contain Zn^{2+} and Ni^{2+} ions, an alkali metal hydroxide and a complexing agent for nickel, such as polyethyleneimine, di-, or triethylenetriamine, N,N'-bis(3-amino-propyl)ethylene-diamine, tetraethylenepentamine, triethanolamine, tartrate, ammonia etc. The use of additives in electrodeposition baths is extremely important due to their influence on the structure of the cathodic deposits, on their physical and mechanical properties and on their corrosion resistance.

In this context, Zn-Ni alloys have been electrodeposited from an alkaline bath containing triethanolamine as complexing agent for Ni^{2+} ions. Polyethyleneglicol, coumarin, piperonal, and vanillin have been tested as brightening agents. Their effect on the codeposition process and on the corrosion resistance of the resulted coatings was investigated by electrochemical and non electrochemical methods.

SDE-P-19

Effect of parameters of pulsating current (PC) regimes on morphology of electrodeposited copper in hydrogen co-deposition range

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The most often employed electrolytes for the electrodeposition of copper are those based on aqueous solutions of sulfuric acid (H_2SO_4) and cupric sulfate ($CuSO_4$). There is an ionic equilibrium of a lot of species in the $CuSO_4$-H_2SO_4-H_2O system. Electrodeposition processes at high current densities and overpotentials are very suitable for experimental verification of this ionic equilibrium, because there is parallelism between copper electrodeposition and hydrogen evolution reaction at high current densities and overpotentials. In this study, it is shown that effects attained by the choice of appropriate parameters of square-waves pulsating current (PC) on morphology of electrodeposited copper were equivalent to those obtained by electrodepositions at the constant overpotential in the hydrogen co-deposition range from six solutions of different concentrations of $CuSO_4$ and H_2SO_4. In this way, it was clear that it is possible to simulate the ionic equilibrium of the species in the $CuSO_4$-H_2SO_4-H_2O system using the only one electroplating solution if the appropriate parameters of PC regimes are used.

SDE-P-20

Electrodeposition of nickel composite coatings with Al_2O_3 and TiO_2

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Composite coatings containing either alumina or titania particles in a nickel matrix were prepared by means of electrochemical deposition from nickel plating baths in which fine submicron size particles of γ-alumina (Buehler USA) or titania (Cinkarna Celje Slovenia) were kept suspended by mechanical stirring. Conventional nickel sulphate plating bath was used in all electroplating experiments. Coatings were prepared under constant stirring rate and temperature but at different current densities and different concentration of particles suspended in the bath. Deposition time was adjusted accordingly to the operating current to obtain an approximately constant coating thickness. Copper plates were used as a substrate for nickel composites coatings. Particles content in the composites was determined by dissolving of samples of coatings and analyzing the obtained solutions by AAS-ICP method. Optical and SEM microscopy were used in studying the surface morphology of coatings.

The structure and mechanical properties of the composites were investigated as a function of applied current density and particles content in the coatings. The surface morphology and microstructure was significantly altered due to the particles embedded in the coatings. Metallographic analysis has shown a uniform particles distribution across the coating. Particles content significantly affects the microhardness of composites as well as the wear resistance. Coatings prepared from a particles-free bath served for comparison with composite ones.

SDE-P-21

Electrodeposition of iron powder particles of different characteristics

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Iron deposits obtained at high current densities and overpotentials are very important from a technological point of view. It has been stated that the open and porous structures of copper or iron deposits obtained at high current densities were ideally suited for use as electrodes in electrochemical devices such as fuel cells, batteries and chemical sensors, while the extremely high surface area is relevant for evaluating some electrochemical reactions. Mainly two types of electrolytes were investigated and these were based on sulfate and chloride electrolytes. With increasing duration of electrolysis, dendrites merge, which is unacceptable for the case of further application. These deposits must be grinded in order to obtain powders. However, in the range of lower acidity the deposits become powdery and, in some cases, may be spongy and sticky. Generally, up to now research indicates that electrodeposition of Fe powders have two steps, deposition of fragile film and grinding. It must be emphasized that we tried and succeeded to obtain Fe powders without grinding process. The aim of this work was to investigate electrodeposition processes of Fe powders from sulfate and chloride electrolytes and morphologies of powder as a function of type of electrolyte and current density.

SDE-P-22

Electrodeposition of Ni/SiC and Co/SiC composites in the presence of Cs$^+$ ions

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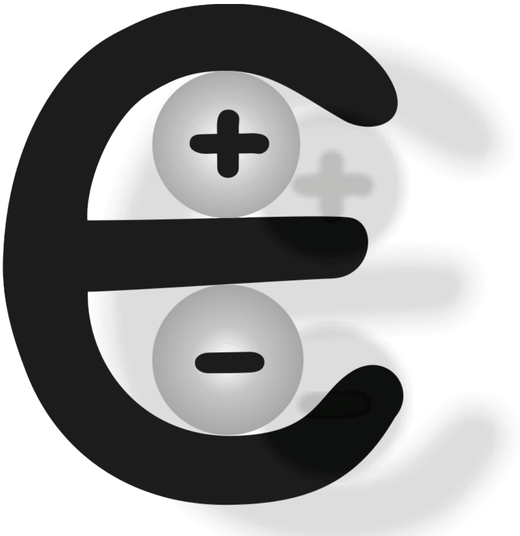
Most of the papers on metal matrix composites were focused on nickel matrix materials, while studies on cobalt matrix composites are relatively limited. It is known that the amount of embedded phase in the composites depends on the metal-particle combination and is governed mainly by powder concentration in the plating bath, current density and agitation rate. However, enhanced incorporation of the particles can be achieved also by addition of some additives to the plating bath. The aim of this work was to find the importance of Cs$^+$ ions as a potential promoter of SiC codeposition with nickel or cobalt. Composites were electrodeposited from Watt's–type baths with various concentrations of Cs$^+$ ions. It was found that despite similarity of properties of both metals their behavior was different. SiC incorporation with cobalt was only little dependent on cesium concentration in the bath, while promoting effect of cesium (in some concentration range) was found during Ni/SiC codeposition. Particles suspended in the bath slightly affected the polarization curves during reduction of metallic ions, whereas cesium ions can inhibit the cathodic process. Linear sweep voltammetry showed better transport of nickel and cobalt ions to the cathode surface in the presence of SiC and Cs$^+$. Some adsorption phenomena on SiC powder were also studied. The presence of Cs$^+$ in the solution enhanced adsorption of ions on SiC, but higher values for Co^{2+} than Ni^{2+} ions were observed. Preferential cesium adsorption occurred simultaneously in both systems. The last phenomena lead to cesium incorporation into the composite coatings.

GEH

General Electrochemistry



ORAL PRESENTATIONS

Niš

Niš is situated on the banks of river Nisava, where Roman Naissus had been bulit, and later on, Byzantine Nysos. It is believed that present names of a city and river were just altering the old names to Slavonic language. One of the most significant Roman emperors, tsar Constantine, who had, by an edict, recognized Christianity as a religion, was born in Naissus. An archeological site Mediana, which represented an elite area of Naissus, also dated from this period.

In the XIX century it had been under Serbian rule, but only for a short period. Turks conquered it in 1385 and they remained there till 1878. After them, the Fortress of Nis remained on the right bank of the river Nišava, being one of the most preserved fortresses on the Balkans, but also the unique monument in the world Skull Tower. A few kilometers away from the city is Cegar, a place where a crucial battle in the First Serbian Rising against the Turks had been fought in 1809. Today it is also very famous by a famed act of Duke Stevan Sindjelic.

Popular picnic grounds around Nis are gorge of Jelasnica, waters of Bojana and gorge of Sicevo. Some of the most famous events are International Jazz festiva - Nisville, Film Festival, Medijana fest, Nisomnia…. .

GEH-O-01

Ethanol oxidation at Pt-based alloys and UPD modified Pt/C catalysts

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Activity of two alloys, Pt_3Sn/C and Pt_3Ru_2/C, was compared with the activity of Pt/C modified with corresponding amounts of Sn_{UPD} (~25 %) and Ru_{UPD} (~40 %) in overall oxidation of ethanol. Pt_3Sn/C, Pt_3Ru_2/C and Pt/C catalysts were characterized by XRD. To establish the activity and stability of the catalysts potentiodynamic, quasi steady-state and chronoamperometric measurements were performed. Both alloys are more active than Sn_{UPD} or Ru_{UPD} modified Pt/C catalysts. Electronic effect determining dominantly the activity of Pt_3Sn/C is the main reason for its higher activity compared to Pt_3Ru_2/C. Since Sn_{UPD} and Ru_{UPD} do not provoke any significant modification of electronic environment, both modified Pt/C catalysts are less active than corresponding alloys. More pronounced difference in activity between Pt_3Sn/C and Sn_{UPD} modified Pt/C than between Pt_3Ru_2/C and Ru_{UPD} modified Pt/C is caused by electronic effect in Pt_3Sn/C. High activity of Pt_3Sn/C modified with small amount of Sn_{UPD} (~10%) can be explained by combining the electronic effect, causing less strongly bonded adsorbate on Pt sites and easier mobility of Sn_{UPD}, with enhanced amount of oxygen-containing species on Sn sites resulting finally in reinforcement of bifunctional mechanism.

GEH-O-02

Electrochemical hydrogen insertion kinetics in electrochemically prepared WO_3 film

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Anhydrous, orthorhombic tungsten trioxide films of about 1.5 μm thick were grown by novel bipolar current pulsing technique in 1 M H_2SO_4 solution. We aimed to elucidate the complexity of the ion insertion process into WO_3 film in aqueous acid media. Combined CV, galvanostatic intermittent titration, and X-ray diffractometric measurements were carried out for the identification of phase transformations during the electrochromic hydrogen insertion/extraction reaction. The observed structural irreversibility of the H insertion process due to $H_xWO_3 \rightarrow WO_{3-x}(OH)_x$ transformation was incorporated into the electrochemical impedance (EIS) model being successfully applied for the CNLS fitting procedures.

GEH-O-03

Electric conductivity study of *o*-substituted phenoxo iron (III) complexes

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The coordination nature of a number of substituted sodiumphenoxides to iron (III) ion has been studied. The *o*-nitrosodiumphenoxide was found to have different coordination behaviour to what the sodium salts of salicylic acid and methylsalicylate showed. The resulting complexes were found to behave as semiconductors.

GEH-O-04

*Moved to Poster Session - **GEH-P-07***

GEH-O-05

Electrochemical considerations regarding the selective dissolution of zinc from zinc ferrite with sulphuric acid

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Zinc ferrite $ZnFe_2O_4$ is a major constituent of the steel-making dusts and different sludges in zinc-metallurgy that should be treated in hydrometallurgical processes in order to recover of zinc separately from iron. The dissolution of zinc ferrite, as shown (Eq. 1), it is investigated in an acidic solution to avoid the loss of its zinc content.

$$ZnFe_2O_4 + 8\,H^+ = Zn^{2+} + 2\,Fe^{3+} + 4\,H_2O \qquad (1)$$

During sulphuric acidic dissolution iron was introduced into the leaching circuits, which has to be removed, because iron is a harmful impurity in the electrowinning process. The rate constant for $ZnFe_2O_4$ is affected by factors such as: temperature, acidity, the type anion and presence of ions such as Cu^+, Fe^{2+} und Fe^{3+}. Because of the above mentioned situation a detailed thermodynamic analysis of stability of zinc ferrite was made in binary Fe-Zn-water system in temperature range between 333 K und 523 K under atmospheric and high pressure using software Factsage, Germany. The solubility of Fe and Zn are very high up to pH-values of 3, but they become low as a result of the formation hematite and ferrites, of which solubilities become low in different potential regions, respectively. Main aim of this work is study is selective dissolution of zinc without iron from zinc ferrite in temperature range between 333 and 523 K. The obtained experimental results of zinc dissolution during sulphuric acid leaching of zinc ferrite will be discussed involving constructed EH-pH diagram in Factsage. The influence of temperature and pressure on zinc recovery will be studied.

POSTER PRESENTATIONS

GEH-P-01

Electrochemical discoloration of acid solution with 4-(phenyldiazenyl)phenyl benzenesulfonate content

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A new azo dye, namely 4-(phenyldiazenyl)phenyl benzenesulfonate (DPB) was synthesized and its discoloration process was investigated. It was studied the electrochemical discoloration process of a synthetic solution solutions of 0.1 M HCl/ 0.035 M NaCl with 4-(phenyldiazenyl)phenyl benzenesulfonate content, using direct electrochemical degradation on Ti electrode. In order to evaluate the contribution of pure adsorption, behavior of DPB in open circuit was studied. Galvanostatic method was applied to evaluate the effect of current density on solution discoloration process. At specified time intervals absorbance values were assessed using an UV-Vis spectrophotometer. Absorbance decreases in time, on the same current density, which demonstrates the DPB degradation and discoloration. The degradation process of dye was clarified determining the color removal. The color removal at 90 min increases of the value of a 50 % calculated at current density of 5mA/cm^2 until the value of 65.8 % at current density equal to 15mA/cm^2. Degradation process of DPB follows a first order kinetic reaction.

Acknowledgements: The results were obtained with financial support of CNCSIS grant 422/2008.

WITHDRAWN

GEH-P-02

Catalytic hydrogen evolution of polyamino acids on mercury electrode

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Polyamino acids can be considered as an intermediate model system between peptides and macromolecular proteins. Here we used polyamino acids such as polylysine, polyarginine and polyhistidine and cyclic voltammetry on hanging mercury drop electrode to explore how different amino acid residues in proteins contribute to the catalytic hydrogen evolution reaction. We found that at pH 6 both the polylysine and polyarginine produced comparable peaks while polyhistidine yielded much smaller peak. It can be thus expected that under the given conditions accessible histidine residues will contribute to the catalytic hydrogen evolution reaction response to a much lesser extent than lysine and arginine residues.

GEH-P-03

The influence of the potential of zero charge of the cathode on the electrochemical reduction of nitrate

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At extremely negative potentials (E < –2.0 V vs. Ag/AgCl) the reduction of nitrate takes place far from the electrode surface, due to the repulsion of the reduced nitrate from the likely charged electrode. The reduction in this potential region is efficient since both the rate of the reduction and the yield to nitrogen, which is the desirable product for environmental purposes, are high.

In this work, the electrochemical reduction of nitrate was studied on six different cathodes including Sn, Pb, Bi, Al, In and Zn. It was found that the rate of the reduction at a constant potential (E = –2.4 V vs. Ag/AgCl) depends only on the distance of the applied potential from the potential of zero charge (pzc) of each metal. In this respect, the rate of the reduction decreases in the order Bi>Sn>Al>Zn>In.

If the electrolysis is performed at equal distance from the pzc of each metal ($E_{applied}$ – pzc = –2.01 V), the rate of the reduction was found to be about the same on all metals.

GEH-P-04

Electrochemical characterisation of antimony deposition from ionic liquid based on choline chloride-urea

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The aim of this work was to study the electrodeposition of Sb using an ionic liquid medium (choline chloride + urea; 1:2 molar mixture). Ionic complex species($SbCl_4^-$) were supposed as participant species at the cathodic process, and were prepared by dissolving $SbCl_3$ in 0.5 - 10 mM concentrations. Cyclic voltammograms on Pt showed redox couples corresponding to cathodic deposition and anodic dissolution of antimony metal at all scan rates (2 – 100 mVs^{-1}) and temperatures (40 – 80 ^0C). Their cathodic peak currents increase with square root of scan rate, thus proving a diffusive controlled electrode process for all systems. Antimony underpotential depositions were observed from CV's corrensponding to 0.5, 1 and 2 mM Sb^{3+} concentrations. Koutecky-Levich diagrams were obtained using rotating disk electrode. Values of diffusion coefficients and activation energy for diffusion were also estimated. Nyquist and Bode spectra, obtained from electrochemical impedance measurements, proved the diffusion control. By fitting the experimental data with an equivalent electrical circuit of modified Randles type the differences in double layer capacitances and also in charge transfer resistances for the cathodic processes of Sb ions were evidenced. Also, Nyquist and Bode diagrams for Sb films obtained by potentiostatic deposition at different time period were shown.

GEH-P-05

Fundamental Electrochemistry in Civil Engineering

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Well known is that steel corrosion in reinforced concrete is of great concern with respect to structures durability. Corrosion in concrete can take place when carbon dioxide has penetrated to the steel surface or when chloride content in the vicinity of the steel bars reaches certain threshold values. Consequently, breakdown of the passive layer, normally deposited on the steel surface in the concrete alkaline medium, is taking place. The assessment of the condition of reinforced structures in terms of: time to initiation of reinforcement corrosion, the level of damage, the performance of the system related to mechanical properties, evaluation of efficiency of protection techniques etc. is always related to estimating corrosion rates i.e. to determination of electrochemical parameters for the steel reinforcement in certain technical and environmental conditions. Further, electrochemical techniques for corrosion prevention and/or protection (e.g. cathodic protection), in terms of assessing their efficiency, is also based on recording electrochemical parameters.
Since steel corrosion and cathodic protection in reinforced concrete are electrochemical processes with high complexity, their investigation and proper interpretation is only possible via the application of fundamental electrochemical techniques. To this end, the present contribution reports on long term monitoring of steel corrosion and protection in reinforced concrete, clarifying fundamental electrochemical principles, supported by surface analysis of the steel reinforcement and chemical analysis of the surrounding bulk matrix.

GEH-P-06

Chronopotentiometric study of the transport of Fe^{3+} through cation-exchange membranes for the regeneration of chromium plating baths

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Emma M. Ortega-Navarro
Departamento de Ingeniería Química y Nuclear, Universidad Politécnica de Valencia,
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The aim of the present work is to study the recovery of hexavalent chromium present in the spent solutions of the chromium-plating industries by means of using electrochemical techniques. Iron is one of the impurities present in the spent baths that reduces the efficiency of the plating process. An electrochemical reactor with a cation-exchange membrane is proposed in order to remove the iron and to regenerate the baths. Chronopotentiometric studies are carried out for the study of the transport of Fe^{3+} through a cation exchange membrane (NAFION 117). The influence of the concentration of iron was analysed. Current-voltage curves are obtained for each case showing an increase in the limiting current for high ferric sulphate concentrations. The presence of Cr(VI), as chromic acid, increases the limiting current due to the contribution of H^+ to the transfer through the membrane. The obtained results confirm also a dependence of the shape of the current-voltage curves on the concentration of ferric sulphate. In this sense, an increase in the Fe^{3+} ions causes a lack of the overlimiting region in the I-E curves of the CEM.

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GEH-P-07

Electrocatalytic reduction of hydrogen peroxide by electrodeposited nano-scale islands of ruthenium oxide

Hamid R. Zare, S. Hossein Hashemi
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Meta oxide nanoparticles have received significant due to their unique properties such as conductivity and excellent electrocatalytic and electroanalysis properties which are due to their nano-siza effect. Hydrogen peroxide (H_2O_2) is the main product of the most enzymatic reactions and it is a significant mediator in various fileds such as food, industrial, enviromental, pharmaceutical and clinical analysis. In this work an electro-deposited nano-scale island of ruthenium oxide was successfully used for electrocatalytic reduction of H_2O_2. It has been found that the reduction of H_2O_2 at the modified electrode occures at a potential of about -210 mV while at the bare glassy carbon electrode no current is observed in the presence of H_2O_2. The diffusion coefficient of H_2O_2 was estimated as 2.0×10^{-6} cm^2 s^{-1} using chronoamperometry. The kinetic parameters such as the electron transfer coefficient, α, and electron transfer rate constant, k', for reduction of H_2O_2 at the modified electrode surface was estimated using cyclic voltammetry. Amperometric methode exhibits a linear dynamic range of 69.0 744.7 μM and detection limit of 29.1 μM for H_2O_2.

ISE Satellite Student Regional Symposium on Electrochemistry

Faculty of Technology and Metallurgy
Karnegijeva 4, Belgrade, Serbia

Sunday, June 6, 2010

Scientific & Organizing Committee:

Chair:

Željka **Jovanović**, *PhD Student, Faculty of Technology and Metallurgy, University of Belgrade, Belgrade*

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Gergana **Raikova**, *PhD Student, Institute of Electrochemistry & Energy Systems, BAS, Sofia*
Suzana **Sopčić**, *PhD Student, Faculty of Chemical Engineering and Technology, University of Zagreb, Zagreb*
Ana **Tomova**, *PhD Student, Faculty of Technology and Metallurgy, Skopje*

PROGRAM

09.00 – 10.45 **Opening -** Faculty of Technology and Metallurgy, Karnegijeva 4, Lecture room, III floor
Addresses by:
Ivanka **Popović**, prezident of the Serbian Chemical Society
Željka **Jovanović**, Chair of the Scientific and Organizing Committe

Chairperson Velizar **Stanković**
Teaching Lecture:
TL **Christos Comninellis**
Ecole Polytechnique Fédérale de Lausanne, Switzerland
Fundamentals in electrochemical treatment of wastewater containing organic pollutants

11.00 – 11.15 **Coffee Break - Refreshment**

Chairperson Željka **Jovanović**

11.15 – 11.30 **Sanja Eraković**, Đorđe Veljović, Miodrag Mitrić*, Papa N. Diouf**, Tatjana Stevanović**,
O-01 Vesna Mišković-Stanković, *Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia, *Vinča Institute of Nuclear Sciences, Belgrade, Serbia, **Département des sciences du bois et de la forêt, Université Laval, Québec, Canada*
The study of electrodeposited HAP/Lig coatings

11.30 – 11.45 **Katalin Neuróhr**, Júlia Dégi, Lajos Pogány, Imre Bakonyi, László Péter
O-04 *Research Institute for Solid State Physics and Optics, Hung. Acad. Sci., Budapest, Hungary*
Codeposition of Co and Pb by d.c. and pulse plating and magnetoresistance properties of the deposits

11.45 – 12.00 **N. Pajkić**, V. D. Stanković, and M. Gojo*
O-06 *Technical Faculty Bor, University of Belgrade, Serbia, *Faculty of Graphic Art, University of Zagreb, Croatia*
Electrodeposition of nickel composite coatings with Al_2O_3 and TiO_2

12.00 – 12.15 **Qamar Abbas,** Leo Binder
O-11 *Institute of Inorganic Chemistry, Graz University of Technology, Graz, Austria*
Electrochemical dissolution of molybdenum in Binary Mixtures

12.15 – 12.30 **Mihael Bučko**, Jelena B. Bajat, Miodrag M. Maksimović
O-10 *Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia*
The electrodeposition and corrosion stability of Zn-Mn alloys

12.30 – 12.45 **Aleksandra Debeljković,** Vesna Mišković-Stanković, Srđan Nešić*
O-21 *Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia, *Institute for Corrosion and Multiphase Technology, Ohio University, Athens OH, USA*
Application of volatile corrosion inhibitors for top of line corrosion in mild steel pipelines

12.45 – 13.00 **Aleksandra Nešić,** Vesna Mišković-Stanković, Srđan Nešić*
O-22 *Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia, *Institute for Corrosion and Multiphase Technology, Ohio University, Athens OH, USA*
Spreading corrosion inhibitors for CO_2 corrosion on mild steel

13.00 – 14.00 **Lunch**

Chairperson Marianna **Kourouzidou**

14.00 – 14.15 **O-16**
Maria-Laura Soare, Magdalena Bujduveanu, Eleonora-Mihaela Ungureanu, Emilian Georgescu*, *Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, Romania, *S. C. Oltchim S.A., Ramnicu Valcea, Romania*
Electrochemical Studies on some Indolizine Carboxylates with Potential Application

14.15 – 14.30 **O-07**
V. Novotný, J. Barek, *Charles University in Prague, Faculty of Science, UNESCO Laboratory of Environmental Electrochemistry, Prague, Czech Republic*
Voltammetric determination of Nitrofen and Oxyfluorfen at a carbon paste electrode

14.30 – 14.45 **O-15**
Cristina Andreea Amarandei, George Octavian Buica, Eleonora-Mihaela Ungureanu, Alexandru C. Razus*, Liviu Birzan*, *Faculty of Applied Chemistry and Material Sciences, University Politehnica of Bucharest, Romania, *Institute of Organic Chemistry C. D. Nenitzescu of Romanian Academy, Bucharest, Romania*
Electrochemical detection of some anions using 4-azulen-1-yl pyranylium salts

14.45 – 15.00 **O-08**
Suzana Sopčić, Marijana Kraljić Roković, Zoran Mandić, András Róka*, György Inzelt*
*Faculty of Chemical Engineering and Technology, Department of Electrochemistry, University of Zagreb, Zagreb, Croatia, *Department of Physical Chemistry, Eötvös Loránd University, Budapest, Hungary*
Ion dynamics and different type of charges in the redox reactions of hydrous RuO_2

15.00 – 15.15 **O-17**
Ivan Ivanov*, Tanja Vidaković-Koch*, Kai Sundmacher*'**, *Otto-von-Guericke University, *Max-Planck-Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany*
Direct glucose enzymatic fuel cell

15.15 – 15.30 **O-18**
Gergana Raikova, D. Vladikova, Z. Stoynov, A. Thorel*, A. Chesnaud*, J. Abreu*, D. Soysal**, Z. Ilhan**, S. A. Ansar**, *IEES – BAS, 10 Acad. G. Bonchev St., Sofia, Bulgaria, *ARMINES, Paris, France, **DLR, Stuttgart, Germany*
Impedance characterization of LSCF/YDC couple obtained by different technologies

15.30 – 15.45 **Refreshment**

Chairperson Suzana **Sopčić**

15.45 – 16.00 **O-12**
Željka Jovanović, Vladimir Panić*, Vesna Mišković-Stanković, Branislav Nikolić
*Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia, *ICTM – Department of Electrochemistry, University of Belgrade, Belgrade, Serbia*
The electrochemical synthesis of different Ag/PVP nanocomposites

16.00 – 16.15 **O-13**
Marianna Kourouzidou, Michael Pagitsas, Dimitra Sazou
Department of Chemistry, Aristotle University of Thessaloniki, hessaloniki, Greece
Electrochemical characterization of the excitable iron-nitric acid system

16.15 – 16.30 **O-03**
Maria Pavlidou, Michael Pagitsas, Dimitra Sazou
Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece
Influence of nitrate ions on the chloride-induced potential oscillations of the iron-sulfuric acid system

16.30 – 16.45 **O-14**
Kyriaki Saltidou, Michael Pagitsas, Dimitra Sazou
Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece
Donor-density effect on the stability of Ti oxide films in bromide-containing solutions

16.45 – 17.00 **O-19**
Kyriaki Michael, Michael Pagitsas, Dimitra Sazou
Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece
Intrinsic coherence resonance in an electrochemical system

17.00 – 17.15 **O-20**
Magdalena Rodica Bujduveanu, Alexandru Anton Ivanov, Eleonora-Mihaela Ungureanu, Haritina Chivu, Cornelia Guran, *Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania*
Electrochemical Properties of some OxotetrabromoMolybdenum (V) Complexes

17.15 – 17.30 **Conclusions –Closing**

Contents Index Print EXIT

PRESENTATIONS

? - Belgrade's oldest tavern (*kafana*)

SERBIA

Serbia is a house by the road, a crossroad of many ways, a place where Europe joins Middle East and Asia. In this house about 10 million people lives in harmony. Not only Serbs, but 37 nationalities! This diversity of people and cultures gives Serbia its strength and make its fortune. Serbs are temperamental people who seem to have red wine instead of blood circulating in their veins. They can love and passionately defend their beliefs, tradition and history! Speaking of honour, one of the best evidence it still exists in Serbia, are typical Serbian taverns (Serbian: KAFANA), very specific for each town. Famous Serbian author ones wrote:

“Tavern is for Serbs what square was for ancient Greeks. Belgrade is breezy city, springs are cold, autumns rainy, and summer sultriness unbearable. And, squares are not among the most beautiful in Europe. People gather on squares rarely, only in key historical moments. Therefore, for public life remained taverns, restaurants, bars and in newer time – cafés; those cradles that swayed away famous Belgrade spirit.”

Tavern is a special institution in Serbia. A place where you can feel the “pulse” of the nation: what people think and what they intend to do. For centuries, in taverns governments have been destroyed, important political decisions have been made, honour has been defended… Even today, in taverns, Serbia lives a parallel, maybe shorter, but far more exciting life!

***http://www.gotoserbia.eu* – May 9, 2010.**

O-01

The study of electrodeposited HAP/Lig coatings

Sanja Eraković, Đorđe Veljović, Miodrag Mitrić*, Papa N. Diouf **,Tatjana Stevanović**,
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**Vinča Institute of Nuclear Sciences, University of Belgrade,*
Mike Petrovića Alasa 12-14, 11000 Belgrade, Serbia
***Département des sciences du bois et de la forêt, Université Laval, Québec, Canada*

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) is used in clinical application as implants, bone defect fillers or coatings on prostheses. Composite materials of HAP with organic polymers can enhance quality of coatings. The nano-sized HAP powder was prepared by a modified chemical precipitation method and Alcell lignin (Lig), natural polymer, was extracted from a mixture of hardwoods by an organosolv process using aqueous ethanol. These two components were used for obtaining novel composite HAP/Lig coatings. The HAP/Lig suspension was prepared using 1.0 g of HAP powder and different percentages of lignin powder– 0.5, 1, 3 and 10 wt. % into 100 ml of absolute ethanol at pH 2. Electrophoretic deposition of HAP/Lig coatings was performed at constant voltage of 60 V for 45 s on titanium plate as working electrode. The HAP coatings were deposited from ethanol suspension on titanium substrate and on modified titanium surface - TiO_2 nanotubes. The morphology and phase composition of the coatings were investigated by ATR-FTIR, TGA, SEM and XRD.

O-02

WITHDRAWN

O-03

Influence of nitrare ions on the chloride-induced potential oscillations of the iron-sulfuric acid system

Maria Pavlidou, Michael Pagitsas, Dimitra Sazou
Department of Chemistry, Aristotle University of Thessaloniki
54124 Thessaloniki, Greece

Chloride-induced potential oscillations emerged under current-controlled conditions of the $Fe|H_2SO_4$ interface are used to investigate the inhibitive effect of nitrates on localized corrosion of iron. The galvanodynamic and galvanostatic curves obtained at various concentration ratios of chloride and nitrate ions indicate distinct differences related to the inhibition action of nitrates on pitting corrosion. Upon increasing gradually the nitrate concentration and depending on the current imposed to the system, the number of potential oscillations decreases whereas the oscillatory waveform becomes more characteristic of a more stable passive state. Above a certain critical nitrate concentration, nitrates suppresed completely the oscillations resulting in a stable passive state. A quantitative characterization of the inhibitive action of nitrates is carried out using diagnostic critiria established previously on the basis of chloride-induced potential oscillations. These critiria include the induction time t_{ind} necessary for the onset of oscillations and the oscillation average firing rate $<r>$. The inhibiting effect of nitrates is discussed in terms of a competitive adsorption of chlorides and nitrates on the oxide surface along with nitrate redox reactions.

O-04

Codeposition of Co and Pb by d.c. and pulse plating and magnetoresistance properties of the deposits

Katalin Neuróhr, Júlia Dégi, Lajos Pogány, Imre Bakonyi, László Péter
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Co and Pb are immiscible metals that both form face-centered cubic crystals. Due to their immiscibility, no data available for the codeposition of Co and Pb. It is expected that multilayer formation from Co and Pb is very hindered because of the large difference in the lattice parameters.

Bath compositions were elaborated by taking into account the chemical compatibility of Co^{2+} and Pb^{2+} with the appropriate anions. Electrolytes containing either acetate, chloride or nitrate anions were tested. Depoits were obtained with constant current or by using various current and potential pulses in order to investigate the possibility of multilayer formation. Composition of the samples was measured with electron probe microanalysis. Variation in the composition as a function of the deposition parameters were elucidated by using cyclic voltammetry and current transient measurements.

Magnetoresistance properties showed that no layer formation occured even in the pulse-plated samples. Regardless of the deposition method, Co and Pb segregated substantially in all samples.

O-05

WITHDRAWN

O-06

Electrodeposition of nickel composite coatings with Al_2O_3 and TiO_2

N. Pajkić, V. D. Stanković, and M. Gojo*
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**Faculty of Graphic Art University of Zagreb, Croatia*

Composite coatings containing either alumina or titania particles in a nickel matrix were prepared by means of electrochemical deposition from nickel plating baths in which fine submicron size particles of γ-alumina (Buehler USA) or titania (Cinkarna Celje Slovenia) were kept suspended by mechanical stirring. Conventional nickel sulphate plating bath was used in all electroplating experiments. Coatings were prepared under constant stirring rate and temperature but at different current densities and different concentration of particles suspended in the bath. Deposition time was adjusted accordingly to the operating current to obtain an approximately constant coating thickness. Copper plates were used as a substrate for nickel composites coatings. Particles content in the composites was determined by dissolving of samples of coatings and analyzing the obtained solutions by AAS-ICP method. Optical and SEM microscopy were used in studying the surface morphology of coatings.

The structure and mechanical properties of the composites were investigated as a function of applied current density and particles content in the coatings. The surface morphology and microstructure was significantly altered due to the particles embedded in the coatings. Metallographic analysis has shown a uniform particles distribution across the coating. Particles content significantly affects the microhardness of composites as well as the wear resistance. Coatings prepared from a particles-free bath served for comparison with composite ones.

O-07

Voltammetric determination of Nitrofen and Oxyfluorfen at a carbon paste electrode

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The optimal conditions for the determination of the herbicides Nitrofen and Oxyfluorfen in a mixed supporting electrolyte consisting of Britton-Robinson buffer and methanol were found. Method for the determination of the substances by differential pulse voltammetry on a carbon paste electrode was developed. The calibration dependences are linear and the achieved limits of detection permit trace analysis.

The finnancial support of The Czech Ministry of Youth and Sports (project LC06035, MSM 021620857 and RP14/63) is gratefully acknowledged.

O-08

Ion dynamics and different type of charges in the redox reactions of hydrous RuO_2

Suzana Sopčić, Marijana Kraljić Roković, Zoran Mandić, András Róka*, György Inzelt*
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*Department of Physical Chemistry, Eötvös Loránd University,
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Electrochemical charging/discharging reaction of hydrous ruthenium oxide was studied by cyclic voltammetry and electrochemical quartz-crystal nanobalance (EQCN) in sulfuric acid as well as in neutral solutions of Na_2SO_4 and K_2SO_4. The ruthenium oxide electrode was prepared by attaching the ruthenium oxide particles on gold covered quartz electrode. The results show that the specific capacitance as well as the apparent molar mass of exchanged species depends on the scan rate. The existence of different mechanisms of the redox reaction depending on the potential range was revealed. The results were interpreted with two different charges, one leading to the mass release and another to the mass loss upon oxidation, taking place simultaneously during the oxidation/reduction reaction of ruthenium oxide.

O-09

WITHDRAWN

O-10

The electrodeposition and corrosion stability of Zn-Mn alloys

Mihael Bučko, Jelena B. Bajat, Miodrag M. Maksimović
Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia

Zinc and its alloys, particularly Zn-Fe, Zn-Co and Zn-Ni, are used for sacrificial protection of ferrous materials in industry nowadays. Several authors have reported that, in Cl^- and SO_4^{2-} medium, Zn-Mn alloy has even better corrosion resistance [1]. However, data about use of Zn-Mn alloys in automobile industry are very scarce [2] because of low current efficiency and bath stability during electrodeposition. Mn is more electronegative metal than Zn, so increased corrosion stability of Zn-Mn alloy can be only due to passive layer on surface. Depending on Mn content in alloy, different corrosion products are formed and some of them behave as passive layer. But, when Mn content in alloy is changed, other corrosion products could be formed, with low protective ability. So, in some cases Zn-Mn alloys have better corrosion resistance than pure Zn, but it is not a rule [3].

The possibility to deposit Zn-Mn alloys with good appearance and increased corrosion stability as compared to pure Zn coating, was investigated in present work. Such alloys could be used in automobile industry. Three different plating baths (chloride, sulphate, and pyrophosphate), without any aditives, were investigated. The influence of deposition current density on current efficiency in Zn-Mn deposition, chemical content, surface roughness, morphology and corrosion stability of alloy coatings was investigated.

The coatings from sulphate bath deposited at current densities up to 4 A dm^{-2} have very small Mn content. Coatings obtained at higher current densities are non-homogeneous and burnt. Pyrophosphate bath is interesting because alloys with appreciable Mn content (up to 10 mass %) were obtained at low current densities. In order to improve the morphology and corrosion stability of coatings deposited from this bath, some changes could be done, like change of complexing agent concentration or use of pulsed electrodeposition. The best results were obtained for alloy coatings deposited from chloride bath. Namely, coatings with homogeneous morphology, appreciable Mn content and increased corrosion stability were obtained at current densities up to 12 A dm^{-2} from this plating bath.

1. J. Crousier, F. Soto, M. Eyraud, *Mater. Tech.* **3–4** (1999) 47.
2. B. Bozzini, V. Accardi, P.L. Cavalloti, F. Pavan, *Met. Finish.* **97** (1999) P33.
3. N. Boshkov, *Surf. Coat. Technol.* **172** (2003) 217.

O-11

Electrochemical dissolution of molybdenum in Binary Mixtures

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Molybdenum is a hard metal, hard to machine and cut; our purpose is to find some suitable solvent that can electrochemically dissolve molybdenum and help in its electrochemical machining. The present work focuses on the electrochemical dissolution of Mo in a bianry mixtures of choline chloride with DMF and DMSO. These solutions possesses physicochemical properties that are comparable to the room temperature ionic liquids (RTILs). Unlike the chloroaluminates and chlorozincates melts, former of which are water sensitive and later are more viscous, choline chloride produces solutions with these polar aprotic solvents that are liquid at ambient temperature and have unusual solvent properties. These solutions showed good conductivity and have corrosive ability to great extent. Galvanostatic measurements show the faradic current efficiency of dissolution upto 60% for DMF and 80% for DMSO mixtures assuming that the molybdenum dissolves in +5 oxidation state in non-aqueous systems. Cyclic voltammeteric measurements show almost no passivation and on cathodic ramp small reduction of cations is observed. The electrodeposition of Mo was checked on copper, iron, zinc and molybdenum at current density as low as 500uA/cm^2, and no electrodeposition of molybdenum was observed.

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O-12

The electrochemical synthesis of different Ag/PVP nanocomposites

Željka Jovanović, Vladimir Panić*, Vesna Mišković-Stanković, Branislav Nikolić
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**ICTM – Department of Electrochemistry, University of Belgrade*
Njegoševa 12, 11000 Belgrade, Serbia

The potential use of Ag/poly(*N*-vinyl-2-pyrrolidone) (PVP) nanocomposites is in wound dressings or soft tissue implants, where Ag nanoparticles (AgNPs) serve as the antimicrobial agent. Ag/PVP nanocomposites were electrochemically synthesized, by the electrochemical reduction of Ag^+ ions into the AgNPs in the PVP aqueous solution and within the crosslinked PVP matrix, forming the non-crosslinked and crosslinked Ag/PVP nanocomposite, respectively. The synthesis of AgNPs was performed in an electrochemical cell with Pt working and counter electrodes and the saturated calomel electrode (SCE) as the reference. The non-crosslinked Ag/PVP nanocomposite was obtained by galvanostatic reduction of Ag^+ ions from the aqueous solution consisted of 0.10 M KNO_3, 3.9 mM $AgNO_3$ and 10 wt. % PVP. The crosslinked Ag/PVP nanocomposite was obtained by *in situ* potentiostatic reduction of Ag^+ ions within PVP hydrogel, previously prepared by γ-irradiation of the 10 wt. % PVP aqueous solution. Hydrogels were swollen in two different aqueous solutions ((a) 3.9 mM $AgNO_3$, (b) 3.9 mM $AgNO_3$ + 0.10 M KNO_3) for 24 h. Ag/PVP nanocomposite systems were characterized by UV-Vis spectroscopy, FTIR, TEM, XRD, Z-sizer analysis and cyclic voltammetry.

O-13

Electrochemical characterization of the excitable iron-nitric acid system

Marianna Kourouzidou, Michael Pagitsas, Dimitra Sazou
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This study addresses the non-linear behavior of the $Fe|HNO_3$ system at concentrated nitric acid solutions (c_{HNO_3} = 11-14.4 M). Three distinct states are distinguished, namely active, partially passive and passive, characterized by equilibrium potential values. Different electrochemical processes dependent on the c_{HNO3} and applied potential control the different states. Within the concentration range 11-14.4, the equilibrium open circuit potential, called also as “mixed potential” takes values ranged between ~800 - 840 mV. This potential regime is located within the passive state of the $Fe|HNO_3$ system and starts at the Flade potential. It is suggested that the passive state within the range determined between the “mixed potential” and Flade potential is a stable but excitable attractor. When an appropriate cathodic current is applied, a dissolution reaction is initiated locally by breaking the passive oxide film.

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The influence of donor density on the stability of titanium oxide films in bromide-containing solutions

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The influence of donor density on the stability of the titanium semiconducting oxide film was investigated in bromide-containing solutions. Titanium oxide films of the same thickness and different donor density were formed at various formation current densities galvanostatically in 0.5 M H_2SO_4. Using the Mott-Schottky analysis the TiO_2 it was found to be an n-type semiconductor whereas the donor density (oxygen vacancies) decreases with increasing formation current density. Passive oxide films of different donor density were used in bromide-containing solutions aiming to trace both the bromide electrochemical oxidation and the breakdown potential of the passive titanium oxide. The peak potential of bromide oxidation remains stable whereas the breakdown potential shifts towards more positive values upon decreasing the donor density. The experimental results are discussed on the basis of the bromide surface adsorption and a point defect model that describes both the oxide growth and its breakdown.

O-15

Electrochemical detection of some anions using 4-azulen-1-yl pyranylium salts

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The design of receptors for the anions coordination is an important aspect in order to get a good electrochemical signal. In the present work, the strategy consisting in the detection of the current/potential change of the redox guest activity when the complex is formed has been applied for the anion electrochemical recognition.

The structure of the proposed receptor is based on the 4-azulen-1-yl pyranylium salts. Cyclic voltammetry and differential pulse voltammetry have been used to characterize the new receptors. The obtained results show that some of the studied receptors present electrochemical recognition properties towards HSO_4^- and I^- anions.

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Electrochemical studies on some indolizine carboxylates with potential application

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Indolizine derivatives have been used in medicine and pharmacology due to their biological activity and therapeutical effects. They also possess a certain capacity to form surface films and to be used as sensors in modern technologies. These aspects justify the interest for more profound studies.

This work is devoted to the study of some indolizine derivatives with structural similarities by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). It is pursued the influence of concentration and that of the scanning domain and scan rate on the CV curves. There are established the number and characteristics of the redox processes for each compound and a comparison of the electrochemical parameters was attributed to the difference between the functional groups grafted on the indolizinic ring. The formation of surface films has been tested.

The financial support of this research, received from CNMP 71-067 REMORESE project, is gratefully acknowledged.

O-17

Direct glucose enzymatic fuel cell

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Enzymatic biofuel cells use biocatalysts (enzymes) instead of noble metal catalysts. Enzymes have high catalytic activity and high substrate selectivity under mild conditions but the electrical communication between the enzyme and the electrode is often difficult to achieve and the resulting bioelectrodes suffer from lack of stability.

An enzymatic anode for glucose oxidation that comprises charge transfer complex (CTC) and enzyme glucose oxidase was developed. The influence of structural parameters such as CTC and enzyme loading was tested. Increased CTC loading was found to extend the linear range in the concentration dependence thus improving the anode performance for biofuel cell and biosensor applications.

The bioanode was employed in a specially-designed flow-through biofuel cell enabling kinetic and mass transport investigations of the anode performance under “fuel cell” conditions as well as long-term stability tests. The influence of different cathode architectures and glucose flow rate was investigated. Under optimized experimental conditions the biofuel cell exhibited high open circuit voltage (up to 0.967V) and reasonable power densities (up to 120 μW cm^{-2}).

O-18

Impedance characterization of LSCF/YDC couple obtained by different technologies

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This work presents conductivity studies of the cathode/electrolyte couple LSCF48/YDC15, which is a buidling block of a new innovative and competitive design of a high temperature fuel cell, operating in the range 600-700°C. It is based on the idea for a junction between a PCFC anode/electrolyte and a SOFC cathode/electrolyte through a mixed H^+ and O^{2-} conducting porous ceramic membrane. Thus, in this concept, hydrogen, oxygen and water are located in three independent chambers, which allows for the avoidance of the gases dilution with water. The applicability of different technologies for electrodes deposition as tape casting, screen printing and plasma spraying is analyzed by electrochemical impedance spectroscopy measurements of electrolyte supported symmetrical half cells $La_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\alpha}/Ce_{0,85}Y_{0,15}O_{2-\alpha}/La_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\alpha}$. The couple LSF48/YDC15 obtained by the three technologies has appropriate microstructure and high conductivity, comparable with data from the literature. The developed materials were applied in the fabrication of the first model cells of the new design.

O-19

Intrinsic coherence resonance in an electrochemical system

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We demonstrate experimentally the existence of intrinsic coherence resonance (ICR) in an electrochemical system in which chlorides induce current oscillations due to localized corrosion of iron in sulfuric acid solutions. ICR is a stochastic resonance-like phenomenon where enhanced regularity in the system dynamics is induced by the system internal noise and not by a finite value of noise imposed externally. At relatively high concentrations of chlorides, two types of oscillatory behavior are induced as a function of the potential representing a passive-active state dissolution (earlier stages of pitting) at lower potentials and an electropolishing state dissolution of iron (late stages of pitting) at higher potentials. The chloride-induced spiking dynamics characteristic at lower potentials was used to quantify the ICR. It is shown that the level of internal noise is regulated by the potential applied at the iron electrode.

O-20

Electrochemical properties of some oxotetrabromo molybdenum (V) complexes

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The oxotetrabromoMolybdenum (V) complexes have been used in medicine and pharmacology due to their biological activity and therapeutical effects. They also possess a certain capacity to form surface films and to be used as sensors in modern technologies. These aspects justify the interest for more profound studies.
This work is devoted to the study of some oxotetrabromomolybdenum (V) complexes with structural similarities by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). It is pursued the influence of concentration and that of the scanning domain and scan rate on the CV curves. There are established the number and characteristics of the redox processes for each complex and a comparison of the electrochemical parameters was attributed to the difference between the functional ligands.

The financial support of this research, received from CNMP 71-067 REMORESE project, is gratefully acknowledged.

O-21

Application of volatile corrosion inhibitors for top of line corrosion in mild steel pipelines

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In wet gas transportation one of the most significant internal corrosion challenges is the so called Top-of-Line-Corrosion (TLC). One possible solution may be the application of the volatile corrosion inhibitors (VCI). It is well known that VCIs such as: 1,3-di-morpholin-4-ylpropan-2-ol,1,3-bis-diethylamino-propan-2-ol, 2-amino-5-phenyl-1,3,4-thiadiazole, 2-hydrazinobenzothiazole and bis-piperidiniummethyl-urea, are very efficient and non-toxic.
In this work, the efficiency of various VCIs will be investigated which are suitable for TLC applications. The corrosion rate and the morphology of the corrosion attack on a mild steel surface covered by corrosion inhibitors will be investigated by different surface analytical methods (SEM-EDXS, TEM, XRD, AFM). Inhibition of carbon steel corrosion by a VCI film forming on the metal surface will be studied using electrochemical measurements (LPR, EIS). The adsorption on the carbon steel surface will be characterized by using a quartz microbalance and adsorption isotherms. The interactions of VCI with the carbon steel will be investigated by XPS and FTIR analysis.

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Spreading corrosion inhibitors for CO_2 corrosion on mild steel

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Internal corrosion of mild steel pipelines constitutes a significant problem for the oil and gas transportation industry. One of the difficult issues is the protection from the so called Top-of-Line-Corrosion (TLC) which occurs when a wet gas stream is cooled and water vapor condenses on the internal walls of the line. TLC inhibition could be achieved with the so called spreading/creeping inhibitors. This type of inhibitor molecules spreads along the surface of the metal against gravity and without the need for a carrier fluid. The aim of this work is to investigate inhibitors that have good spreading characteristics and are effective at corrosion inhibition. The effect of spreading will be investigated by surface tension, contact angle and spreading tests. The structure of the metal surface covered by spreading inhibitors will be investigated by different methods for surface analysis (SEM-EDXS, TEM, XRD, AFM, XPS). Inhibition of mild steel corrosion by spreading inhibitors will be studied by electrochemical measurements (LPR, EIS and Tafel analysis).

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