Regional Symposium on Electrochemistry

RSE-SEE

South-East Europe

Fourth Regional Symposium on Electrochemistry
South-East Europe

Programme &
Book of Abstracts

Ljubljana, Slovenia, May 26–30, 2013

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Ljubljana, Slovenia, May 26-30, 2013

PROGRAMME & BOOK OF ABSTRACTS

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RSE-SEE is organized by National societies:

Slovenian Chemical Society
Bulgarian Chemical Society
Czech Chemical Society
Croatian Society of Chemical Engineering
Electrochemical Committee of the Hungarian Academy of Sciences
Romanian Chemical Society
Electrochemical Division of the Serbian Chemical Society
Society of Chemists and Technologists of Macedonia

We are honoured of having the opportunity to host the Fourth Regional Symposium on Electrochemistry – South East Europe (RSE-SEE) in Ljubljana. The idea about establishing the RSE-SEE meetings emerged in 2007 to facilitate dissemination and discussion of the newest scientific results across the national borders. The first meeting was held in Croatia (Red Island, 2008), the second in Serbia (Belgrade, 2010) and the third in Romania (Bucharest, 2012). RSE-SEE was established primarily to bring together scientists from the South-Eastern European region, but it immediately "crossed its borders" as many scientists from numerous other countries were eager to participate at the these conferences. Internationally distinguished plenary speakers have additionally contributed to the attractiveness and importance of the RSE-SEE series of conferences.

Maintaining the tradition of previous conferences, this RSE-SEE meeting aims to bring together researchers from scientific and industrial institutions to present and communicate their newest results, to create personal contacts, to promote research, to find possibilities of cooperation in bilateral or multilateral projects, and to stimulate the participation of doctoral students. PhD and postdoctoral students of electrochemistry will present their work at the one-day Satellite Student Regional Symposium on Electrochemistry (SSRSE), which traditionally takes place on the Sunday preceding the conference.

The conference covers broad aspects of electrochemistry fields in order to stimulate and promote research on all core topics of traditional and emerging research areas of electrochemistry. The conference comprises nine sessions, from physical and analytical electrochemistry, to energy conversion and storage devices.

We hope that you will enjoy the scientific activities as well as in pleasant gathering in the warm atmosphere of this conference.

It is our great pleasure welcoming you in Ljubljana,

Conference co-chairs

Milošev

Miran Gaberšček

Ingrid Milošev

RSE-SEE4 PROGRAMME

SUNDAY, May 26, 2013	
13.00-	Registration
Student Symposium RSE-SEE	
Hall: Janus Chairpersons: M. Gaberšček and I. Milošev	
14.00-14.20 SS-IL-01	**Mechanism(s) of Li-S Batteries Derived from In-Situ Measurements** R. Dominko, M.U.M. Patel, A. Vižintin, V. Lapornik, I. Arčon
14.20-14.40 SS-IL-02	**Molecular Modeling of Corrosion Inhibitors: Can It Provide Some Useful Insight?** A. Kokalj
Hall: Janus Chairpersons: M. Gaberšček and S. Hočevar	
14.45-14.55 SS-O-01	**Electrodeposition and Electrochemical Propreties of Nickel Oxide Electrodes** H. Vučić, S. Sopčić, Z. Mandić, M. Kraljić Roković
14.55-15.05 SS-O-02	**Characterization of Reactively Co-Sputtered Cu-Ni Material Libraries Using a Scanning Kelvin Probe** W. Burgstaller, A. W. Hassel
15.05-15.15 SS-O-03	**1,2,4,5-Tetramethoxybenzene as a Redox Shuttle** K. Pirnat, R. Dominko, M. Gaberšček
15.15-15.25 SS-O-04	**Electrochemical and Microstructural Investigations on Al-Cu-Ni Thin Films** M. Hafner, A. I. Mardare, A. W. Hassel
15.25-15.35 SS-O-05	**Electrochemical Characterization of Glass Like Carbon and Graphite Electrodes: Influence of Varying Degree of Oxidation in H_2SO_4 Solution** K. Magdić, V. Horvat-Radošević, K. Kvastek
Hall: Kronos Chairpersons: I. Milošev and L.M. Muresan	
14.45-14.55 SS-O-06	**Comparison of Results from Standardized Cyclic Corrosion Testing and Flowing Electrolyte on the Corrosion Behaviour of Hot Dipped Galvanized Steel** M. Voith, A.W. Hassel, T. Keppert, G. Luckeneder, K. Stellnberger
14.55-15.05 SS-O-07	**Protection of Bronze Works of Art from the Effects of Polluted Urban Atmospheres** Z. Hajdari, M. Warde, K. Marušić, H. Otmačić Ćurković
15.05-15.15 SS-O-08	**Corrosion Protection Of Copper, Zinc and Their Alloys With Carboxylic Acids** G. Žerjav, I. Milošev
15.15-15.25 SS-O-09	**Evaluation of the Performance of Corrosion Inhibitor for Mild Steel in CO_2 Containing NaCl Solution** I. Jevremović, M. Singer, S. Nešić, V. Mišković-Stanković
15.25-15.35 SS-O-10	**Investigation of Chloride Adsorption on Oxide Covered Steel Samples with the Novel 'Thin Gap' Method** D. Horváth, Zs. Kerner, T. Kovács, K. Varga, T. Pintér
15.35-16.00	Coffee break

Hall: Janus **Chairpersons: I. Milošev and M. Gaberšček**	
16.00-16.20 SS-IL-03	**Bismuth- and Antimony-Based Electrodes in Contemporary Electroanalysis** S. Hočevar
16.20-16.40 SS-IL-04	**On the Role of Dipole and Quadrupole Moment of Water Molecules in Spatial Variation of Permittivity in Electrolyte Solution near a Highly Charged Surface** A. Iglič, E. Gongadze, A. Velikonja, V. Kralj-Iglič
Hall: Janus **Chairpersons: M. Gaberšček and S. Hočevar**	
16.45-16.55 SS-O-11	**Enhancing Electrochemical Performance of Titanium Oxide Nanotubes-Based Materials** J. Bitenc, A. Rozman, B. Erjavec, E. Chernyshova, M. Bele, M. Gaberšček
16.55-17.05 SS-O-12	**Spectroscopic and Electrochemical Sensing of Lanthanides with Azulene Chromophores** C.-A. Amarandei, E.-M. Ungureanu, A. C. Razus, L. Birzan
17.05-17.15 SS-O-13	**Voltammetric Study for the Detection of Food Dyestuff Red Allura Ac in Soft Drinks** M.M. Jurcovan, E. Diacu, E. M Ungureanu, A.A. Ivanov
17.15-17.25 SS-O-14	**Severe Accelerated Degradation of a Thin Film Platinum Based Catalysts** N. Hodnik, M. Zorko, B. Jozinović, M. Bele, G. Dražič, S. Hočevar, M. Gaberšček
Hall: Kronos **Chairpersons: I. Milošev and L.M. Muresan**	
16.45-16.55 SS-O-15	**The Electrochemical Behaviour of Some Metallic Materials Used as Implants in the Presence of Lactic Acid Addition in Human Serum** G. Totea, I. Demetrescu, D. Ionita
16.55-17.05 SS-O-16	**Cerium-Conversion Coatings for Corrosion Protection of Aluminium and Aluminium Alloy 7075-T6** P. Rodič, I. Milošev
17.05-17.15 SS-O-17	**Synthesis of Silver Nanoparticles in Poly(Vinyl Alcohol) Solution by Electrochemical Method** R. Surudžić, Ž. Jovanović, V. Mišković-Stanković
17.15-17.25 SS-O-18	**PLD Deposited Thin Films on Titanium Modified by TiO_2 Nanotubes** S. Eraković, A. Janković, C. Ristoscu, L. Duta, N. Serban, A. Visan, G. Stan, M. Socol, C. R. Luculescu, I. N. Mihailescu, V. Misković-Stanković
Hall: Janus **Chairperson: M. Korenčan**	
17.30-19.00	**Seminar «INTERNATIONAL COLLABORATION«** **EU Financial Instruments for Research** S. Možina, Research Adviser, Permanent Representation of the Republic of Slovenia to the EU **Coordination of EU FP7 Project - Experience from Eurolis** R. Dominko, National Institute of Chemistry
19.00-	Welcome drink (Marco Polo Restaurant at the Austria Trend Hotel)

MONDAY, May 27, 2013	
8.15-	**Registration**
Hall: Janus **Chairpersons: M. Gaberšček and I. Milošev**	
9.00-9.30	**Opening ceremony**
9.30-10.10 PL-01	**Building the Energy Highway** N.M. Markovic
10.10-10.50 PL-02	**Electrochemistry of Solid Oxide Fuel Cells: What Makes the Difference to the World of Aqueous Electrochemistry?** J. Fleig
10.50-11.10	Coffee break
Chairpersons: M. Gaberšček and J. Jamnik	
11.10-11.35 KN-01	**Permittivity Spectroscopy – Principles and Application** Z. Stoynov, E. Mladenova, D. Levi, D. Vladikova
11.35-11.50 ECS-O-01	**Synchrotron-Based in situ Characterization of PEMFC, SOFC and Supercapacitor Components** B. Bozzini, P. Bocchetta, A. Gianoncelli, L. Gregoratti, C. Mele, M. Kiskinova
11.50-12.05 ECS-O-02	**Catalytic Properties of Ir/EBonex On Non-Carbon Gdl As Anode In Pem Water Electrolysis** K. Pirnat, R. Dominko, M. Gaberšček
12.05-12.20 ECS-O-03	**Catalytic Properties of Ir/EBonex on Non-Carbon GDL os Anode in PEM Water Electrolysis** G. Borisov, E. Slavcheva
12.20-12.35 ECS-O-04	**PtNi On Hollow Graphitc Spheres: Activity and Stability** C. Baldizzone, S. Mezzavilla, J.C. Meier, A. Kostka, C. Galeano, F. Schüth, K.J.J. Mayrhofer
12.35-12.50 ECS-O-05	**Comparative Study on The Electrochemical Behaviour of Iridium Oxide Prepared by Magnetron Sputtering and Sol Gel Deposition Methods** E. Slavcheva, G. Borisov, E. Lefterova
12.50-13.05 ECS-O-06	**Initial Conditioning of Pem Fuel Cell by Temperature and Potential Cycling** F. Barbir, D. Bezmalinović, J. Radošević
13.05-15.00	Lunch
15.00-15.15 ECS-O-07	**Hybrid 3D Analytic-Numerical Approach for Computationally Efficient Modelling of Species Transport in PEM Fuel Cells** G. Tavčar, T. Katrašnik
15.15-15.30 ECS-O-08	**Nitrogen-Doped Hollow Core Mesoporous Shell Carbon as Advanced Electrocatalysts for Oxygen Reduction Reaction** M. Young Song, J.-S. Yu
15.30-15.45 ECS-O-09	**Mesoporous Silicas in Lithium Sulfur Batteries** V. Lapornik, N. Novak-Tušar, M. Gaberšček, R. Dominko
Hall: Janus **Chairpersons: E. Daciu and N. Vaszilcsin**	
15.50-16.15 KN-02	**Heteroatom-Doped Mesoporous Carbon as Efficient Cathode Material for Oxygen Reduction** D.-S.Yang, M. Young Song, H. Park, N. Chaudhari, J.-S. Yu
16.15-16.35	Coffee break

16.35-16.50 EOE-O-01	**Fischer Aminocarbene Complexes: Effects of Structure on Redox Properties** R. Metelková, H. Kvapilová, I. Hoskovcová, J. Ludvík
16.50-17.05 EOE-O-02	**Fluorenone Dianion Protonation. Unusual pK_1/pK_2 Ratio** A.S. Mendkovich, M.A. Syroeshkin, M.N. Mikhailov, D.V. Ranchina, A.I. Rusakov
17.05-17.20 EOE-O-03	**Correlation of UV-VIS, NMR and EPR Spectra in Electrochemical Reduction of a New Explosive Fox-7** L. Šimková, J. Klíma, J. Ludvík
17.20-17.35 EOE-O-04	**Treatment of Pharmaceutical Substances in Medical Waste Water by a Combination of Anodic Oxidation and Sterilization** H. Menapace, R. Sarc, W. Staber, H. Katschnig
Hall: Kronos **Chairpersons: J. B. Bajat and G.G. Láng**	
15.50-16.15 KN-03	**New Challenges in the Design of Electrochemical (Bio)Sensors** C. Bala
16.15-16.35	Coffee break
16.35-16.50 ESG-O-01	**Effects of (Poly)-Ethylene Glycol on the Stability and Electrochemical Properties of Pedot: PSS Films** A. B. Stoian, C. Pirvu, I. Demetrescu
16.50-17.05 ESG-O-02	**Generation and Electrochemical Nanogravimetric Response of The Third Anodic Hydrogen Peak on a Platinum Electrode in Sulfuric Acid Media** G. Inzelt, B.B. Berkes
17.05-17.20 ESG-O-03	**Electrochemical Immunoassays for the Detection of Mucines Cancer Biomarkers** A. Florea, A. Ravalli, C. Cristea , R. Săndulescu, G. Marrazza
17.20-17.35 ESG-O-04	**Methanol Oxidation at Platinum-Based Electrocatalysts** N. Hodnik, M. Bele, S. Hočevar
17.35-19.00	**POSTER Session I: ECS, EOE, ESG, BIO, FSM, NTM**
19.00-	Welcome party (Marco Polo Restaurant at the Austria Trend Hotel)

TUESDAY, May 28, 2013	
Hall: Janus **Chairpersons: I. Milošev and M. Gaberšček**	
9.00-9.40 PL-03	**Electrochemical Reactivity and Nanostructure of Metal Surfaces and Thin Oxide Films: Key Issues for Corrosion and Passivation** P. Marcus
Chairpersons: I. Milošev and V. Mišković-Stanković	
9.40-10.05 KN-04	**Corrosion Behaviour of Plasma Electrolytic Coatings on Aluminium in Sodium Chloride Solution** J.B. Bajat
10.05-10.20 CPA-O-01	**Thiadiazole Derivatives as Inhibitors for Acidic Media Corrosion of Artificially Patinated Bronze** R. Bostan, S. Varvara, L. M. Muresan
10.20-10.35 CPA-O-02	**The Relation Between Adsorption Bonding and Corrosion Inhibition of Azoles on Copper** N. Kovačević, A. Kokalj, I. Milošev
10.35-10.50 CPA-O-03	**The Effect of Soiling and Oxidation on Titanium Exposed to Outdoor Environments** M. P. Pedeferri, M. V. Diamanti
10.50-11.10	Coffee break
11.10-11.25 CPA-O-04	**Preparation and Characterization of Self- Assembled Monolayer of Stearic Acid for Protection of Cupronickel Alloy** N. Šimunčić, Z. Hajdari, K. Marušić, H. Otmačić Ćurković
11.25-11.40 CPA-O-05	**Investigation of Chloride Adsorption on Oxide Covered Steel Samples with the Novel 'Thin Gap' Method** D. Horváth, Zs. Kerner, T. Kovács, K. Varga, T. Pintér
11.40-11.55 CPA-O-06	**Designing Corrosion Inhibitor Formulations for Acid Stimulations** M. Finšgar, J. Jackson
11.55-12.10 CPA-O-07	**Comparison of Results from Standardized Cyclic Corrosion Testing and Flowing Electrolyte on the Corrosion Behaviour of Hot Dipped Galvanized Steel** M. Voith, A.W. Hassel, T. Keppert, G. Luckeneder, K. Stellnberger
12.10-12.25 CPA-O-08	**Corrosion Protection of Hot Dip Galvanized Low Carbon Steel using Conducting Polyaniline Based Paints** P. P. Deshpande
12.25-15.00	Lunch / Meeting of Scientific and Organizing Commitees
Hall: Janus **Chairpersons: D. Vladikova and J. Ludvik**	
15.00-15.25 KN-05	**Origin of Pseudocapacitances in Transition Metal Oxides and Conducting Polymers** Z. Mandić
15.25-15.40 PAE-O-01	**Chemically Modified Electrodes Based on Polyazulene Complexing Films for Lead and Cadmium Metal Ions Electroanalysis** E.-M. Ungureanu, G.-O. Buica
15.40-15.55 PAE-O-02	**Effect of Photo-Oxidation of Ascorbic Acid on The Analysis of Hydrogen Peroxide using Titanium-Porphyrin Reagent** K. Takamura, T. Matsumoto
15.55-16.10 PAE-O-03	**Electrochemical Analysis of Polysaccharides on Static Mercury Drop Electrode** S. Strmečki Kos, M. Plavšić
16.10-16.25 PAE-O-04	**Investigation of Platinum Stability by In-Situ Mass Spectrometry** A. A. Topalov, S. Cherevko, A. R. Zeradjanin, K. J. J. Mayrhofer

16.25-16.40 PAE-O-05	**Investigation of the Reduction of Perchlorate Ions on Rhodium and Ruthenium** G.G. Láng, M. Ujvári
16.40-17.00	Coffee break
Hall: Kronos **Chairpersons: B. Nikolić and G. Inzelt**	
15.00-15.25 KN-06	**Improvement of Electrocatalytic Activity of Non-Platinum Electrode Materials as Result of Carbonaceous Support Material Modification** P. Paunović, O. Popovski, A.T. Dimitrov
15.25-15.40 SDE-O-01	**Pulse Plated and Laser Ablated Silver Nanocoatings for Biomedical Applications** M. Lakatos-Varsányi, T. Pozman, M. Furko, Z. Kónya, Á. Kukovecz, Cs. Bodor, L. Rosivall, T. Perlaky, M. Szendrői, M. Soós
15.40-15.55 SDE-O-02	**Electroplated Ferromagentic Nanostructures for Different Applications** K. Žužek Rožman, D. Pečko, N. Kostevšek, U. Maver, P. Nadrah, M. Zorko, M. Bele, S. Kobe
15.55-16.10 SDE-O-03	**Study of Electrolytic Reduction into Lithium and Sodium Molten Salts** A. T. Dimitrov, A. Ademi, P. Paunović
16.10-16.25 SDE-O-04	**Electrochemical Synthesis of Titania Nanopowder Involving Choline Chloride Based Ionic Liquids with Extended Visible Light Response** L. Anicai, A. Petica, S. Costovici
16.25-16.40 SDE-O-05	**Composition Depth Profile of D.C.-Plated and Pulse-Plated Fe-Ni Alloys** K. Neuróhr, K. Vad, A. Csik, G. Molnár, I. Bakony, L. Péter
16.40-17.00	Coffee break
17.00-19.00	**POSTER Session II: CPA, SDE, PAE**
20.00-	Dinner (Marco Polo Restaurant at the Austria Trend Hotel)

WEDNESDAY, May 29, 2013

Hall: Janus **Chairpersons: I. Milošev and M. Gaberšček**	
9.00-9.40 PL-04	**TiO_2 Nanotubes and Other Self-Organized Anodic Structures: Formation and Applications** P. Schmuki
Chairpersons: D. Vladikova and J. Ludvik	
9.45-10.00 PAE-O-06	**On The Nature of the Electrochemical Double Layer** T. Pajkossy
10.00-10.15 PAE-O-07	**Faradaic Adsorption of Lithium on the Surface of Carbon Fiber Studied by Cyclic Voltammetry and Raman Spectroscopy** T. Takamura, F. Mouri
10.15-10.30 PAE-O-08	**On the Applicability of Maxwell Relations in Surface Thermodynamics and Electrochemistry** E.M. Gutman
10.30-11.00	Coffee break

Hall: Janus **Chairpersons: I. Milošev and L.M. Muresan**	
11.00-11.25 KN-07	**Electrochemical Properties and Surface Characterisation of Anodic Zirconium Oxide Grown in Phosphoric Acid for Permanent Implants** S. Ceré
11.25-11.40 BIO-O-01	**New Procedure in Electrochemical Synthesis of Silver Nanoparticles: Inside Poly(N-Vinyl-2-Pyrrolidone) Hydrogel** Ž. Jovanović, B. Nikolić, V. Mišković-Stanković
11.40-11.55 BIO-O-02	**On The Role of Dipole and Quadrupole Moment of Water Molecules in Spatial Variation of Permittivity in Electrolyte Solution near a Highly Charged Surface** A. Iglič, E. Gongadze, V. Kralj-Iglič
11.55-12.10 BIO-O-03	**Studies on Application of Metalloporphyrins as Potential Protein Labels** K. Konopińska, M. Pietrzak, E. Malinowska
12.10-12.25 BIO-O-04	**Electrochemically Assisted Formation of Hydroxyapatite Coatings on Nitinol** J. Katić, M. Metikoš-Huković, R. Babić
12.25-12.40 BIO-O-05	**Optimization of Two Pulse-Based Amperometric Detection of Selected Bio-Molecules** M. Novič, D. Kotnik, B. Pihlar
Hall: Kronos **Chairpersons: E.-M. Ungureanu and P. Paunović**	
9.45-10.10 KN-08	**Material Science Aspects of Conducting Polymer Based Hybrid Assemblies for Electrochemical Sensing** Cs. Janáky, Cs. Visy
10.10-10.25 FSM-O-01	**Gases Permeability Study in Dual Membrane Fuel Cell** E. Mladenova, D. Vladikova, Z. Stoynov, A. Chesnaud, A. Thorel, M. Krapchanska
10.25-10.40 FSM-O-02	**Electrochemical and Microstructural Investigations on Al-Cu-Ni Thin Films** M. Hafner, A.I. Mardare, A.W. Hassel
10.40-11.00	Coffee break
11.00-11.15 FSM-O-03	**Rational Design of Morphological Pattern for Efficient Electrocatalytic Gas Evolution** A.R. Zeradjanin, A.A. Topalov, S. Cherevko, W. Schuhmann, K.J.J. Mayrhofer
11.15-11.30 FSM-O-04	**Advanced Electrochemical Interfaces** D. Strmcnik, N.M. Marković, V.R. Stamenkovic
11.30-11.45 FSM-O-05	**New Electroactive Polyaniline/Polyacrylamide Hydrogel Composites** M. A. Smirnov, P. V. Vlasov, I. Yu. Dmitriev, V. Bukošek, G. K. Elyashevich
11.45-12.00 FSM-O-06	**Copper Corrosion in Saline/Bentonite Environment, Studied by Coupled Multi Electrode Arrays** T. Kosec, B. Rosborg, A. Legat
12.00-12.15 FSM-O-07	**Geometry-Performance Relationship of Organic Electrochemical Transistors** P. Hütter, T. Rothländer, H. Gold, G. Jakopic, P. Hartmann, B. Stadlober
12.15-12.30 FSM-O-08	**Thickness and Structure of Thin Anodic TiO_2 Films** M.V. Diamanti, M.P. Pedeferri
12.30-12.45 FSM-O-09	**Characterization of Reactively Co-Sputtered Cu-Ni Material Libraries Using a Scanning Kelvin Probe** W. Burgstaller, A.W. Hassel
12.45-15.00	Lunch
14.30-	Excursion to Škocjan Cave

THURSDAY, May 30, 2013

Hall: Janus **Chairpersons: M. Gaberšček and I. Milošev**	
9.00-9.40 PL-05	**Electrochemistry of Nucleic Acids: Label-Free DNA Sensing and DNA Redox Labeling** M. Fojta
Chairpersons: Z. Mandić and V. Horvat-Radošević	
9.40-10.05 KN-09	**Computational Modeling of New Materials for Electrochemical Solar-To-Fuel Energy Conversion** S. Fabris, S. Piccinin, C. Ma, X. L. Hu, A. Laio
10.05-10.20 NTM-O-01	**Polarographic Study of Antioxidants Interactions with Hg(II) and its Hydroxo-Perhydroxyl Complex** D. Sužnjević, F. T. Pastor, S. Gorjanović, S. Milić
10.20-10.35 NTM-O-02	**Reversible Electrochemical Contact Angle Switching of Hexagonal Boron Nitride Nanomesh** S. F. L. Mertens, S. Muff, A. Hemmi,R. Küng, S. De Feyter, J. Osterwalder, T. Greber
10.35-10.50 NTM-O-03	**Anodic Titanium Nanotubes with Crystallinity Prepared in Organic Electrolytes** C. Dumitriu, C. Pirvu, I. Demetrescu
10.35-11.00	Coffee break
Chairpersons: Z. Mandić and A. Dimitrov	
11.00-11.15 NTM-O-04	**Ambiguitiy in Modelling and Interpretation of Impedance Spectra of Gc Electrodes** V. Horvat-Radošević, K. Magdić, K. Kvastek
11.15-11.30 NTM-O-05	**Chloride Adsorption Investigation Using Combined Electrochemical Quartz Crystal Microbalance Radiotracer Technique** Zs. Kerner, R. Répánszki
11.30-11.45 NTM-O-06	**Combination of Nanogravimetry and Visible Spectroscopy: A Tool for the Better Understanding of Electrochemical Processes** B.B. Berkes, S. Vesztergom, G. Inzelt
11.45-12.00 NTM-O-07	**Rotating Ring-Disk Electrode with Dual Dynamic Potential Control: Theory and Practice** S. Vesztergom, G.G. Láng
12.00-12.15 NTM-O-08	**Impedance Investigation of Bace$_{0.85}$y$_{0.15}$o$_{3-\delta}$ Properties for Hydrogen Conductor in Fuel Cells** G. Raikova, M. Krapchanska, I. Genov, G. Caboche, L. Combemale, A. Thorel, A. Chesnaud, D. Vladikova, Z. Stoynov
12.15-12.30 NTM-O-09	**Mathematical Models, Dynamical Analysis and Synthesis in Fields of Electrochemistry and Bioelectrochemistry** N. A. Kablar, V. Kvrgić
12.30-12.40	Closing remarks
12.40-14.00	Lunch
14.00-	Walking tour through Ljubljana

PL: Plenary lecture, IL: Invited lecture, KN: Key-note lecture

Sessions:

1. **ECS** - Energy Conversion and Storage Devices
2. **EOE** - Environmental and Organic Electrochemistry
3. **ESG** - Electrochemical and Electronic Sensors and General Electrochemistry
4. **CPA** - Corrosion, Passivation and Anodic Films
5. **PAE** - Physical and Analytical Electrochemistry
6. **SDE** - Electrochemical Synthesis, Deposition and Electrolysis
7. **BIO** - Bioelectrochemistry and Biomedical Applications
8. **FSM** - Electrochemistry of Functional Structures and Materials
9. **NTM** - Nanoscale and Molecular Electrochemistry, and Experimental and Theoretical Methods of Electrochemistry

PL

PLENARY LECTURES

PL-01

BUILDING THE ENERGY HIGHWAY

Nenad M. Markovic
Materials Science Division, Argonne National Laboratory,
Lemont, IL 60 559 USA

Design and synthesis of energy efficient and stable electrochemical interfaces (materials and double layer components) with tailor properties for accelerating and directing chemical transformations is the key to developing new alternative energy systems – fuel cells, electrolizers and batteries. In this lecture, we address the importance of covalent and non-covalent interactions in controlling catalytic activity at electrochemical interfaces. Although the field is still in its infancy, a great deal has already been learned and trends are beginning to emerge that give new insight into the relationship between the nature of bonding interactions and catalytic activity/stability of electrochemical interfaces. In addition, to bridge the gap between a “water battery” (fuel cell ↔ electrolyzer) and a Li-oxygen battery systems we demonstrate that this would require fundamentally new knowledge in several critical areas. We conclude that understanding the complexity (simplicity) of electrochemical interfaces would open new avenues for design and deployment of alternative energy systems.

PL-02

ELECTROCHEMISTRY OF SOLID OXIDE FUEL CELLS: WHAT MAKES THE DIFFERENCE TO THE WORLD OF AQUEOUS ELECTROCHEMISTRY?

J. Fleig
Vienna University of Technology, Institute of Chemical Technologies and Analytics,
Vienna, Austria

The kinetic processes taking place in operating electrochemical cells are always the same: anodic oxidation, ion conduction, cathodic reduction. At first glance it may therefore be surprising that a substantial gap in mutual understanding can often be found between “solid state electrochemists” and “liquid electrochemists”. In this contribution, the science of solid oxide fuel cells (SOFCs) is taken as an example in order to illustrate that indeed approaches, concepts and tools used in solid state electrochemistry are partly different from those of established aqueous electrochemistry: Ion conduction based on point defects, electrode reactions not taking place at the electrode/electrolyte interface, electrodes not only being electron but also ion conductors, etc..

PL-03

ELECTROCHEMICAL REACTIVITY AND NANOSTRUCTURE OF METAL SURFACES AND THIN OXIDE FILMS: KEY ISSUES FOR CORROSION AND PASSIVATION

Philippe Marcus
Laboratory of Physical Chemistry of Surfaces, Chimie ParisTech-CNRS (UMR 7045), Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, 75005, Paris, France

Recent advances in the understanding of corrosion mechanisms, including passivity and passivity breakdown of metals and alloys, have been achieved by investigating the electrochemical reactivity of well-defined surfaces at the nanoscale.

The aim of this lecture is to present a selection of examples in which the relationship between nanostructure and reactivity of metal surfaces has been revealed, with emphasis on applications to corrosion and passivation .

The following points will be addressed:

- The metal-water interface: early stages of interaction studied *in situ* by Electrochemical Scanning Tunneling Microscopy (Cu, Ag)
- Formation of structurally ordered monolayers of sulphur on silver electrodes studied by EC-STM
- Nanostructure of passive films on metals and alloys
- Local electronic properties of ultra-thin oxide layers investigated by Tunneling Spectroscopy
- Atomistic modeling (DFT) of the interactions of chloride ions with hydroxylated oxide surfaces (mechanisms of localized corrosion initiation)

PL-04

TIO$_2$ NANOTUBES AND OTHER SELF-ORGANIZED ANODIC STRUCTURES: FORMATION AND APPLICATIONS

Patrik Schmuki
University of Erlangen Nuremberg, Dept. of Materials Science, LKO, Martensstr. 7, 91058 Erlangen, Germany

The presentation demonstrates approaches to achieve electrochemical fabrication of self-organized high aspect ratio titanium oxide layers with robust meso-scale feature sizes. Several highly promising geometries, nanotubular, nanochannel and nanosponge materials, are being compared. These different self-organized morphologies can be produced by anodic oxidation of Ti metal surfaces but the resulting oxides have considerably different physical chemical and mechanical properties.Titanium oxide is a wide band-gap semiconductor that is extremely stable to photocorrosion. The material is highly functional and has, for example, unique surface catatytic properties and provides a high degree of biocompatibility Therefore it has a high potential for various technological exploitation. The talk will address synthesis and applications of the different TiO$_2$ nanoscale architectures.

For reviews on TiO$_2$ nanotubes:

- P. Roy, S. Berger, P. Schmuki, Angew. Chem. . (2011) 50, 2904
- Paramasivam, I., Jha, H., Liu, N., Schmuki, P. (2012) *Small* 8,. 3073

PL-05

ELECTROCHEMISTRY OF NUCLEIC ACIDS: LABEL-FREE DNA SENSING AND DNA REDOX LABELING

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Nucleic acids (NAs) possess intrinsic electrochemical activity due to reduction (at mercury and amalgam electrodes) or oxidizable (usually at carbon electrodes) nucleobases and/or characteristic adsorption/desorption processes. These properties have been utilized in label-free electrochemical DNA sensing techniques, particularly detection of DNA damage and other changes in DNA structure. In other applications, typically focused on analysing DNA sequences, utilization of electroactive labels has appeared advantageous. A labelled DNA probe or a nucleotide encoded by a tag giving specific electrochemical signal can be detected in a large excess of nonspecific DNA sequences with a high selectivity and sensitivity. Several approaches to introducing redox-active or enzymatic labels into NA have been developed, including chemical modification with oxoosmium complexes and incorporation of labelled nucleotides by enzymes.

References

1. E. Palecek, M. Bartosik: *Chem. Rev.* **2012,** *112*, 3427-3481.
2. M. Hocek, M. Fojta, *Chem. Soc. Rev*. **2011**, *40,* 5802-5814

KN
KEY NOTE
LECTURES

KN-01

PERMITTIVITY SPECTROSCOPY – PRINCIPLES AND APPLICATION

Z. Stoynov, E. Mladenova, D. Levi, D. Vladikova
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The permittivity spectroscopy which is a kind of the Impedance Spectroscopy has shown to be a powerful method for studying objects with dielectric properties, yielding valuable insights into the characteristics of wide range of materials, including polymers, ceramics, rubber, wood, adhesives, waxes, oils etc.

The basic principles of the permittivity spectroscopy will be discussed together with the necessary advanced techniques for its application. They will be elucidated by practical examples of permittivity spectroscopy studies of selected objects – lubricating oils and formation of liquid films in porous ceramic systems, where unexpected phenomenon of gigantic enhancement of the effective capacitance has been found.

KN-02

HETEROATOM-DOPED MESOPOROUS CARBON AS EFFICIENT CATHODE MATERIAL FOR OXYGEN REDUCTION

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Platinum based materials have long been investigated as active catalysts for oxygen reduction reaction (ORR) in fuel cells[1-2]. However, the large-scale application of fuel cells has been disturbed by the high cost, shortage and instability of the precious Pt metal. In this work, we report the fabrication of novel heteroatom (N, P, and S)-doped mesoporous carbons through nanocasting method using corresponding N, P,or S precursor as heteroatom and carbon source[3-4]. As-made hetero atom-doped porous carbon exhibits comparable or better catalytic activity and long-term stability than a commercial Pt/C catalyst towards ORR.

References

1. B. Fang, J. H. Kim, M.-S. Kim, J.-S. Yu, *Chem. Mater.*, **2009**, *21*, 789.
2. J. Zhang, K. Sasaki, E. Sutter, R. R. Adzic, *Science* **2007**, *315*, 220 .
3. D.-S, Yang, D. Bhattacharjya, S.Inamdar, J. Park, J.-S. Yu, *J. Am. Chem. Soc.*, **2012**, *134*, 16127.
4. B. Fang, M. S. Kim, J. H. Kim, J.-S. Yu, *Acc. Chem.Res.*, 10.1021/ar300253f

KN-03

NEW CHALLENGES IN THE DESIGN OF ELECTROCHEMICAL (BIO) SENSORS

Camelia Bala
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This lecture will present the design of new biosensors and bioanalytical systems based on different materials which allow real applications to solve analytical problems. Acetylcholinesterase is the target of many neurotoxins and drugs that bind specifically to its active site. The electrocatalytic behavior of carbon nanotubes/ionic liquids nanocomposite materials towards oxidation of enzymatically generated thiocholine was recently reported[1]. Different composite materials promoted electron transfer reaction at a lower potential and catalyzed electrochemical oxidation of thiocholine leading to electrochemical enhancements with respect to response time, sensitivity and stability of the biosensors will be reported [2,-4].

1. L. Rotariu, L-G. Zamfir, C. Bala, *Sens. Actuat. B.,* **2010**, 150, 73–79.
2. L-G. Zamfir, L. Rotariu, C. Bala, *Biosens. Bioelectron*., **2011,** 26, 3692–3695.
3. L. Rotariu, L.-G. Zamfir, C. Bala, Anal. Chim. Acta, **2012**, 748, 81-88.

KN-04

CORROSION BEHAVIOUR OF PLASMA ELECTROLYTIC COATINGS ON ALUMINIUM IN SODIUM CHLORIDE SOLUTION

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Plasma electrolytic oxidation (PEO) is a technique in which the surface of metals or metallic alloys can be used to form thick oxide coatings by plasma discharges in suitable electrolytes[1]. Tungsten containing oxide layers on aluminium are widely investigated due to their catalytic, electro-optic and corrosion protection properties. Novel PEO coatings, containing additional small amounts of zirconium, were synthesized, at different current densities (*j*) and anodization time. Morphology, chemical and phase composition of PEO coatings are strongly associated to PEO time. Electrochemical impedance measurements (EIS) were performed in 3% NaCl to characterize the degradation of PEO coatings. The evolution of EIS spectra with immersion time for coatings deposited at 5 and 7.5 min at small *j*, as well as at 2 min at higher *j* suggest increased corrosion stability.

References

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KN-05

ORIGIN OF PSEUDOCAPACITANCES IN TRANSITION METAL OXIDES AND CONDUCTING POLYMERS

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Development of electrochemical supercapacitors as high power and storage devices are in the focus of scientific and technological interest in the last decade. They are based on either double layer charging of the interface between electrolyte and highly-porous polarisable materials such as carbon or on the utilization of the fast and reversible solid state faradaic reaction. The most promising pseudocapacitive materials are transition metal oxides and conducting polymers. Due to the great variety of different solid state structures, chemical compositions and morphology of these materials, a great attention has to be paid when preparing and designing these materials in order to achieve sufficient energy density, long term stability and reversibility.

Recent results obtained on electrochemical properties of thin layers of transition metal oxides (RuO_2, MnO_2 and NiOOH), conducting polymers (polyaniline, polypyrrole) and their composites reveal the complexity of pseudocapacitive reactions and importance of the optimization of properties such as combined proton/electron conduction, chemical stability in the wide potential range, fast ion dynamics and different physico-chemical interactions.

KN-06

IMPROVEMENT OF ELECTROCATALYTIC ACTIVITY OF NON-PLATINUM ELECTRODE MATERIALS AS RESULT OF CARBONACEOUS SUPPORT MATERIAL MODIFICATION

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[2]*Military Academy "Mihailo Apostolski", Skopje, R. Macedonia*

The modern electrode materials are composed of nanostructured catalytic phase dispersed over the support material which has to possess several very important characteristics, such as: *i*) highly developed surface area to provide better dispersion of the nano-scaled catalytic particles; *ii*) high electric conductivity to allow efficient electron transfer to ions involved in the electrochemical reactions, *iii*) mechanical and chemical stability and *iv*) to improve intrinsic catalytic activity of the active catalytic phase through the strong metal-support interaction (SMSI).

Carbon nanostructured materials such as carbon blacks are commercially the most used support material. The subject of this paper is to show a comparison of performances of nano-scaled Co-based catalytic material deposited on several support materials such as: i) Vulcan XC-72, ii) Vulcan XC-72 with TiO_2, iii) multiwalled carbon nanotubes (MWCNTs) TiO_2 and iv) Magneli phases – nonstoichiometric titanium oxides. Comparison of catalytic activity of Co-based electrocatalysts deposited on all mentioned support materials is given.

KN-07

ELECTROCHEMICAL PROPERTIES AND SURFACE CHARACTERISATION OF ANODIC ZIRCONIUM OXIDE GROWN IN PHOSPHORIC ACID FOR PERMANENT IMPLANTS

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The rapid increase in demand of medical implants requires materials of high chemical resistance in biological environments. For this, the mechanical properties and good biocompatibility of zirconium and some of its alloys make them highly suitable for biomedical applications. The aim of this work is to study the electrochemical properties and film structure of zirconium anodic oxides grown in phosphoric acid for eventual use as permanent biomedical implants. Zirconium oxide films were electrochemically grown by anodisation in phosphoric acid solution to induce surface modifications. The films were electrochemically characterised. The flat band potential calculated from the Mott-Shottky analysis confirms the formation of a bilayer structure of the oxide film. The problems associated with the determination of film thickness from impedance measurements are discussed.

KN-08

MATERIAL SCIENCE ASPECTS OF CONDUCTING POLYMER BASED HYBRID ASSEMBLIES FOR ELECTROCHEMICAL SENSING

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[2]*Dept. Chemistry and Biochemistry, Univ. of Texas at Arlington, USA*

During the last two decades, the progress achieved in amperometric sensing of different analytes over conducting polymer based hybrid electrocatalysts has shown an exponential trend. In this paper representative examples are given for conducting polymer based hybrids – with the incorporation of special dopant ions, noble metal nanoparticles, carbon based nanomaterials, inorganic compounds – demonstrating that they play a notable role in the field of electrochemical sensing. Numerous approaches to obtain both binary and ternary composites of real synergistic effect – including purely chemical, electrochemical and mixed methods – are also summarized.

References
1. Cs. Janáky, C. Visy, *Anal Bioanal Chem, in press: DOI 10.1007/s00216-013-6702-y*

KN-09

COMPUTATIONAL MODELING OF NEW MATERIALS FOR ELECTROCHEMICAL SOLAR-TO-FUEL ENERGY CONVERSION

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[1]*CNR-IOM DEMOCRITOS and SISSA – Via Bonomea 265, Trieste, Italy*

The conversion and storage of solar energy into chemical fuels rely on finding novel catalytic materials for the electrochemical splitting of water. These catalysts should be stable, inexpensive, efficient and easily integrable in photovoltaic units. The quest for catalyst optimization is plagued by the elusive description of the active sites on oxide surfaces. In this talk I will discuss how state-of-the-art computational modeling can provide the missing insight into the structure and function of nano-sized molecular catalysts (Ru4–polyoxometalate) and nanocrystalline amorphous cobalt-phosphate catalysts. The calculated results[1-3] allow for rationalizing the available experimental data and identify the origins of the high reactivity and stability of these novel catalysts.

References

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2. X.L. Hu, A. Laio, S. Piccinin, and S. Fabris, *ACS Nano* **2013***, 6*, 10497.
3. S. Piccinin, A. Sartorel, Aquilanti, Goldoni, M. Bonchio, S. Fabris, PNAS (2013).

ECS
Energy Conversion and Storage Devices

ORAL PRESENTATIONS

ECS-O-01

SYNCHROTRON-BASED IN SITU CHARACTERIZATION OF PEMFC, SOFC AND SUPERCAPACITOR COMPONENTS

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Luca Gregoratti[2] , Claudio Mele[1] and Maya Kiskinova[2]
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Fuel cells and supercapacitors are electrochemical devices providing efficient and pollution-free production and transformation of electricity. Notwithstanding their environmental appeal, a host of materials-science problems – chiefly related to the limited durability of crucial functional components – are hindering the widespread application of these otherwise promising devices. Nanotechnology is foreseen to play a key role in the elimination of such drawbacks. Some nanotechnology solutions have already led to sensitive improvements of properties, functionality and performance of some components. However, the present knowledge is mostly at the macroscopic and empirical trial-and-error level and the answers to many questions require much deeper scientific understanding of the origin of degradation processes. In this regard, the development and implementation of appropriate methods for in-situ characterization of cell components at the functionally relevant length scales is highly required. Soft X-ray spectroscopies, namely X-ray absorption spectroscopy, X-ray emission (fluorescence) spectroscopy, resonant inelastic X-ray spectroscopy and X-ray photoelectron spectroscopy have been extensively employed for ex-situ characterization of materials used in electrochemical systems. Furthermore, adding spatial resolution capabilities by implementing proper optical solutions has opened unique opportunities for monitoring material changes and mass transport events occurring at submicron length scales. The input from these methods is providing correlative information about the status of the electrode surface and of the electrode/electrolyte interface and also of the processes occurring under operation conditions at the three phase boundary, namely the electrode-electrolyte-reactant interface[1-7].

References
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2. B. Bozzini et al., *J. Power Sources*, **2012**, *211*, 71–76.
3. B. Bozzini et al., *Electrochem. Comm.*, **2012**, *24*, 104–107.
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ECS-O-02

1,2,4,5-TETRAMETHOXYBENZENE AS A REDOX SHUTTLE

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Redox shuttles are compounds used for overcharge protection of commercial Li-ion batteries. They are soluble in electrolyte and are oxidized at high potential to a stable radical cation, which migrates to the opposite electrode, where it is reduced to the initial oxidation state again. The shuttle molecule therefore carries the charging current during overcharge and prevents increase of potential. Most of the redox shuttles are different dimethoxybenzenes and other organic molecules.[1] Recently, we synthesized and characterized a new compound 1,2,4,5-tetramethoxybenzene (MB) with a redox potential 3,65 V vs. lithium. Initial tests in Li/$LiFePO_4$ battery showed good results when we used 3 % (wt.) solution of MB in electrolyte 1 M $LiPF_6$ EC/DEC=1:1.[2]

References
1. C. Buhrmester, J. Chen, L. Moshurchak, J. Jiang, R. L. Wang, J. R. Dahn, *J.Electrochem. Soc*., 2005, *152 (12)*, A2390–A2399.
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ECS-O-03

CATALYTIC PROPERTIES OF IR/EBONEX ON NON-CARBON GDL AS ANODE IN PEM WATER ELECTROLYSIS

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A composite nano scaled catalyst was synthesised by dispersion of iridium on electrically conductive oxide - Magnelli phase titania (Ebonex®). The supporting material was mechanically pre-treated to reduce the particle size and thus, to achieve higher surface area. The composition, surface structure and morphology of the catalyst were characterized by XRD, EDX, and SEM analysis. Then, a catalytic ink was prepared and spread out as a thin film over a non-carbon gas diffusion layer, integrated in a membrane electrode assembly (MEA) with Nfion 117 proton exchange membrane and tested as anode for hydrogen generation via PEM water electrolysis. The electrochemical behaviour and the catalytic activity toward OER were investigated using cyclic voltammetry, polarization curves and long term potentiostatic experiments. The Ir/Ebonex showed an improved catalytic efficiency compared to the reported literature data for similar systems, reaching a current density of more than 1 $A.cm^{-2}$ at potential of 1.8 V, 80 ^{o}C, and catalytic loading of 0.2 $mg.cm^{-2}$. The MEA demonstrated stable performance during a 240 h long durability tests.

ECS-O-04

PtNi ON HOLLOW GRAPHITC SPHERES: ACTIVITY AND STABILITY

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Due to pore confinement, Pt catalysts supported on mesoporous graphitic spheres demonstrate a significant increase in stability versus commercial carbon supported cathode catalysts and are therefore excellent candidates for PEM fuel cells (1). Moreover, by extending this approach to Pt alloys even higher mass activity can be achieved. The thorough analysis of the catalyst structure and composition by means of XRD, TEM and ICP-MS, and electrochemical characterization by rotating disk electrode and Identical-Location TEM (2), enables a detailed insight into the peculiarities of this catalyst system and its benefits.

References
1. C. Galeano, J.C. Meier et al., *J. Am. Chem. Soc.*, **2012**, *134*, 20457–20465.
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ECS-O-05

COMPARATIVE STUDY ON THE ELECTROCHEMICAL BEHAVIOUR OF IRIDIUM OXIDE PREPARED BY MAGNETRON SPUTTERING AND SOL GEL DEPOSITION METHODS

E. Slavcheva, G. Borisov, E. Lefterova
Institute of Electrochemistry and Energy Systems, Academy of Sciences, Sofia, Bulgaria

The work presents a research on the preparation of iridium oxide by two alternative deposition techniques – PVD of magnetron sputtering and the common chemical sol gel method. The substrates used are a commercial carbon paper and Magnelli phases titania, respectively. Both materials are characterised in regards to their surface structure, morphology, mechanical and chemical stability in acidic aqueous and polymer electrolytes. The influence of the substrate on the active surface area, electronic surface state, electrochemical performance, and catalytic activity toward oxygen evolution are elucidated and compared using XPS analysis, cyclic voltammetry, steady state polarisation techniques and electrochemical impedance spectroscopy. They are integrated in membrane electrode assemblies using Nafion 117 PEM and tested as anodes in PEM water electrolysis. The results obtained show higher active surface area and enhanced efficiency toward OER of the sputtered IrO_x, particularly at cell voltage below 1.8V. On the other hand, the Ebonex supported catalyst is less prone to degradation and demonstrates long term performance stability.

ECS-O-06

INITIAL CONDITIONING OF PEM FUEL CELL BY TEMPERATURE AND POTENTIAL CYCLING

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University of Split, Faculty of Electrical Engineering Mechanical Engineering and
Naval Architecture, Split, Croatia

PEM fuel cells need initial conditioning, activation or breaking-in the first time they are operated after being assembled. The exact mechanism of this initial conditioning has not been completely clarified, but it can be well assumed that during the conditioning process the polymer membrane and the polymer in the catalyst layer, get humidified, and the number of active catalyst sites increases. As a result the fuel cell performance gradually improves during the conditioning process. Several conditioning protocols have been applied, patented and/or proposed1, which include both on-line (such as current and potential control, short-circuiting, temperature control, hydrogen-pumping and air-braking) and off-line (before the cell is assembled) procedures. A procedure of both temperature and current cycling is proposed, described and characterized. It is assumed that cycling to high currents results in more water being produced inside the fuel cell, and temperature cycling allows the water to condense inside a fuel cell. It is well known that a membrane equilibrated with liquid water can take in more water than the same membrane equilibrated with water vapor in saturated gas. The temperature and current cycling procedure will be described, the results will be presented and compared to conventional conditioning procedure.

References

1. X.-Z. Yuan et al., Journal of Power Sources, 196 (2011) 9097–9106.

ECS-O-07

HYBRID 3D ANALYTIC-NUMERICAL APPROACH FOR COMPUTATIONALLY EFFICIENT MODELLING OF SPECIES TRANSPORT IN PEM FUEL CELLS

Gregor Tavčar and Tomaž Katrašnik
University of Ljubljana, Faculty of Mechanical Engineering, Ljubljana, Slovenia

An innovative hybrid analytic-numerical approach to modelling species transport in fuel cells suitable for application on the system level is presented. The innovative idea behind this modelling approach is taking 1D numerical model for gas-flow and superimposing onto it a 2D analytic solution for concentration distribution in the plane perpendicular to the gas-flow. This coupling of 1D numerical and 2D analytical modelling gives a 3D information on species concentration in the fuel cell. The hybrid analytic numerical approach is applied to modelling a simple geometry isothermal fuel cell and it is comparatively evaluated by benchmarking it against a professional full 3D CFD simulation tool. This evaluation shows: on one side a very close agreement with the benchmarking 3D CFD simulation, and on the other side computational times comparable to 1D models. The model’s analytic nature in the other two dimensions is the reason of this computational efficiency making it suitable for system level application.

ECS-O-08

NITROGEN-DOPED HOLLOW CORE MESOPOROUS SHELL CARBON AS ADVANCED ELECTROCATALYSTS FOR OXYGEN REDUCTION REACTION

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Electrocatalyst for oxygen reduction reaction (ORR) is a key component of fuel cells.[1] Nitrogen-doped hollow core mesoporous shell carbon (N-HCMSC) was prepared by nanocasting method using Iron (II) phthalocyanine as carbon source. The synthesized material has excellent properties like high surface area of 1700 m^2g-1 along with 3D interconnected macro-meso-microporous network. It also has N atom covalently bond in carbon framework along with some Fe oxide. Performance results indicates that N-HCMSC shows ORR onset potential (-0.01 V) and current density comparable to commercial 20 wt% Pt/VC catalyst along with four electron transfer pathway, and illustrates much better durability, selectivity to oxygen reduction, and tolerance to methanol crossover. This outstanding electrocatalytic activity of N-HCMSC is attributed not only to presence of N and Fe atoms, but also to excellent surface properties of HCMSC.

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ECS-O-09

MESOPOROUS SILICAS IN LITHIUM SULFUR BATTERIES

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The possibility of achieving high-energy, long-life storage batteries has tremendous scientific and technological significance. A prime example is the Li−S cell, which can offer a 3-5-fold increase in energy density compared with conventional Li- ion cells, at lower cost1. Despite significant recent advances, there are still some challenges. Upon sulfur reduction, intermediate soluble lithium polysulfides readily diffuse into the electrolyte, causing capacity fading and poor Coulombic efficiency in the cell. Recently, improved capacity fading of cathode composite has been achieved by combining mesoporous carbon, mesoporous silica (SBA-15), and elemental sulfur.2 Herein, we report the capacity retention and cycle life of the Li−S cell through the use of different mesoporous silicas and zeolite additives as polysulfide reservoirs and examine the role of surface and pore absorption.

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POSTER PRESENTATIONS

ECS-P-01

CARBON FREE Pt CATALYSTS FOR FUEL CELLS APPLICATIONS

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Tin oxide based supports have been synthesized by hydrazine reduction method. Physical characterization of the synthesized supports was performed by BET, X-ray diffraction and TEM techniques. Presence of SnO_2 belonging peaks has been detected in Sb-SnO_2 support powder, while Ru-SnO_2 XRD diffraction spectra contained RuO_2 and SnO_2 peaks. Pt catalysts on Sb-SnO_2 and Ru-SnO_2 supports have been synthesized by borohydride reduction method. Electrocatalytic activity and stability of these catalysts for oxygen reduction have been studied by cyclic voltammetry and linear sweep voltammetry at rotating disc electrode (RDE). Pt catalysts on Sb and Ru doped SnO_2 support exhibited catalytic activities comparable to Pt on commercial carbon based support. Stability tests were performed by repetitive cycling in the potential range from 0 - 1.45 V vs RHE. Determined small loss of electrochemical active surface area of the Pt catalysts on tin oxide based supports after repetitive cycling indicated high stability and high durability of this cathode for prospective polymer electrolyte fuel cell application.

ECS-P-02

NANOCRYSTALLINE AND COARSE GRAINED POLYCRYSTALLINE NICKEL CATALYSTS FOR THE HYDROGEN EVOLUTION REACTION

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The objective of this work was to study electrocatalytic properties of the coarse grained polycrystalline nickel cathodes: bulk Ni, foam Ni, and electrodeposited Ni in comparison with those of nanocrystalline nickel catalyst for the hydrogen evolution reaction (HER) in 1.0 M NaOH solution.

According to voltammetry and electrochemical impedance spectroscopy results, the intrinsic reactivity of polycrystalline Ni-cathodes, investigated for the HER, increases as follows: electrodeposited < foam < bulk Ni. The highest catalytic reactivity of nanocrystalline Ni cathode results from its favourable microstructural properties. The intercrystalline volume fraction contributes to the overall rate of the HER using spillover effect. It was found that spillover effect plays a major role in determining the overall catalytic activity of nanocrystalline catalyst.

ECS-P-03

ENHANCING ELECTROCHEMICAL PERFORMANCE OF TITANIUM OXIDE NANOTUBES-BASED MATERIALS

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Wide use of renewable resources is inseparably connected with energy storage materials that possess both high energy and high power density. Li-ion batteries seem to be the system of choice, but to achieve demanded characteristics we need to nanostructurize battery materials in a highly controlled way. Short transportation paths, good electronic and ionic wiring are crucial parameters to be optimized. Titanium dioxide nanotubes (TONT) are a promising anode material due to their high surface area and good stability [1]. We prepared TONT by hydrothermal method, and added various salts to create spacers that were supposed to prevent aggregation and phase transformation of TONT-derived anatase materials during annealing. We noticed improvement of the electrochemical performance of material when using Rh, especially at high current densities.

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ECS-P-04

FORMIC ACID OXIDATION AT PLATINUM-COATED BISMUTH DEPOSITS ON GLASSY CARBON SUBSTRATE

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The aim of this work is to prepare and examine the electrocatalytic activity of multicomponent Pt(Bi)/GC electrodes for formic acid oxidation. Platinum-coated bismuth deposits on glassy carbon substrate have been prepared by a two-step process. The controlled amount of Bi was electrodeposited onto GC substrate and subsequently coated with a thin Pt layer using chronocoulometry. Stable electrode was obtained after the selective electrochemical oxidation of Bi from the binary surface. The electrode was characterized electrochemically using a rotating disk electrode configuration and by microscopic and spectroscopic methods (STM, EDX). The obtained Pt(Bi)/GC electrode exhibits significantly increased electrocatalytic activity and stability for formic acid oxidation in comparison to Pt/GC or bulk Pt electrodes. This behavior is attributed to an ensemble effect of Bi oxide(s) formed in Pt surface layer and electronic effect of the underlying Bi onto the Pt surface atoms.

ECS-P-05

DETERMINATION OF THE “WIRING” PARAMETERS OF A TYPICAL LITHIUM ION ELECTRODE

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In the present work we have for the first time determined the values of the “wiring” parameters of a typical Li ion electrode. Based on the previous research[1,2] we here present experimentally determined values of the electronic composite resistance – separately of the value of the “contact resistance” between the composite and the current collector. We have also determined the value of the ionic resistance of the composites introduced into the battery cell. We demonstrate how the electrical properties of the “wetted” electrode differ from the one in the starting “dry” state. The results are indicating that the softening of the composite accompanying the volume changes during cycling might have an important role in the regularly observed increase of the total impedance during aging of the Li ion cells.

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ECS-P-06

ANALYTICAL TECHNIQUES FOR LITHIUM SULPHUR BATTERY

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In the recent years a lot of effort has been put to create high performance Li-S battery, which at present has problems because of the loss of sulphur from cathode in the form of lithium polysulfides during battery operation. However results till now obtained has not reached the expectations. One of the reasons for this is the absence of proper analytical techniques to monitor the Li-S system. Till recently new kind of analytical techniques like 4 electrode Swagelok cell(1), in-situ UV-Visible spectroscopy and XAS (X-ray absorption spectroscopy) have been developed, which are helpful in monitoring the Li-S system and give proper feedback about material, electrolyte and other parameters, using these information changes can be made to achieve the goal of high performance Li-S battery.

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ECS-P-07

SODIUM INTERCALATION IN $LiFePO_4$/C COMPOSITE FROM AN AQUEOUS SOLUTION OF SODIUM NITRATE

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The olivine based composite, $LiFePO_4$/C, synthesized by gel-combustion technique[1] was subjected to potentiodynamic cycling in saturated aqueous $NaNO_3$ solution. Successful sodium intercalation in $FePO_4$/C composite from an aqueous solution was presented for the first time. In the initial stage of potentiodynamic cycling, lithium in solid phase was replaced by sodium, and in the next cycles, an reversible intercalation/deintercalation processes took place, in a manner analogous to that observed in organic electrolyte solution[2]. A satisfactory coulombic capacity amounting to 118 mAh g^{-1} was found for a scan rate of 10 mV s^{-1}. By both cyclic voltammetry and impedance measurements in aqueous electrolyte, the intercalation/deintercalation kinetic of $NaFePO_4$/C composite was evidenced to be faster in comparison to than of $LiFePO_4$/C composite.

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ECS-P-08

CHEMICAL SYNTHESIS AND CHARACTERISATION OF SnO_2 FOR SUPERCAPACITOR APPLICATIONS

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In the recent years, supercapacitors have attracted significant attention as they provide high power and high energy densities. Metal oxides are promising materials for such applications [1]. SnO_2 is interesting candidate because of its low cost, nontoxicity and abundant presence in nature. In this work, crystalline SnO_2 was prepared by sol–gel process using alcoholic solution of tin(II) chloride. Obtained material was characterized using X-ray diffraction (XRD) and it was applied onto platinum and glassy carbon supports. Electrochemical properties were investigated using cyclic voltammetry (CV), chronoamperometry and quartz crystal microbalance (QCMB) in 0.5 mol dm^{-3} KCl. Cyclic voltammograms showed high currents in wide potential range indicating capacitive behavior of SnO_2. Mass change *vs.* potential data reveal that charging/discharging mechanism of SnO_2 does not involve intercalation/deintercalation of cations as is the case with other other metal oxides such as RuO_2 and MnO_2 [1].

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ECS-P-09

EFFECT OF CHEMISORBED CO ON Sb-SnO_2 SUPPORTED Pt ELECTRODE ON THE KINETICS OF HYDROGEN OXIDATION

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The influence of poisoning of Sb-SnO_2/Pt anode by CO on the kinetics of H_2 oxidation reaction (HOR) in 0.5 mol dm^{-3} $HClO_4$ saturated with H_2 containing 100 ppm CO, was examined on rotating disc electrode (RDE). Based on Tafel-Heyrovsky-Volmer mechanism the corresponding kinetic equations from a dual pathway model were derived to describe oxidation current-potential behavior on RDE over entire potential range, at various CO coverages. The fitting showed that the HOR proceeded most likely via the Tafel-Volmer (TV) pathway. A very high electrocatalytic activity observed at Pt catalyst for the hydrogen oxidation reaction in the presence of 100 ppm CO is achieved through chemical surface reaction of adsorbed CO with Sn surface oxides.

ECS-P-10

SONOCHEMICAL ACTIVATION AND SONOSYNTHESIS OF PERSPECTIVE MATERIALS

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This work presents an innovative approach for sonoactivation of elecroconductive oxides used as catalytic supports (Magnelli phase titania) and solid state synthesis of ceramic materials (Bi_2O_3-TiO_2-SiO_2-Nd_2O) to obtain ferroelectric high temperature phases at ambient conditions. The approach is based on the physical phenomena called cavitaion in liquids under strong ultrasound field, using the ability of ultrasonic waves to de-agglomerate and disintegrate hard solid powders and to accelerate chemical, physicochemical and electrochemical processes. The method is extremely simple and energy saving since it avoids the usage of high temperature equipment. The current results show that it is possible to synthesize high-temperature phases $Bi_{12}TiO_{20}$ with specific optical properties at room temperature. This is verified by XRD analysis, optical microscopy and IR spectroscopy. It is proven that this method is a good alternative or a complimentary step to the mechanochemical methods for both activation and synthesis of materials with application in electrochemical energy conversion systems as well.

ECS-P-11

FORMIC ACID OXIDATION AT Pt-Sn BIMETALLIC CATALYSTS

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PtSn bimetallic catalysts are extensively studied due to their activity for CO oxidation. The activity of PtSn is mainly explained by bi-functional mechanism since Sn can supply surface oxygen-containing species at lower potentials in comparison to Pt. CO is the main poison of polycrystalline Pt in formic acid oxidation, yet this reaction has been rarely studied on Pt-Sn catalyst. The aim of our work is to study this reaction at PtSn/C catalysts with different Pt to Sn ratio. The catalysts were prepared by microwave assisted pollyol method and characterized by STM, XRD and EDX techniques. The onset potential of formic acid oxidation is shifted to the lower values and currents are significantly higher in comparison to Pt, thus the reaction is shifted towards direct path. The results are discussed and explained by Sn influence through bi-functional mechanism, morphology changes and electronic effect.

ECS-P-12

EFFECT OF SURFACE MODIFIED $LiNi_{0,5}Mn_{1,5}O_4$ PARTICLES ON ITS ELECTROCHEMICAL PERFOMNACE

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Li-ion batteries are receiving enormous attention in the renewable energy field. Due to its high energy and power density and low cost high voltage LiNi0,5Mn1,5O4 cathode is an important option for new generation batteries. On the other hand, its high working potential enhances the occurrence of side reactions[1]. Examples are electrolyte decomposition and spinel dissolution both of which lead to a decrease of electrochemical stability. It has been reported that surface modification can protect material from these side reactions and consequently improve stability[2].

We report on the effect of surface layer formation on the capacity retention and on the resistance measured by Impedance spectroscopy.

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EOE
Environmental and Organic Electrochemistry

ORAL PRESENTATIONS

EOE-O-01

FISCHER AMINOCARBENE COMPLEXES: EFFECTS OF STRUCTURE ON REDOX PROPERTIES

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Basing on systematic electrochemical investigation of more than 40 Fischer-type aminocarbene complexes of chromium, tungsten and iron, a more detailed insight into electronic and redox properties of the title compounds, their reactivity and reaction mechanisms is presented. As a result, important structural parameters influencing reduction / oxidation potentials and stability of intermediates were described and discussed [1-3]. In addition to this, analogous hetaryl derivatives and their dimeric species were recently synthesized, investigated and the experimental results correlated with quantum chemical calculations.

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EOE-O-02

FLUORENONE DIANION PROTONATION. UNUSUAL pK_1/pK_2 RATIO

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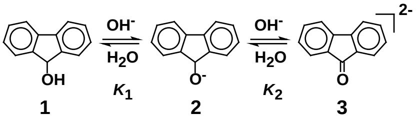
Protonation of dianion **3** by water (1) has been investigated by cyclic voltammetry and digital simulation in 0.1M Bu_4NClO_4/DMF solutions. It was shown that anion **2** is more acidic than alcohol **1**. The ratio of equilibrium constants K_1/K_2 was estimated as $8{,}1\cdot10^{-3}$ what was close to the value $7.1\cdot10^{-3}$ obtained by DFT B3LYP/PCM/6-311++G(d,p) calculations. According our knowledge this is the first case when K_1/K_2 value for alcohol is less than unity. The unusual value of the ratio is explained in terms of π^*-anions specificity, in particular, its anomalous low basicity in compare with other anions[1]. The role of reaction (1) in mechanisms of fluorenone and fluorenol electroreduction has been investigated as well.



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EOE-O-03

CORRELATION OF UV-VIS, NMR AND EPR SPECTRA IN ELECTROCHEMICAL REDUCTION OF A NEW EXPLOSIVE FOX-7

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The title compound FOX-7 (2,2-dinitroethene-1,1-diamine) is a relatively novel, powerful insensitive explosive[1]. Its applicability is broadly investigated, but fundamental research of its chemical structure on molecular level is very scarce and any electrochemical investigation is missing. The molecule involves electron-donating and electron-withdrawing part. Its structure is stabilized by push-pull effect which allows tautomeric changes connected with electron transfer[2]. FOX-7 can be present in several different structures in various solvents. Correlation of UV-vis, NMR and EPR spectra recorded before and/or during reduction process helps to identify the present structure which influences the redox behaviour of FOX-7. It has been found that surprisingly only 2-electron reduction takes place[3], which is associated with adsorption in dependence on material of working electrode and involves radicalic intermediates. The reduction mechanism is discussed.

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EOE-O-04

TREATMENT OF PHARMACEUTICAL SUBSTANCES IN MEDICAL WASTE WATER BY A COMBINATION OF ANODIC OXIDATION AND STERILIZATION

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This Paper deals with treatment methods for pharmaceutical substances in waste water and fluid waste from medical establishments (laboratories, hospitals). During the last years, several projects were settled at the chair for waste processing technology with a focus on waste water treatment and tap water disinfection by using boron doped diamond (BDD) electrodes. These BDD-electrodes, produced by the pro aqua GmbH, are used to generate in-situ oxidation substances like OH-radicals, O_3 and H_2O_2 directly from the waste water. This substances can be used for the degradation of e.g. pharmaceuticals. In laboratory and small technical tests degradation rates up to 99,99 % were achieved for Carbamazepine, Diazepam and other pharmaceuticals. In an actual research project, a combination between the already praxis proven continuous flow METEKA sterilization system and Anodic Oxidation with BDD-electrodes, is used for practical tests with carbamazepine spiked water.[3] Used Technology, reached results and scientific recommendation will be presented in the presentation.

POSTER PRESENTATIONS

EOE-P-01

NEW COMPOSITE MATERIALS BASED ON CLAY NANOPARTICLES AND CELLULOSE MEMBRANES

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This research aims at combining the ion exchange and the adsorbent properties of Romanian clay with the specific properties of a cellulose membrane deposited on glassy carbon electrode previously coated with the clay particles. The new composite materials were characterized by electrochemical methods, scanning electron microscopy, Raman spectroscopy, and X-ray diffraction. The results indicate extension of the interlayer of the clay upon treatment with the cationic surfactant (TBAB), which was reversible upon removal of this template. The film permeability after template removal, as tested by cyclic voltammetry in $K_4Fe(CN)_6$, ferrocene dimethanol, and $Ru(NH_3)_6Cl_3$ solutions, revealed significant enhancement of mass transport rates and accumulation efficiency (for cationic species) when passing from the pristine clay film to the composite one. Good surface coverage of the electrode with the films was confirmed by suppression of CV signals prior to surfactant extraction. The novel material showed attractive adsorbent properties, which could be exploited for the development for heavy metal detection sensors.

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EOE-P-02

ENVIRONMENTAL ELECTROCHEMICAL APPROACH TO POLLUTION CONTROL IN KOSOVO

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Protection of environment is one of the main concerns in the world, especially in developing countries, where the pace of industrial transformation has been relatively fast. So, it is important to ensure any work activity is investigated, and any risk from dangerous leftover waste mitigated (reduced/eliminated). The LLAMKOS plant has consistently produced the galvanized metal sheet \`LLAMKOS\`from its inception. The wastes that remains from usage of \`Passerite\` and used oil from lubrication of machinery are kept in metallic and plastic drums, which are stored in one place with concrete base.

The process of digestion (reduction) for a long time for the passivity of the galvanized sheet brings about the changes of the overall digested mixture (leftovers), because contamination with zinc changes the mixture composition, so this is treated as dangerous waste. For this reason the reduction process and neutralization is done. These processes reduce the amount of dangerous waste. Main recommendations that come out of these work practices are:

- With reduction of Cr6+ composition in to Cr3+ composition and its neutralization, risk is reduced from this matter (this chemical) which is dangerous and cancerous.

EOE-P-03

ENHANCEMENT OF HYDROGEN EVOLUTION REACTION BY PROTON CARRIERS

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This work presents the catalytic effect of aniline and benzylamine on hydrogen evolution reaction on platinum electrode in sulfuric acid aqueous solution. Aniline and benzylamine catalytic effect has been studied by linear voltammetry and electrochemical impedance spectroscopy. Electrochemical behavior of aniline and benzylamine has been studied by cyclic and square wave voltammetry. Kinetic parameters (cathodic transfer coefficient, exchange current density) have been determinate using Tafel plots. The exchange current density value in a blank sulfuric acid solution is rather low (i_o = 2.9 A m^{-2}), while in the presence of the aromatic amines, at the same temperature, the values are 22.9 A m^{-2} for 10^{-2} mol L^{-1} benzylamine, respectively 67.6 A m^{-2} for 10^{-2} mol L^{-1} aniline. A correlation between obtained results and molecular parameters of aromatic amines has been performed. Activation energies for hydrogen evolution reaction have been calculated with and without addition of aromatic amines.

EOE-P-04

THE ELECTROLYTIC DISSOCIATION OF CROCONIC ACID

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Croconic acid (1,2-dihydroxycyclopentenetrione) belongs to the dihydroxycycloalkane-polyones group. The representatives of this group: deltic, squaric, croconic and rhodizonic acids are the rare examples of organic acids with two acidic hydroxyl groups. Their comparatively high acidity is attributable to the resonance stabilization of dianions which consist only of carbon and oxygen atoms and are completely symmetrical. Croconic acid is ferroelectric. Its salts are of interest in supramolecular chemistry research. In this communication with the aid of original method suggested by authors for determination of the dissociation parameters for the dilute solutions of weak multibasic organic acids the values of usual and "partial" degrees of dissociation for both steps, concentrations of mono- and dianions, hydrogen ions and undissociated acid molecules in the acid concentration range 0.0001-0.01M are determined. In our work the mass action law equations suggested by us were used. The values of the activity coefficients of all charged particles were approximated by Debye-Huckel equation.

EOE-P-05

COMPARATIVE ASSESSMENT OF NANOSTRUCTURED CARBON BASED COMPOSITE ELECTRODES FOR APPLICATION IN ELECTROCHEMICALLY-ASSISTED PHOTODEGRADATION OF PCP FROM WATER

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Pentachlorophenol (PCP) is a highly toxic and persistent pollutant, which can be formed as a by-product in water chlorination processes and as a metabolite from the degradation of some pesticides[1]. In this study, the performances of the carbon nanotubes-based composite (CNT-Epoxy, CNT-TiO_2-Epoxy) and the carbon nanofibers-based composite electrodes (CNF-Epoxy, CNF-TiO_2-Epoxy) were assessed comparatively for the degradation of PCP from water by application of electrochemically-assisted photocatalysis process. The electrode surface morphology was examined by scanning electronic microscopy. A synergetic effect was found for electrochemically-assisted photocatalysis process in PCP degradation in comparison with application of individual process (photocatalysis and electrooxidation).

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EOE-P-06

ENZYMATIC SYSTEM FOR BOD DETERMINATION

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For the fast determination of Biochemical Oxygen Demand, microbial sensors are typically used. Various types of microorganisms were employed in these devices, depending on the type of analyzed wastewater. However, river water samples can contain persistent organic compounds, such as lignin, humic acid and tannic acid, that are not readily assimilable by the microorganisms. In this presentation, we propose novel, enzymatic method for the electrochemical determination of BOD of such samples. Laccase was used as a bioactive component of proposed sensors due to its wide substrate range and low cost. Different types of working electrodes, as well as laccase of various origin were used to prepare BOD sensors. Preliminary results show that developed electrodes can be used for the BOD determination for artificial wastewater samples.

The study was accomplished thanks to the funds allotted by the National Centre for Research and Development within the framework of the research project No NR15-0049-10/2011.

EOE-P-07

ELECTROCHEMICAL DETERMINATION OF HYDROGEN SULFIDE FROM SIMULATED SEAWATER AT CARBON BASED ELECTRODES

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Free sulfide (H_2S, HS^-, S^{2-}) is an exceedingly important substance in the aquatic environment and serve as a very important pollution index for water, especial due to its potential to poison many aquatic organisms, even at micromolar concentrations[1]. In this study, the performances of the carbon based electrodes, e.g., boron-doped diamond (BDD), carbon nanofibers-epoxy composite (CNF-EP) and carbon nanotubes-epoxy composite (CNT-EP) electrodes were assessed comparatively for the voltammetric/ amperometric direct detection of hydrogen sulfide from simulated seawater water. Carbon nanotubes exhibited the catalytic effect towards sulfide oxidation, which lead to highest sensitivity. Several mechanistic aspects were discussed based on the influence of the scan rate and pH in direct relation with sulfide speciation.

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EOE-P-08

ELECTROCHEMICALLY INITIATED DEGRADATION OF HENRY REACTION PRODUCT

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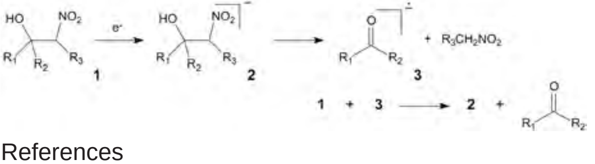
Despite electrochemically induced Henry reaction was the subject of some investigations*1* the electrochemical behavior of its product **1** did not attract attention of the researchers. We have found that electron transfer to **1** in DMF and MeCN solutions initiates cyclic process of its degradation which should be taken in account when the Henry reaction is induced electrochemically.



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EOE-P-09

NITROPHENOLIC COMPOUNDS CONTROL AND ELIMINATION FROM WASTEWATERS

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Nitrophenols and nitrophenolic herbicides are toxic and biorefractory substances and they are classified as priority pollutants, dangerous for the environment, in USA and E.U., where production, merchandising and utilization is banned or restricted. Thus is important to develop simple, widely applicable and low-cost methods for detection, quantification and monitoring these pollutants and their degradation products in soil and water. 4-Nitrophenol and 2,4-dinitrophenol are initially and major degradation product of nitrophenolic herbicides and will be used as model molecules in experimental determinations. The obtained results were applied to some dinitrophenolic herbicides.

Experimental methods used for nitrophenolic herbicide and their degradation compounds elimination are: electrochemical transformations (reduction and oxidation), in different experimental conditions, and the decreasing of these compounds concentration during electrochemical treatment was realized by the mean of TOC, UV-Viz and electrochemical methods.

EOE-P-10

ELECTROCHEMICAL DECOLORIZATION OF REACTIVE ORANGE 16 DYE AT Ti/Bi_2O_3 ANODE

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Ti/Bi_2O_3 anode was synthesized by electrodeposition[1,2] from Bi (III) solution on Ti substrate and calcination. Ti surface was covered with mixture of α-Bi_2O_3 and β-Bi_2O_3[3]. Dye was completely decolorized at synthesized anode in the presence of H_2O_2, fallowing the pseudo-first order kinetics model[4,5]. Optimal values of pH and current density are found to be: 7±0.2 and 30 mA cm^{-2}, respectively.

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EOE-P-11

IN SITU EPR-UV/VIS/NIR SPECTROELECTROCHEMISTRY OF SUBSTITUTED DIARYLAMINOTHIOPHENES

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In this contribution, 1,4-bis-(2-diphenylamino-thiophen-5-yl)-benzene, (1,4-bis-[2-(phenothiazin-10-yl)-thiophen-5-yl]-benzene and 1,4-bis-(5-diphenylamino-[2,2´]bithiophen-5´-)-benzene consisting of three different groups, namely the diphenylamino-, bithiophene- and central phenylene moiety, respectively, were studied in detail to get insights to their oxidation mechanism. Different voltammetric techniques, in situ EPR-UV/Vis/NIR and NMR spectroelectrochemistry as well as a theoretical study based on DFT calculations were used to achieve this goal[1].

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ESG

Electrochemical and Electronic Sensor Devices

ORAL PRESENTATIONS

ESG-O-01

EFFECTS OF (POLY)-ETHYLENE GLYCOL ON THE STABILITY AND ELECTROCHEMICAL PROPERTIES OF PEDOT: PSS FILMS

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By mixing the same concentrations of (poly)-ethylene glycol of different molar masses, a series of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) composite thin films were prepared by spin coating. The morphology of the films was inspected by Atomic Force Microscopy. Electrochemical characterizations performed in phosphate buffer solution included Surface Plasmon Resonance Spectroscopy combined with Cyclic Voltammetry, Electrochemical Impedance Spectroscopy and Mott–Schottky analysis. Experimental results showed that the inclusion of (poly)-ethylene glycol influenced the properties of PEDOT-PSS films significantly. The tests were performed over a time span of ten days to determine the stability of the films. The PEG molecular weight played an important role on the properties of PEDOT-PSS/PEG thin films.

ESG-O-02

GENERATION AND ELECTROCHEMICAL NANOGRAVIMETRIC RESPONSE OF THE THIRD ANODIC HYDROGEN PEAK ON A PLATINUM ELECTRODE IN SULFURIC ACID MEDIA

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Platinum is one of the most thoroughly studied and used electrode materials. Despite all the efforts even the problem of the nature of the strongly and weakly adsorbed hydrogen has not been solved entirely, yet. In this lecture we present our recent results obtained by EQCN experiments on the generation of the third voltammetric peak which is situated between the two main peaks during the oxidative desorption of hydrogen from Pt in sulfuric acid media. It is shown that applying appropriate potentials and waiting time during the adsorption of hydrogen the magnitude of the third peak appearing in the course of the oxidative desorption can be comparable with the two main peaks. Moreover, the anions also occupy the liberated sites just as in the case of the weakly and strongly adsorbed hydrogen.

ESG-O-03

ELECTROCHEMICAL IMMUNOASSAYS FOR THE DETECTION OF MUCINES CANCER BIOMARKERS

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In recent years increasing attention has been focused on the development of immunosensors for cancer biomarkers detection. MUC1 serves as a tumor marker, being over expressed in various types of cancer. Four strategies have been employed and compared for the development of an electrochemical sandwich assay for MUC1 detection based on magnetic beads functionalised with either antibodies or aptamers in order to bind MUC1. The amount of captured protein was quantified detecting the enzymatic product of the enzyme used as label by DPV. Under optimal conditions a calibration plot has been obtained for each assay. For the dual antibody assay a DL of 0.69 was obtained in the range of 0-10 ppb when AP was used as label; instead, when HRP was used as label a DL of 1.34 ppb with a linear range of 0-5 and 5-25 ppb was obtained. The aptamer-based sensors exhibited a linear response in the range of 0-10 ppb with a DL of 1.69 for aptamer-antibody assay and 2.10 for aptamer-aptamer assay. The sensors were applied for serum samples, providing promising perspectives for future clinical applications.

ESG-O-04

METHANOL OXIDATION AT PLATINUM-BASED ELECTROCATALYSTS

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Adsorbing properties of the catalyst have a profound impact on reactions proceeding in proton exchange membrane fuel cells: oxygen reduction, methanol oxidation and, additionally, carbon monoxide oxidation and nitrous oxide reduction. A new way for predicting MOR activity is proposed based on surface coverages of adsorbing species, specifically OH_{ad} and CO_{ad} which are simulated from ORR polarization and CO stripping curves. The change in ORR activities of platinum alloy catalysts (MxPt/C, M = Co, Ni, Cu and Ru) measured as shift in potential at 0.02 mA/cm^2 current density show nice correlation with a shift in the potential of total zero change (PTZC), hence indicating importance of surface interaction with adsorbing species such as OH_{ad} [1]. A new catalyst for MOR (PtCu+Ru/C) is presented. Its superior activity is explained by two synergic effects: a decreased platinum surface coverage of spectators by ligand and/or strain effect and the bifunctional effect caused by the addition of ruthenium that lowers OH_{ad} formation.

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POSTER PRESENTATIONS

ESG-P-01

NONOXIDATIVE IMPEDIMETRIC SENSOR BASED ON POLY(3-AMINOPHENYLBORONIC ACID) MODIFIED SKELETON NICKEL ELECTRODES FOR DOPAMINE DETECTION

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In this work a nonoxidative dopamine sensor has been obtained by electro-polymerization of 3-aminophenylboronic acid in aqueous solutions on a preformed polyaniline layer electrochemically deposited on smooth and skeleton nickel electrodes. Poly(anilineboronic acid) (PABA) has the ability to selectively bind dopamine over ascorbic acid, eliminating the problem of interferents. The modified electrodes have been tested as impedimetric sensors for detection of dopamine in aqueous phosphate buffer at pH 7.4. Both sensors gave a linear response for dopamine concentrations between 10^{-5} and 10^{-10} mol L^{-1}. PABA modified skeleton nickel electrode has the advantage of an increased specific surface area, that leads to a high density of boronic acid groups and hence to a better sensitivity.

ESG-P-02

CANTILEVER PROBES WITH SUBMICRON-SIZED Pt-ELECTRODES FOR COMBINED SECM-AFM

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Combined scanning electrochemical microscopy (SECM)-atomic force microscopy (AFM) has become a powerful tool for investigating small electrochemically active structures and a wide range of processes occurring at interfaces[1]. Although SECM-AFM is a well-known method for over one decade[2], its application is limited by the insufficient availability of sensors which can fulfill the requirements regarding topography resolution and stability of the insulating layer in electrolytic solutions. Hence we have developed a reliable probe for SECM-AFM which combines an outstanding lateral resolution and stable ion sensitivity in liquids. Corresponding cyclic and differential pulse voltammetry measurements will be presented and discussed.

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ESG-P-03

MODIFIED CARBON BASED ELECTRODES AS PLATFORM FOR THE DEVELOPEMENT OF NOVEL SENSORS

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Different carbon based electrodes, i.e. glassy carbon, graphite based screen printed electrode or graphite porous electrode were used as platform for the development of innovative sensors, applied for the determination of a wide range of compounds, going from drugs to food or environmental samples analysis. The single and multiwall carbon nanotubes were used to modify the surface of a conventional glassy carbon electrode, but also to modify and improve the electrochemical behavior of carbon based screen printed electrodes. The biosensors were applied to the assay of acetaminophen in various drug formulations by the standard addition method. The SPEs were also modified with cali[4] arenes in order to develop a specific sensor for the quantification of procaine.

ESG-P-04

CYCLIC AND STRIPPING VOLTAMMETRY OF IRON-PHYTATES IN ALKALINE HYROXIDE SOLUTION AT THE HMDE

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Ubiquitous presence of phytates and corresponding complexes with iron(III) in the cytosol and nucleus of eukaryotic cells indicate on their significant biological importance, which hitherto has not been fully explained. Therefore, the main aim of present research was to characterize the soluble complexes of Fe(III)-phytates with the voltammetric measurements, particularly in the range of neutral and alkaline pH. Depending on the pH, molar ratio, deposition time and potential applied three cathodic and two anodic peaks may appear on the curves obtained by the hanging mercury drop electrode, employed for the first time for the study of iron(III)phytate system. It was demonstrated that the ligand to metal molar ratio equals 6 : 1 and the product formed during the reduction of Fe(III)-phytate is deposited/adsorbed on the mercury surface, resulting in the appearance of anodic adsorption peak.

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ESG-P-05

LANTHANIDES SENSING USING AZULENES DERIVATED CHROMOPHORES

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1-azulenylmethylenemalonodiamides substituted at the nitrogen atoms with alkyl or hydroxyalkyl groups were synthesized[1]. Their interaction with lanthanide cations (Eu^{3+}, Ce^{3+}, Sm^{3+}, Yb^{3+}) was studied using both spectroscopic and electrochemical methods. The increased adding of a lanthanide solution showed a corresponding increase of response suggesting that these ligands have molecular recognition properties.

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ESG-P-06

NEW WAY OF CATALYST ACTIVITY EVALUATION VIA ROTATING DISK ELECTRODE METHOD

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Over the past decades much effort has been devoted to development of efficient and less expensive Pt-alloy catalyst for proton exchange membrane fuel cells (PEMFC) reactions. In most cases, fast screening of material is done with the rotating disk electrode (RDE) method. Thereby, following the strict benchmarks for RDE method is mandatory for the correct interpretation of the oxygen reduction reaction (ORR) polarisation curve[1]. However this can sometimes be very difficult, or even impossible, because many parameters such as catalyst suspension stability, catalyst loading, film formation, drying procedure can mask the real catalyst ORR activity. We demonstrate that measuring the potential at fixed low-kinetic current density enables us to correctly evaluate the activity of even relatively "low quality" catalyst films. A correlation between the classical specific activity at 0.9 V and our fixed low-kinetic activity is also given.

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ESG-P-07

DISPOSABLE MICROBABRICATED ANTIMONY-FILM SENSORS FOR THE DETERMINATION OF TRACE METALS BY STRIPPING VOLTAMMETRY

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This work describes a novel type of antimony electrode for stripping voltammetry (SV). The sensor was microfabricated by coating a silicon chip with a thin antimony-film by means of sputtering and the active area of the electrode was defined by photolithography1. The resulting antimony-film electrodes (SbFEs) were characterized by optical and electrochemical techniques, and were tested for the trace determination of Ni(II) and Pb(II) by stripping voltammetry. Acknowledgments. The research project is implemented within the framework of the Action «Supporting Postdoctoral Researchers» of the Operational Program “Education and Lifelong Learning” (Action’s Beneficiary: General Secretariat for Research and Technology), and is co-financed by the European Social Fund (ESF) and the Greek State.

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CPA
Corrosion, Passivation and Anodic Films

ORAL PRESENTATIONS

CPA-O-01

THIADIAZOLE DERIVATIVES AS INHIBITORS FOR ACIDIC MEDIA CORROSION OF ARTIFICIALLY PATINATED BRONZE

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Electrochemical impedance spectroscopy and SEM-EDX observations were used to evaluate the inhibiting effect of four thiadiazole derivatives on the corrosion of naked and artificially patinated bronze surface exposed to an acidic solution (pH 3) that simulates a strongly polluted rainfall. For comparison reasons, the inhibiting effect of benzotriazole (BTA) was also examined. It was concluded that 2-mercapto-5-methyl-1,3,4-thiadiazole (MMeT) and 2-mercapto-5-amino-1,3,4-thiadiazole (MAT) allow the stabilization of the patina layer, leading to the protection of the bronze substrate and their effectiveness significantly increase with the immersion time. Finally, a possible inhibition mechanism of the thiadiazole protonated species on bronze corrosion was proposed.

CPA-O-02

THE RELATION BETWEEN ADSORPTION BONDING AND CORROSION INHIBITION OF AZOLES ON COPPER

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A detailed analysis of the results of density-functional-theory based molecular modeling of interaction of imidazole and triazole corrosion inhibitors with copper surfaces suggests that in near neutral conditions the imidazoles are active against corrosion in their neutral forms, whereas triazoles are active in their deprotonated forms. This inference is based on the finding that for triazoles the chemisorptive bonding is by and large the strongest for deprotonated inhibitors, whereas for imidazoles the aqueous-phase adsorption free energy of the neutral form is comparable to that of deprotonated form. In order to corroborate this inference, we performed corrosion experiments of imidazole, triazole and their 1-methyl derivatives (1-methyl-imidazole and 1-methyl-triazole) as copper corrosion inhibitors in 3 wt.% NaCl solution. Namely, 1-methyl-triazole should be less active against corrosion of copper than plain triazole, because its methyl group prevents the formation of deprotonated form, whereas imidazole and 1-methyl-imidazole should behave similarly. The experimental measurements indeed confirmed these expectations thus validating the relation between the adsorption bonding of inhibitors and their corrosion inhibition.

CPA-O-03

THE EFFECT OF SOILING AND OXIDATION ON TITANIUM EXPOSED TO OUTDOOR ENVIRONMENTS

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Anodized titanium can exhibit fascinating interference colours due to the presence of a thin oxide layer on its surface. The hue produced depends on oxide thickness, therefore it can provide information on the oxidation degree of the surface itself. In outdoor applications the amphiphilic surface of titanium undergoes both soiling and a slow oxidation; few experimental studies have been carried out to understand its durability when exposed to the atmosphere[1], and none of them considers this dual surface modification. This work investigates through spectrophotometry the two contributions to titanium surface alterations upon outdoor exposure, and evaluates different anodising treatments to improve its behaviour.

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CPA-O-04

PREPARATION AND CHARACTERIZATION OF SELF- ASSEMBLED MONOLAYER OF STEARIC ACID FOR PROTECTION OF CUPRONICKEL ALLOY

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Cupronickel alloys are often used for marine applications due to their good corrosion resistance to seawater. However, corrosion may be facilitated in the presence of pollution or biofouling and additional protection may be needed. The aim of this work was to investigate the possibility of protection of cupronickel in near neutral chloride media. For that reason stearic acid was used as an environment friendly corrosion inhibitor that may form a protective hydrophobic layer on the metal surface. In order to obtain high corrosion protection properties various methods of surface pretreatment were examined (various inhibitor concentrations, adsorption duration, reduction of cupronickel oxide layer or surface covered with oxide layer). Stability and efficiency of such obtained protective monolayers of stearic acid were examined by the means of electrochemical methods (polarization measurements and electrochemical impedance spectroscopy) as well as by contact angle measurements. Results obtained in this work confirm that stearic acid may significantly decrease corrosion rate of cupronickel alloy in chloride media.

CPA-O-05

INVESTIGATION OF CHLORIDE ADSORPTION ON OXIDE COVERED STEEL SAMPLES WITH THE NOVEL ‘THIN GAP’ METHOD

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The in-situ radiotracer ‘thin gap’ method combined with cyclic voltammetry was developed towards the application on rough surfaces. The basic equations of the new model were discussed and validated.

Then, the chloride adsorption on oxide-covered austenitic stainless steel samples was investigated and the following aspects were studied:

- Optimization of the parameters for the formation of proper oxide layers.
- Determination of the extent of chloride adsorption on oxide–covered steel samples.

CPA-O-06

DESIGNING CORROSION INHIBITOR FORMULATIONS FOR ACID STIMULATIONS

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One of the most important parts of acidizing applications in oilfield and gas industry is the need to give adequate corrosion inhibition in diverse media. Single organic compounds as corrosion inhibitors are usually not effective for low grade steel corrosion control under typical acidizing conditions and in particular this is relevant at elevated temperatures. A common acidizing formulation is multicomponent and will included corrosion inhibitor actives, intensifiers, surfactants and solvents. In this paper, we will address how a corrosion inhibitor formulation design could be conducted under severe steel corrosion conditions (elevated temperature, high pressure and high acid content) using different corrosion tests, electrochemical methods and surface analytical techniques. The aim is to understand the factors that influence component selection for acidizing applications. Safer and environmentally more acceptable alternatives will also be explored.

CPA-O-07

COMPARISON OF RESULTS FROM STANDARDIZED CYCLIC CORROSION TESTING AND FLOWING ELECTROLYTE ON THE CORROSION BEHAVIOUR OF HOT DIPPED GALVANIZED STEEL

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Corrosion behaviour of conventionally hot dipped galvanized steel (Z) and Al-Mg-Zn coated steel (ZM) is investigated by standardized cyclic corrosion tests namely VDA 233-102[1]. The development of flow cells with downstream analytics allow a time resolved investigation of corrosion mechanism in a flowing electrolyte[2]. In this work results obtained from cyclic corrosion tests and experiments with flowing electrolytes in a flow cell setup are compared. Because of the particular importance in civil engineering and automotive industry, the influences of chloride containing, acidic electrolytes to hot dipped galvanized steel are presented.

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CPA-O-08

CORROSION PROTECTION OF HOT DIP GALVANIZED LOW CARBON STEEL USING CONDUCTING POLYANILINE BASED PAINTS

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Metals corrode in environments encountered during their use. The most common corrosion control method is the use of coatings containing toxic materials As such, it encouraged to search for alternatives. Recently, conducting polymers shown promise in this direction. A lot of work has been carried out on electrochemical deposition of conducting polymer on steel in recent years; however, it is difficult to use this approach on massive engineering structures. Since hot dip galvanizing is an established technique, it was thought that conducting polyaniline based paint on hot dip galvanized steel might provide an alternative. The aim of work was, therefore, to study corrosion performance of chemically synthesized conducting polyaniline based paint coating on hot dip galvanized low carbon steel samples. It was found that 1 wt % PANI-HCl based paint coatings offer significant corrosion protection to hot dip galvanized low carbon steel and the coating remains intact even after 120 hours of immersion in 3.5 % NaCl.

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POSTER PRESENTATIONS

CPA-P-01

CHARACTERIZATION OF STEEL CORROSION IN CONCRETE BY ELECTRODE ARRAYS

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There are several methods for the detection of steel corrosion in concrete, but all of them have some specific disadvantages. Most of conventional methods (potential mapping, Rp measurements) provide general corrosion conditions in shorter time intervals. In addition, none of them detects the type of corrosion (general, pitting). In the present work two relatively new methods were implemented: measurements of partial current by means of coupled multi-electrode arrays (CMEA), and assessment of general corrosion rate with electrical resistance (ER) probes. Measuring with an electrode array is by some means the advancement of electrochemical noise (EN): with electrically connected micro-electrodes, which are spatially arranged, the assessment of anodic and cathodic currents distribution in time is possible. An electrical resistance (ER) probe provides reliable general corrosion rate, which is calculated from the thickness reduction, however its response to localized corrosion is limited. Beside these two techniques, electrochemical impedance spectroscopy (EIS) was used as an upgrade of Rp measurements.

The measurements were performed in concrete specimens, which were exposed to periodic wetting and drying cycles. In the second wetting cycle, the chlorides were introduced by wetting the mortar with 3.5% NaCl solution. The methods detected the initiation of corrosion in the beginning of the wetting cycles, and the retardation of corrosion at the end of the drying cycles. Most of the methods clearly indicated the change in corrosion rate in the chloride presence.

The distribution of anodic and cathodic currents obtained by CMEA indicated that the localized corrosion rates were significantly higher that the measured general corrosion rates. The results of both used methods were compared and related to the conditions of steel after the test was finished. In certain cases, especially at CMEA, X-ray micro-tomography was used, in order to characterize the initial phase of corrosion.

CPA-P-02

STABILITY OF CARBON SUPPORT FOR PEMFC

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Fuel cells have emerged as a very promising substitute for selected conventional energy conversion technologies. To some extent, carbon-supported Pt alloy catalysts have fulfilled the expectation when used in contemporary PEM fuel cells. At the moment, a more critical concern seems to be the durability of PEMs. Together with platinum dissolution carbon corrosion is the main cause of a decrease in the electrochemical surface area (ESA) during typical operation of PEM[1,2]. Our preliminary modeling based on a wide range of thermogravimetric data suggests that the rate of oxidation of carbon support follows the same trend as the oxygen reduction activity measured with thin-film rotating disc electrode method. In other words, the catalyst activity seems to be inversely proportional to stability of carbon support which sheds a new light on the problem of catalyst stability.

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CPA-P-03

ANODIC OXIDATION OF MAGNESIUM ALLOY AZ31 TO BE USED AS BIODEGRADABLE ALLOY

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Magnesium alloy AZ31 can be used as a biodegradable implant material in different orthopaedic applications, especially for healing of fractures of small joints. Unfortunately, the corrosion rate of this material is so high that its degradation may occur before the end of the healing process[1]. To reduce the corrosion rate, various methods can be applied. We used the method of anodic oxidation in an alkaline environment in order to form passive oxide layers on the alloy surface.
The oxide layers were formed at different anodic potentials in 1 M NaOH aqueous solution. The corrosion characteristics of anodized samples were then assessed in simulated physiological solution (SPS) by electrochemical polarization methods. Morphology and composition of the anodized samples were analyzed by scanning electron microscopy and X-ray photoelectron spectroscopy. To follow the degradation of anodized AZ31 alloy, immersion tests were performed in SPS. The concentration of dissolved Mg^{2+} ions was determined by complexometric titration. Anodized layers successfully reduced the degradation rate of Mg alloy.

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CPA-P-04

LANTHANIDE SALTS AS CORROSION INHIBITORS FOR ALUMINIUM ALLOY IN CHLORIDE MEDIUM

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Aluminium alloy 7075-T6 is commonly used in different applications in industry. For many decades, chromate conversion coatings have been applied to protect metals and their alloys against corrosion. Their use has been recently restricted due to the cancerogenicity of chromate compounds. As alternative, rare earth salts, especially cerium, have been identified.[1] The aim of this study was to investigate various rare earth salts as corrosion inhibitors for the 7075-T6 alloy, i.e. cerium chloride, cerium nitrate, lanthanum chloride, lanthanum nitrate and neodymium nitrate. Two methods of inhibition were tested: the addition of rare earth salts directly in chloride solution, and the preparation of conversion coatings followed by measurements in chloride solutions. The corrosion properties were studied by electrochemical measurements in 0.1 M NaCl solution, as well as by testing in salt spray chamber. Among various salts, the addition of 0.01 M CeCl$_3$ was most effective against corrosion in chloride solution.

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CPA-P-05

SELF-HEALING EFFECT OF CERIA ELECTRODEPOSITED THIN FILM ON STAINLESS STEEL IN 0.5 M NaCl

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The electrodeposition of Ce_2O_3-CeO_2 on stainless steel (SS) significantly improves its corrosion resistance in nitric and sulfuric acids [1]. In this study we have proven the self-healing effect of electrochemically deposited Ce_2O_3-CeO_2 on SS in 0.5 M NaCl. The sinusoidal changes in the open circuit potential after 200 h exposure in the corrosive media are associated with the formation of a secondary passive oxide / hydroxide films in the area of its mechanical removal, established by XPS. SEM and EDS analyzes showed partial accumulation of cerium in the scratched surface area, protect significantly the local corrosion at the scratch area.

Acknowledgment: The authors gratefully acknowledge the financial support of Project BG 051PO001-3.3.06-0038.

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CPA-P-06

MICROSTRUCTURAL EVOLUTION AND CORROSION BEHAVIOR OF $Al_{25}Ti_{25}Ga_{25}Be_{25}$ EQUI MOLAR COMPOSITION ALLOY

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The microstructure of light element containing Al25Ti25Ga25Be25 equi-molar composition alloy were investigated by X-ray diffractometry and scanning electron microscopy, while the corrosion behavior was tested in 1M sulfuric acid solution (H2SO4) at ambient temperature (298 K). The results show that the alloy displays good general corrosion resistance. The influence of the microstructure and morphology of the constituent phases is also evaluated.

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CPA-P-07

CORROSION INHIBITION OF CARBON STEEL IN 3.5 % NaCl SOLUTION USING GLUCONATE, ZINC SULPHATE AND GREEN CLAY ELUATE

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The effect of sodium gluconate, $ZnSO_4$ and green clay eluate on the corrosion inhibition of carbon steel (EN S235 JRG) in 3.5 % sodium chloride solution has been evaluated using Tafel polarization technique. Substantial general corrosion inhibition using sodium gluconate solely can be obtained with moderate concentrations. The corrosion inhibition is predominately obtained by anodic mechanism and is limited to general corrosion, whereas carbon steel becomes liable to localised pitting corrosion. When sodium gluconate is combined with $ZnSO_4$ and/or green clay eluate both general and localized corrosion are diminished which indicates good synergy between applied inhibitors.

CPA-P-08

TARTRATE AS CORROSION INHIBITOR IN CONCRETE – THE PITTING CORROSION INHIBITION

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Electrochemical measurements performed in a solution simulating concrete pore solution have shown that tartrate postpones pitting corrosion initiation of steel. EIS and capacitance measurements have shown that tartrate affects the electrochemical and semi-conductive properties of passive film. It was postulated that tartrate adsorbs on the passive film surface effectively competing with chloride ions in the pitting initiation process by blocking the surface active sites. ATR FTIR measurements have confirmed the presence of tartrate at the steel surface.

The addition of tartrate to mortar was shown to affect the properties of fresh and hardened mortar resulting in increased compressive strength and penetrability resistance of mortar. Electrochemical measurements performed on rebar embedded in mortar and exposed to chloride media have shown significantly higher interfacial resistances of the samples to which the tartrate was admixed. Such behavior may be an indicator of an enhanced corrosion resistance of rebar.

CPA-P-09

L–TRYPTOPHAN AND L–HISTIDINE AS CORROSION INHIBITORS FOR CARBON STEEL IN WEAK ACID SOLUTIONS

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The inhibitory properties of L-tryptophan and L-histidine on the corrosion process of carbon steel in weak acid media, containing acetic acid/sodium acetate, has been investigated by weight loss, Tafel polarization and electrochemical impedance spectroscopy measurements. The results obtained indicate that the amino acids exhibit good inhibition efficiencies which increase with concentration. The adsorption of these compounds obeys Langmuir adsorption isotherm and the negative value of Gibbs energy indicate the nature of interactions between inhibitor molecules and metal surface. Further, the inhibition effect was studied using scanning electron microscopy and energy dispersive X-ray analysis. The electrochemical behavior of L-tryptophan and L-histidine has been determined by cyclic voltammetry method.

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CPA-P-10

ELECTRODEPOSITION AND CORROSION PROPERTIES OF TERNARY Zn-Ni-P ALLOYS

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The investigation reports about the electrochemical obtaining of alloy coatings Zn-Ni-P from sulfate-chloride electrolyte the later containing b-alanine, $NaH_2PO_2.H_2O$ and H_3PO_2. Important characteristics like surface morphology, chemical and phase composition of the alloys are determined. CVA curves demonstrate that at these electrodeposition conditions Zn does not co-deposit with phosphorus in the absence of nickel ions in the electrolyte. The alloys deposited under galvanostatic conditions at pH 2-3 and current density values of 1-2 A/dm^2 contain an amorphous phase and are practically Ni-Zn-P coatings with different phosphorus content. The corrosion properties and protective ability of the alloy coatings obtained are investigated by using the potentiodynamic polarization method and polarization resistance (Rp) measurements in model corrosion medium of 5% NaCl. Highest Rp values and best protective ability against the iron substrate, respectively show the alloy with composition Zn-92%, Ni-5%, P-3%.

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CPA-P-11

EVALUATION OF EUGENOL AND LINALOOL AS CORROSION INHIBITORS FOR ALUMINIUM IN HCL SOLUTION

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The use of corrosion inhibitors is one way of protecting Al against corrosion in acidic media.1,2 Two non-toxic organic compounds, namely, eugenol and linalool were investigated as corrosion inhibitors for aluminium in 0.5 M HCl solution by weight loss, potentiodynamic polarization and EIS methods. Gravimetric measurements showed that the corrosion rate of aluminum in 0.5 M HCl was significantly reduced in the presence of compounds investigated. Potentiodynamic polarization curves indicated that presence of eugenol and linalool in HCl solution causes a prominent decrease in current densities. EIS measurements confirmed the existence of protective inhibitor film on the Al surface. The optimum concentration of eugenol was 0.012 mol L^{-1}, while for linalool a concentration of 0.035 mol L^{-1} was necessary to attain its maximum inhibition eficinecy.

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CPA-P-12

INHIBITING EFFECT OF SOME ANTIBIOTICS ON BRONZE CORROSION

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Inhibition performance of three antibiotics, namely streptomycin, doxycycline and ciprofloxacin as corrosion inhibitors for bronze in acidic solution (pH = 4) has been studied. Results of electrochemical impedance and Tafel polarization measurements consistently showed that the three compounds exert to some extent an inhibiting effect on bronze dissolution. The highest inhibition efficiency value was around 85% for all investigated compounds. EIS measurements also revealed that the antibiotics effectiveness as bronze corrosion inhibitors is time-dependent. Langmuir isotherm is found to provide an adsorption description of the studied compounds on bronze surface.

CPA-P-13

CORROSION STUDIES OF Ag/TiO_2-COATED Ti−6Al−7Nb SURFACES IN SIMULATED PHYSIOLOGICAL SOLUTION

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The physico-chemical and electrochemical properties of the composite oxide film on Ti alloys surface play a decisive role for the bio-compatibility of titanium-based implants[1]. Starting from the fact that silver has a high antibacterial activity and Ti alloys are widely used as implant materials[2], Ag/TiO_2 composite layers were electrodeposited on a mechanically polished Ti−6Al−7Nb surface, in different experimental conditions (oxidation potential, electrolyte type etc). Linear and cyclic polarization methods were used to investigate the corrosion behaviour of the Ag/TiO_2 composite layers in Hank's simulated physiological solution. The obtained results were compared to those recorded on Ag/TiO_2 modified Ti in the same experimental conditions.

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CPA-P-14

PHYTIC ACID AS GREEN CORROSION INHIBITOR FOR COPPER

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Copper is used in many industrial applications due to its favourable thermal and electrical conductivity and good corrosion resistance. Nevertheless, the protection of copper in aggressive chloride media can still be improved. Corrosion inhibitors have been commonly used, but they may be toxic to the environment[1]. In this study, phytic acid was considered as a corrosion inhibitor for copper. Phytic acid, with a molecular formula $C_6H_6[OPO(OH)_2]_6$, inositol hexaphosphate (IP_6), is a natural plant compound, and it is commonly found in rice, beans, wheat bran, etc[2]. Phytic acid contains 12 replaceable protons and expresses highly pH dependent chelating properties. Using self-assembling process the protective layer was formed at the surface of copper. Its electrochemical characteristics in 3 % NaCl solution were studied as a function of preparation method including surface roughening, time of immersion and inhibitor concentration. Electrochemical polarization methods were used complemented by scanning electron microscopy.

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CPA-P-15

CERIUM-CONVERSION COATINGS FOR CORROSION PROTECTION OF ALUMINIUM AND ALUMINIUM ALLOY 7075-T6

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Due to favourable physical and chemical properties aluminium and its alloys are commonly used metals in aerospace, automobile and construction industries. Chromate conversion coatings which have been used for decades for corrosion protection of Al alloys must be replaced due to the restricted use of Cr^{6+}-based compounds in European Union[1]. Rare-earths conversion coatings, especially prepared with cerium salts, have been reported as one of the alternatives[2]. Two types of cerium based conversion coatings were investigated on Al and its alloy 7075-T6: (i) addition of cerium salt solution directly to chloride solution, and (ii) formation of cerium conversion coating prior to immersion to chloride solution. Various cerium salts were tested: nitrate, chloride, acetate and sulphate. Corrosion properties of the modified metal surface were studied in 0.1 M NaCl, while its morphology and composition were analysed by SEM/EDS.

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CPA-P-16

IMPROVEMENT OF CORROSION PROTECTION ABILITY OF CERIA LAYERS DEPOSITED ON ALUMINUM

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The influence of copper ions as component of cerium salts-based-electrolyte has been studied with a view to conversion treatment of aluminum. Thereupon the processes of formation of cerium oxides films on Al have been investigated and the occurring changes in the corrosion protection behavior of the system Al/conversion layer have been monitored. It has been established that the addition of Cu^{2+} ions to the working electrolyte determines the formation of copper clusters on the surface of aluminum, which is leading to electrochemical "activation" of the Al surface. The presence of additional active sites of copper on Al increases considerably the rate of deposition of the conversion layer of Ce_2O_3+CeO_2 and it improves the corrosion behavior of the Al/conversion layer. The chemical state and the chemical composition of the conversion films have been defined on the basis of the XPS measurements.

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CPA-P-17

ELECTROCHEMICAL BEHAVIOUR OF NANOTUBES FORMED ON TiAlZr

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The electrochemical characterization of nanostructures area with various sizes is the mail goal of this present work. The nanotubes were formed via one step anodization in a mixture of Glycerol+15vol.%H_2O+0.2M NH_4F using different voltages. The surface was characterized using SEM, AFM and contact angle determinations. Electrochemical behaviour was characterized by Tafel plots, cyclic voltammetry and electrochemical impedance spectroscopy. All the electrochemical experiments were performed in HANK solution with the following composition:
NaCl - 8; KCl – 0.4; $NaHCO_3$ – 0.35; $NaH_2PO_4 \cdot H_2O$ – 0.25; $Na_2HPO_4 \cdot 2H_2O$ – 0.06; $CaCl_2 \cdot 2H_2O$ – 0.19; $MgCl_2$ – 0.19; $MgSO_4 \cdot 7H_2O$ – 0.06; glucose - 1.

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CPA-P-18

ELECTROCHROMISM IN ANODIC Nb_2O_5 FILMS

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Over a long period of time our researchers conducted a number of researches dealing with electrochrome effect (EChE) in certain transition-metal oxides, primarily in Nb_2O_5 anode oxide films (AOF). We were the first to obtain AMORPHOUS AOF of niobium pentoxide [1] that show pronounced electrochrome effect, i.e. retain high contrast during numerous “coloring-discoloration” cycles.. We have patented a technique for preparation of amorphous anode electrochrome films on niobium, comprising a totally ingenious electrolyte composition and anode oxidation mode. Besides, we have developed the pulsed electrochemical polarization conditions for already known electrochrome structures which permit to raise coloring voltage, and consequently, electrochrome process rate, still preserving the predominance of hydrogen injection into oxide over gas discharge .

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CPA-P-19

CORROSION PROTECTION OF COPPER, ZINC AND THEIR ALLOYS WITH CARBOXYLIC ACIDS

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The use of carboxylic acids as a means to modify the surface of Cu, Zn, Cu10Zn and Cu40Zn and thus to increase their corrosion resistance was investigated. The carboxylic acids form by self-assembling a hydrophobic layer[1] on the surface which improves the corrosion resistance of underlying metals.[2] The samples were immersed in ethanol solution of different carboxylic acids: hexanoic, decanoic, myristic and stearic. Their corrosion properties were investigated in artificial rain. The longer the aliphatic tail of carboxylic acid, the better the corrosion resistance. The effect of surface roughness prior the self-assembling process was studied, especially in terms of its effect on the corrosion resistance and degree of hydrophobicity. The increased surface roughness implies better corrosion resistance and higher hydrophobicity.

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PAE
Physical and Analytical Electrochemistry

ORAL PRESENTATIONS

PAE-O-01

CHEMICALLY MODIFIED ELECTRODES BASED ON POLYAZULENE COMPLEXING FILMS FOR LEAD AND CADMIUM METAL IONS ELECTROANALYSIS

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New complexing polymer-coated electrodes have been synthesized by oxidative electropolymerization of 4-azulen-1-yl-2,6-bis(2-thienyl)pyridine in acetonitrile solutions[1]. The electrodes were used for the detection of Pb(II) and Cd(II) ions by means of the chemical preconcentration-anodic stripping technique. The electrode material showed a selectivity towards Pb(II) ions. Detection limits of 0.7 nM and 10 nM were obtained for Pb(II) and Cd(II) ions, respectively. The modified electrodes have been used for the determination of lead in natural water and tap-water.

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PAE-O-02

EFFECT OF PHOTO-OXIDATION OF ASCORBIC ACID ON THE ANALYSIS OF HYDROGEN PEROXIDE USING TITANIUM-PORPHYRIN REAGENT

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The Ti-TPyP reagent, *i.e*. an acidic aqueous solution of oxo[5,10,15,20-tetra(4-pyridyl) porphyrinato]titanium(IV) complex, denoted as TiO(tpyp), was first developed by us as an effective reagent for determining trace hydrogen peroxide in electroanalytical chemistry. The reagent is characterized by very high sensitivity and specificity to hydrogen peroxide[1]. In the course of the uses of the reagent in biomedical analysis, ascorbic acid concurrently present in the samples was found to cause a positive error in the analytical results. In the present paper, the source of the error was revealed to be due to the production of hydrogen peroxide through the oxidation of ascorbic acid by singlet oxygen arising from the energy transfer between oxygen molecule and the photo-excited TiO(tpyp) complex. The reaction mechanism was proposed for the photo-oxidation processes of ascorbic acid to produce dehydroascorbic acid and hydrogen peroxide.

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PAE-O-03

ELECTROCHEMICAL ANALYSIS OF POLYSACCHARIDES ON STATIC MERCURY DROP ELECTRODE

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Chronopotentiometric features of peak recorded in the buffer solutions of selected marine polysaccharides (PS) at different conditions (accumulation potential, accumulation time, stripping current, buffer concentrations) will be presented. According to the electrochemical properties and rules serving as a tool to differentiate between faradaic and catalytic current[1,2], it will be proven that obtained peak possess catalytic characteristics on mercury electrode, so it is called "peak H_{PS}"[2]. Sulpho- and carboxyl groups could be identified as catalytic groups in the PS structure. Dependence of "peak H_{PS}" on accumulation potential could give the information about PS conformation. Reproducibility could be assured in the buffered electrolyte only.

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PAE-O-04

INVESTIGATION OF PLATINUM STABILITY BY IN-SITU MASS SPECTROMETRY

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Electrochemical energy conversion and storage play a key role in a proclaimed movement to clean and sustainable power supply. This makes technologies like fuel cells, electrolysers, and batteries more attractive than ever. All of these approaches have their pros and cons. Commercialization of fuel cells is limited by a lag in long-term performance, particularly of catalysts, and dissolution is one of the main causes of degradation. Employment of traditional electrochemical approaches for investigation of electrode dissolution is, however, not satisfactory. In order to address this phenomenon, our group has developed a unique coupled system, which allows local electrochemical experiments in parallel with time resolved multi-elemental analysis of the electrolyte by ICP-MS[1,2]. This approach was successfully utilized in a first study for the investigation of polycrystalline platinum dissolution. Obtained results will be presented and discussed.

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PAE-O-05

INVESTIGATION OF THE REDUCTION OF PERCHLORATE IONS ON RHODIUM AND RUTHENIUM

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The stability of perchlorate ions is interesting from electrochemical point of view, since perchlorate salts or perchloric acid are often used as supporting electrolytes. On the other hand, in many countries perchlorate is present as contaminant in soils and drinking water. There are several metals which can either reduce perchlorates themselves, or at least can act as an electrode material, on which the perchlorate ions can be electrochemically transformed to chloride. In this study new results concerning the reduction of the perchlorate ions on ruthenium and rhodium in contact with perchlorate solutions are shown. Results of various measurements are presented with special attention to cyclic voltammetry, chronoamperometry, and impedance spectroscopy. Changes of the interfacial stress were measured by the electrochemical bending beam (cantilever bending) method as functions of the electrode potential and of the concentration of chloride ions. It could be shown that chloride ions change the interfacial stress and exert an inhibiting effect on the reduction process indicating the role of competitive adsorption. These findings provide a warning that the reduction process may also significantly influence the electrocatalytic activity of metals in solutions containing perchlorate ions.

PAE-O-06

ON THE NATURE OF THE ELECTROCHEMICAL DOUBLE LAYER

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

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

PAE-O-07

FARADAIC ADSORPTION OF LITHIUM ON THE SURFACE OF CARBON FIBER STUDIED BY CYCLIC VOLTAMMETRY AND RAMAN SPECTROSCOPY

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During the course of studying carbon fibers by cyclic voltammetry in an organic electrolyte containing Li cation we incidentally found the appearance of sharp pre-peak on the main peak due to the Li insertion/deinsertion. The pre-peak appeared not only on the graphitized carbon but also activated carbon after the mild oxidation treatment. This means that the appearance of the peak is possible only on the cleaned surface. We attempted to identify the cause of the peak. After detailed examination we attributed the peak is due to the Faradaic adsorption of Li on the carbon surface. We tried to detect the vibrational band of the C-Li bond by constructing electrochemical in situ Raman cell. A new band at 442 cm-1 was detected only when the polarization potential was sufficiently cathodic to 10 mV vs. Li|Li+. The amount of the adsorbed Li was enhanced by nano-ionics mechanism.

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PAE-O-08

ON THE APPLICABILITY OF MAXWELL RELATIONS IN SURFACE THERMODYNAMICS AND ELECTROCHEMISTRY

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We have shown that two known conditions of the applicability of Maxwell's relations (mutual independence of the chosen pair of variables and conformity of the fundamental thermodynamic equation to the requirements for the thermodynamic potential to be a 'characteristic function') make these relations inapplicable for the description of capillary and electrocapillary phenomena, as they lead, if used correctly, to trivial results. Attempts to use Maxwell's relations for the case of solid electrodes available in the literature are based on mathematical defects and, consequently, yield erroneous results[1, 2]. Attempts to use the fundamental equation transformed to the *per-unit-area basis* (in densities) have been erroneous because a correct transformation excludes the surface area from the set of independent variables.

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POSTER PRESENTATIONS

PAE-P-01

MODIFIED ELECTRODES BASED ON POLY(MALONAMIDE-LIKE) FILMS FOR HEAVY METAL ELECTROANALYSIS

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New complexing chemically modified electrodes (CMEs) have been obtained by oxidative electropolymerization of (3-pyrrole-1-ylpropyl)N,N,N',N'-tetraethyl-malodiamide (**L**). Poly**L** films could be grown onto carbon disk electrodes from millimolar solutions of **L** in acetonitrile-TBAP in the presence of 2 equivalents of perchloric acid[1]. Upon transfer into clean supporting electrolyte, the resulting modified electrode retains this electroactivity. Poly**L** films could also be grown by controlled potential oxidation. Apparent surface concentration of complexing sites Γ_L was assessed. Dark-blue films with Γ_L ranging from 2×10^{-9} to 10^{-8} mol cm^{-2} have been obtained. The complexing properties of these CMEs have been evaluated for lead and mercury ions electroanalysis.

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PAE-P-02

A SPECTROELECTROCHEMISTRY STUDY OF THE OXIDATION OF ADENOSINE AND ADENOSINE-THYMIDINE PAIR

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The IR absorption spectra of one electron oxidized adenosine (A) and adenosine-tymidine H-bonded pair (A:T) have been recorded in an electrochemical cell, during oxidation at controlled potential.

Spectroelectrochemical measurements of the A:T H-bonded complex[1] show a broad absorption in the IR spectral region attributed to photoinduced electron transfer from neutral thymidine to adenosine cation, which localizes the electron hole on the thymidine moiety, similar in shape and bandwidth to that observed for the guanine-cytosine pair.[2]

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PAE-P-03

STACKING INTERACTIONS BETWEEN ADENINES IN DNA OLIGONUCLEOTIDES

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Stacking interactions play a major role in DNA oxidation, because they finely modulate the redox potential of DNA nucleobases, in a way which depends on the primary and higher order structures. Here, we present a series of voltammetric measurements -a well suited experimental tool for detecting the effects of inter-base interactions on the oxidation potentials of the nucleobases-[1-3] of oligonucleotides containing adenines in different sequences and ratios, which in physiological conditions exhibit multiple signals, characteristic of pi stacked molecular systems, which allow a quantitative determination of the strengths of stacking interactions between two stacked adenine units.

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PAE-P-04

ION EFFECTS ON SELF-ASSEMBLED MONOLAYERS OF L-CYSTEINE ON p-GaAs (100) ELECTRODES

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L-Cysteine is a natural amino acid containing a thiol group with high affinity for solid surfaces, be the carboxyl and amino functional groups that can be conjugated with other biomolecules. Cysteine-modified electrodes proved already to be useful in the electroanalytical detection of cytochromes, proteins and vitamin B12. The effects of magnesium and chlorine ions on the self-assembled monolayers of cysteine on p-GaAs (100) electrodes were investigated by electrochemical impedance spectroscopy (EIS) coupled with photoelectron X-ray spectroscopy (XPS) and atomic force microscopy (AFM). The results revealed changes both in the capacitive and resistive contributions of the cysteine-thiolate monolayer and the electronic properties of the semiconductor electrode.

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PAE-P-05

HEMIN MODIFIED GRAPHITE ELECTRODE FOR H_2O_2 ELECTROCATALYTIC REDUCTION: A COMPARISON OF DIFFERENT IMMOBILIZATION TECHNIQUES

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The integration of biomolecules (enzyme or part of enzyme) with nanosized materials (single wall carbon nanotubes, SWCNT) into a polymer matix can achieve to a new composite electrode material that combine the special recognition and catalytic properties of biomaterials with the unique electronic, optical and catalytic functions of nanomaterials. Due to its iron (III) redox active center, hemin (Fe^{III} protoporphyrin IX chloride, Hm) was used as prototype of biomolecule[1]. In this work, three different approaches for Hm immobilization: Hm electropolymerisation or incorporation in negative (Nafion) and positive (chitosan) charged polymer matrixes were compared. Cyclic and square-wave voltammetric measurements were used to find out the most performance modified electrode for H2O2 electroreduction.

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PAE-P-06

BISMUTH-DISPERSED SOL-GEL-MODIFIED SCREEN PRINTED GRAPHITE ELECTRODES FOR THE DETERMINATION OF LEAD AND CADMIUM

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The effectiveness of bismuth-dispersed xerogel as a modifier for the development of sensors for lead and cadmium [Anal. Chim. Acta in press], led us to explore the possibility to massively fabricate cheap and reliable sensors, based on this material, by employing the screen-printing technology. A key parameter for the implementation of this objective was the preparation of properly sized bismuth-dispersed sol-gel (Bi-SG) particles to allow them to be screen-printed. For this purpose, diferrent synthetic routes were tested and the resulting materials were characterized with SEM, IR spectroscopy and SW voltammetry. Under certain experimental conditions a granular material of grain size <25 μm, as evidenced by SEM inspection, was received and used as a blend of 4% w/w Bi-SG with a commercial graphite ink to fabricate Bi-SG-modified screen-printed electrodes for the determination of lead and cadmium ions with stripping voltammetry. Acknowledgements**:** The research Project is co-funded by the European Union - European Social Fund (ESF) & National Sources, in the framework of the program “HRAKLEITOS II” of the “Operational Program Education and Life Long Learning” of the Hellenic Ministry of Education, Life Long Learning and religious affairs.

PAE-P-07

GOLD NANOPARTICLE-DECORATED CYSTEAMINE-MODIFIED GRAPHENE OXIDE AS SENSING LAYER FOR THE VOLTAMMETRIC DETERMINATION OF ARSENIC

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This work reports on the synthesis and characterisation of cysteamine-modified graphene oxide (GO-CYS) before and after its reaction with chloroauric acid ($HAuCl_4$). Materials were characterized with XRD, FTIR and TGA/DTA analysis. The so produced hybrid material was applied over screen-printed graphite electrodes (GRA-SPEs) and then, the formation of gold-nanoparticle (Au-NP) was achieved by cathodic polarization at different applied potentials. Optimum conditions for the formation of Au-NP were investigated and confirmed with XPS studies. Finally, GO-CYS@Au-NP-modified GRA-SPEs were used as sensors for the determination of arsenic by anodic stripping voltammetry. Various experimental varialbles were investigated in detail and optimized.

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PAE-P-08

PERFORMANCE OF LAYER-BY-LAYER DEPOSITED LOW DIMENSIONAL BUILDING BLOCKS OF GRAPHENE-PRUSSIAN BLUE AS SENSORS FOR HYDROGEN PEROXIDE

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Thin films of reduced graphene oxide (rGO)-prussian blue (PB) hybrids were deposited on graphite screen-printed electrodes (SPEs) using a novel layer-by-layer approach that combines the self-assembly with the Langmuir-Schaefer method. A water solution of GO was used as subphase in a Langmuir-Blodgett (LB) deposition system while a long-chain amino surfactant (octadecylamine, ODA), that binds covalently with the GO, was injected at the air-water interface for the formation of hybridized organo-GO. GO hybrid films were deposited on hydrophobic graphite SPEs by horizontal dipping in the LB through. Then, GO platelets were further modified by bringing the surface of the transferred Langmuir film in contact with ODA, and finally, the ODA-GO-ODA films were brought in contact with PB solution. The so produced modified electrodes were tested as sensors for hydrogen peroxide by employing cyclic voltammetry and amperometric measurements. The effect of Rb(II) and Cs(I) as counter ions and of various polymers as protective membranes on the sensitivity and working stability of the sensors was also investigated.

PAE-P-09

ZIRCONIA-MODIFIED SCREEN PRINTED GRAPHITE ELECTRODES FOR THE DETERMINATION OF LEAD AND COPPER

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The fabrication of zirconia (ZrO_2)-modified screen-printed graphite electrodes (GRA-SPEs), and their performance as chemical sensors for the simultaneous determination of lead and copper is presented for the first time. GRA-SPEs with diferrent loadings of 2, 4 and 6% w/w zirconia were fabricated and examined with respect to their efficiency to serve as sensors for metal cations by employing anodic stripping voltammetry. ZrO_2-GRA-SPEs showed an excellent performance for Pb(II) and Cu(II) ions, while the highest response for Pb and Cu (stripping) peaks was observed at 4% w/w loading. Various experimental variables were investigated. Under selected working conditions and for a preconcentration period of 60 s, the 3σ limit of detection was 1.1 μg L^{-1} for Pb(II) and 3.0 μg L^{-1} for Cu(II), while the reproducibility of the method was 3.6% for lead (n=8, 15.9 μg L^{-1} Pb(II)) and 2.5% for copper (n=8, 24.4 μg L^{-1} Cu(II)). ZrO_2-GRA-SPEs showed a remarkable working and storage stability by retaining their original activity for more than 30 successive runs and six months, respectively. The effect of potential interferences was also examined and the sensors were succesfully applied to the determination of Pb(II) and Cu(II) in water samples.

PAE-P-10

DETERMINATION OF ASCORBIC ACID IN PHARMACEUTICAL SAMPLES BY CYCLIC VOLTAMMETRY

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The aim of this work was to determine ascorbic acid content pharmaceutical samples by cyclic voltammetry and standard titrimetric method[1]. A Pt disc electrode was used as working electrode. The reference electrode was a Ag/AgCl in saturated KCl solution. The counter electrode was a Pt strip. A stock solution of ascorbic acid, 20mmol·L^{-1}, was prepared daily in a 0.34mol·L^{-1} KCl solution. Standard solutions of ascorbic acid with concentrations ranging between 1,25 and 20 mmol·L^{-1} were obtained by diluting the stock solution with the respective volumes of 0.34mol·L^{-1} KCl solution. Obtained results by cyclic voltammetry showed good correlation with titrimetric method. The proposed procedure was successfully applied to the determination of L - ascorbic acid in the pharmaceutical preparations.

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SDE

Electrochemical Synthesis, Deposiotion, Electrolysis and Engineering

ORAL PRESENTATIONS

SDE-O-01

PULSE PLATED AND LASER ABLATED SILVER NANOCOATINGS FOR BIOMEDICAL APPLICATIONS

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Bacterial biofilm formation on the surface of implanted metal objects is a major clinical problem. Removing bacteria being in a biofilm is impossible and the local or systematic antibiotic treatment is not effective. In view of increasing bacterial resistance to antibiotics and antiseptic, silver coating can be an effective strategy to prevent the bacterial induced infections.

This work presents the development of nanostructured silver coatings or silver grains on TiAl6V4 and CoCrMo metallic implants with controlled and sustained silver release. Nanocrystalline silver layers and/or independent silver grains on metallic implants have been deposited using two different techniques, namely pulse current technique and laser ablation methods.

Long-term corrosion potential measurements carried out on pure silver, different substrate materials and silver coated metallic implants showed that the potential of substrate materials are more positive than that of pure silver and silver coated metallic implants. Consequently galvanic corrosion can take place when the silver coated metallic implants are exposed to a corrosive environment such as chloride or Ringer solutions. In this case the silver in the bimetallic corrosion acts as anode.

The release of silver deposited on metallic substrates has been traced by EIS measurements under open circuit conditions in chloride solution. Local dissolution of the silver was also confirmed by other methods, such as SEM micrographs, and solution analysis by ICP-MS methods.

The antibacterial activity and the antifungal efficiency of silver coated Ti alloy samples were tested against frequently used bacterial species and funguses.

The biocompatibility aspects were taken with high importance throughout the whole project.

Since the initial experiments when the silver was deposited by pulse plated technology with the thickness of the silver coating of 10 micrometer, showed that the silver coated samples compared to the substrate had negative effect on the growth and viability of bone cells, therefore we moved the focus to produce silver grains also by electrochemical technique. In this case some parts of the substrate remained without silver, which ensures the growth of bone cells on the metallic implant. Testing of these samples proved that the assumptions were correct, and the result of these experiments with modified pulse plating" will be presented.

SDE-O-02

ELECTROPLATED FERROMAGENTIC NANOSTRUCTURES FOR DIFFERENT APPLICATIONS

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Chemically ordered and disordered Co-Pt and Fe-Pd nanostructures represent a promising magnetic storage media and potential as nano- and micro-magnets which can be used in micro- and nano-systems. In addition the magnetic shape memory alloys like $Fe_{70}Pd_{30}$, where reversible strains of several percents are achieved in modest magnetic fields, also represent an interesting class of materials. Co-Pt and Fe-Pd-based nanotubes and nanowires produced via template assisted electroplating will be discussed from the magnetic properties point of view, with the emphasis on the composition, morphology and the crystal structure influence. Furthermore the magnetic shape memory $Fe_{70}Pd_{30}$ nanostructures will be assessed as a potential smart drug delivery system. In addition the electroplating of Tb from a non-aqueous solution on the hard magnetic substrates and its influence on the final magnetic properties will be presented.

SDE-O-03

STUDY OF ELECTROLYTIC REDUCTION INTO LITHIUM AND SODIUM MOLTEN SALTS

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Electrolytic reduction of both lithium and sodium molten salts on carbon and molybdenum cathodes accompanied with formation of carbon nanotubes (CNTs) was studied by means of cyclic voltammetry. As an electrolyte LiCl, Li_2CO_3, LiOH and NaOH were used. The measurements were performed in temperature interval from 400 to 900°C. It was found that start potential of Li and Na reduction depends on type of electrolyte and cathodic material as well as working temperature. Due to intercalation of Li and Na into graphite bulk, electrochemical reduction on graphite cathode occurs at more positive potentials related to molybdenum one. Increase of working temperature intensifies electron transfer on graphite electrode, shifting potential at more positive values. It should mention that the process of lithium and sodium intercalation generates a high mechanical stress at the graphite surface that causes exfoliation of the graphite cathode. This phenomenon enables electrochemical synthesis of CNTs to be possible.

Key words: Carbon nanotubes (CNTs), Molten salts, Lithium, Sodium, Graphite,, Molybdenum

SDE-O-04

ELECTROCHEMICAL SYNTHESIS OF TITANIA NANOPOWDER INVOLVING CHOLINE CHLORIDE BASED IONIC LIQUIDS WITH EXTENDED VISIBLE LIGHT RESPONSE

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Recently it has been demonstrated the possibility of forming of ionic liquids from eutectic mixtures of quaternary ammonium salt such as choline chloride with hydrogen bond donor species such as amides, glycols or carboxylic acids, also known as “deep eutectic solvents (DES)”, with a good air and water stability. Unlike the conventional ionic liquids, the use of DES for a large range of metal surface treatments may be an attractive alternative due to their easy synthesis and manipulation. The paper presents some preliminary experimental results dealing with the synthesis of TiO_2 nanopowder using anodic dissolution of Ti in DES. The obtained nanocrystalline oxide has crystallite sizes of 10-20 nm, a high surface area and enhanced photocatalytic effect also extended under visible light irradiation. Moreover, an anodic synthesis efficiency of min.92% has been determined.

SDE-O-05

COMPOSITION DEPTH PROFILE OF d.c.-PLATED AND PULSE-PLATED Fe-Ni ALLOYS

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Fe-Ni alloys have been produced by electrodeposition using. both d.c. plating and pulse plating. Ccomposition depth profile measurements were carried out with the so-called reverse mode, in which the deposit was peeled off from the substrate and the sputtering process started at the substrate side. It has been found that the molar fraction of iron near the substrate is higher than during the steady-state deposition when d.c. plating is applied. In the pulse-plating mode, however, samples with nearly even composition could be obtained. The duty cycle at which deposits with even composition could be obtained was the smaller, the lower the Fe^{2+} concentration. This indicates the importance of the mass transport effects during the deposition at low Fe^{2+} concentrations.

POSTER PRESENTATIONS

SDE-P-01

EIS ASSAYS OF POLY(3-AMINOPHENYLBORONIC ACID) FILMS ON PLATINUM ELECTRODES

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Compared to polyaniline, self-doped polyanilines such as poly(anilineboronic acid) (PABA), show improved redox activity and conductivity in neutral pH solutions that simulate the physiological environment of the human body, which makes them good candidates in the design of biosensors. In this work several PABA films have been electrochemically deposited on platinum electrodes from acidic solutions in the presence of NaF. The influence of monomer and NaF concentration on the electrochemical properties of the resulting PABA films has been studied by cyclic voltammetry and electrochemical impedance spectroscopy (EIS). It has been found that the concentration of NaF affects the degree of oxidation of PABA and the diffusion resistance.

SDE-P-02

ELECTROSYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF POLYTYRAMINE NANOCOMPOSITE

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Multi-walled carbon nanotubes (MWNT) with polytyramine (PT) composite electrodes with good uniformity for electrochemical capacitors are prepared by the in situ electropolymerization by using the ionic surfactant as electrolyte, for alignment disordered CNTs within conducting polymer/carbon nanotube composite films [1]. The capacitance properties are investigated with cyclic voltammetry, charge–discharge tests and ac impedance spectroscopy. The composite electrode shows much higher specific capacitance, better power characteristics and is more promising for application in capacitor than pure PT electrode. The effect and role of MWNT in the composite electrode are also discussed in detail.

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SDE-P-03

ELECTRODEPOSITION OF COPPER SELENIDES

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The Cu–Se system includes several stoichiometric (CuSe, Cu_3Se_2, Cu_2Se, $CuSe_2$) and non-stoichiometric ($Cu_{2-x}Se$) compound compositions, so that the development of a simple and adjustable preparation process leading to well-defined products is very important for material growth in this system. In this work, aspects of the aqueous electrochemical synthesis of copper selenide films have been examined. Cathodic electrodeposition was carried out onto conductive glass (ITO) and metal (Ti) substrates from aqueous acidic solutions of $Cu(NO_3)_2$ and SeO_2 precursors. The influence of the precursor concentration ratio in solution, the deposition potential and the bath temperature were investigated. The electrodeposited films were characterized by XRD, SEM, and EDX analysis. It was found that the berzelianite ($Cu_{2-x}Se$ or $Cu_{1.8}Se$) content of the films is increased when the deposition potential is made more negative. In general, Cu-rich selenides, i.e., berzelianite and umangite (Cu_3Se_2), rather than klockmannite (CuSe), were preferably obtained at the more negative potentials and higher growth temperatures. The evaluation of the experimental results showed that under similar working condition, use of the ITO substrate leads to better results that Ti, at least with respect to the prospect of “cuprous” selenides formation.

SDE-P-04

ELECTRODEPOSITION OF CHROMIUM AND COBALT FROM IONIC LIQUIDS BASED ON CHOLINE CHLORIDE

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The electrodeposition of chromium and cobalt layers on copper, aluminum, steel and nickel substrates was investigated in ionic liquids consisted in mixtures of choline chloride with malonic acid or oxalic acid with 1 : 1 mole ratio. Hexahydrate chromium trichloride and cobalt dichloride were employed as precursor salts for Cr^{3+} and Co^{2+} species. The operating current densities and temperatures were in the ranges of 5-30 mA/cm^2 and 60-90^{0}C, respectively. Cyclic voltammetry and electrochemical impedance spectroscopy were used to evidence the cathodic processes. The surface characteristics of Cr and Co deposits were established using optical, SEM and AFM microscopies, as well as XPS, Vickers microhardness tests and magnetic tests (for Co).

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SDE-P-05

"COPPER-DIAMOND" COMPOSITE COATINGS DEPOSITED BY ELECTROLESS AND ELECTROCHEMICAL PLATING ON POLYETHYLENE TEREPHTHALATE SUBSTRATE

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Two possibilities of obtaining copper composite coatings are investigated, applicable to the fabrication of tools for mechanical, finishing, surface processing of rock materials, quartz, non-ferrous metals and alloys.

The first approach is based on electroless deposition of composite „copper-diamond" coatings of trilonic electrolyte with diamond particles sized up to 20/28 μm.

The second approach was aimed at checking the possibilities of electrochemical deposition of composite coatings with larger-sized (up to 200 μm) diamond particles from a sulphur-acidic electrolyte.

Using SEM and XRD analysis, the morphology and structure of the composite coatings, including the distribution of the diamond particles were investigated.

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SDE-P-06

COMPARISON OF LEAD ELECTRODEPOSITION PROCESSES FROM THE BASIC AND COMPLEX ELECTROLYTES

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Electrodeposition of lead from the basic (nitrate) and complex (acetate) electrolytes was investigated by the analysis of their polarization characteristics and by the scanning electron microscopic (SEM) analysis of deposits obtained at the different overpotentials[1]. The shape of regular crystals formed in the ohmic control did not depend on the type of electrolytes. Contrary, the shape of dendrites formed under the diffusion control strongly depended on the type electrolyte. The dendrites composed of stalk and weak developed primary branches (the primary (P) type in Wranglen`s classification of a dendrite[2]) were predominantly formed from the basic electrolyte. On the other hand, the very branchy dendrites composed of stalk and of both primary and secondary branches (the secondary (S) type) were mainly electrodeposited from the complex electrolyte.

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SDE-P-07

INFLUENCE OF THE ELECTRODEPOSITION CURRENT REGIME ON THE CORROSION RESISTANCE OF Zn-CeO_2 NANOCOMPOSITE COATINGS

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The present work aims to study the influence of the current regime on the electrodeposition of zinc-ceria composites obtained from a chloride based electrolyte, by using both direct and pulsed current electrodeposition techniques. The microstructure, microhardness, composition profile and the corrosion parameters of the samples were evaluated *via* SEM, GDOES, microhardness tests and polarization curves. Blank pure zinc samples obtained under the same experimental conditions were used as a reference. The addition of CeO_2 nanoparticles lead to finer grained deposits, and the pulsed current further enhanced the coating properties.

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SDE-P-08

ELECTROPLATING OF ALUMINIUM FROM IONIC LIQUIDS

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Ionic liquids (IL) are a novel class of solvents which consist of organic salts with melting points below 100°C[1]. Due to their ionic character they might be used as electrolytes for electroplating of materials that are not accessible from aqueous solutions[2]. Recently, it has been demonstrated that the electrodeposition of dense, matt to bright Al layers from electrolytes based on a Lewis acidic mixture of $AlCl_3$ and 1-ethyl-3-methylimidazolium chloride (EMIM*Cl) with some additives is feasible on lab scale[3]. However, decomposition products from the electrolyte may affect the quality of the coating.

In this contribution we present a study of long term electrodeposition and storage experiments of EMIM*Cl/$AlCl_3$. The ionic liquid electrolytes were analyzed by NMR and HPLC. Furthermore, the morphology and adhesion of the Al coating on steel substrates was characterized by optical microscopy, SEM, FIB and cross-cut tests.

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SDE-P-09

INVESTIGATION OF MORPHOLOGICAL ALTERATION OF T24 CELLS BY TITANIUM FLAT SURFACE AND TITANIUM DIOXIDE NANOTUBES.

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TiO_2 nanotubes were synthesized by electrochemical anodization method for application in cancer therapy. To investigate morphological alterations of malignant cancer cells, (T24) of urothelial origin were cultured on flat titanium (Ti) surface as reference and nanotubular titanium dioxide (TiO_2) surface. The alteration in the morphology of cancer cells was evaluated using scanning electron microscopy (SEM). Statistical analysis of cell surface area shows big difference in the size of cancer cells cultured on titanium flat surface and titanium dioxide nanotubes surface. The surface topography of urothelial cells reveals smaller cell diameter, smaller contact area of adhesion ($P<0.0001$) and numerous membrane protrusions (eg, nanotubular structures – thin arrows and pleomorphic microvilli – arrowheads) on the TiO_2 nanotube, whereas, on the flat titanium surface, the cells are considerably larger in size and the cell membrane is smoother (asterisks)

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SDE-P-10

HYDROGEN PERMEABILITY OF ELECTRODEPOSITED Zn-Cr ALLOY COATINGS

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The development of Zn-Cr alloy coatings for corrosion protection of steel is directed towards the automotive industry. In order to face the demands for weight reduction of the car body and respectively for lower fuel consumption, high-strength steels have been introduced. It is generally known that the hydrogen embrittlement susceptibility increases with increasing the strength of the materials. Studies on the hydrogen permeation in Zn-Cr alloy coatings showed that as soon as the first coatings' layers are formed, the hydrogenation of the steel is strongly inhibited and that the Zn-Cr coatings protect steel effectively under conditions, which cause hydrogen ingress. The quantity of trapped hydrogen in the high-strength steel/Zn-Cr system was determined by thermal desorption analysis (TDA).

SDE-P-11

OBTAINING OF NICKEL-PHOSPHORUS DISPERSION MATRIX WITH DIAMOND PARTICLES DIAFORMED CHEMICALLY ON FLEXIBLE SUBSTRATES

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Obtainment and investigation of disperse Ni-P coatings with diamond particles deposited on a flexible substrate of pressed polyethylene terephthalate material (PETF) is quite interesting. Investigations are carried out to find the influence of the concentration and size of the dispersoid (3/7 ÷ 225/300 μm) on the coating thickness and the number of particles contained in it. To optimise the operating conditions investigations were conducted on the influence of the temperature, the deposition rate and hydrodynamic regime. Microscopic photographs reveal the morphology of the disperse coatings as a function of the deposition kinetics. Owing to their high hardness, the diamond coatings obtained have a considerable wear resistance and abrasive capacity and can find application in the production of efficient flexible grinding tools.

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SDE-P-12

EFFECTS OF CALCINATION TEMPERATURE ON THE ELECTROCHEMICAL PERFORMANCE OF $LiMnPO_4$ PREPARED BY A SCALE-UP TWO-STEP SYNTHESIS

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Among various cathode poly-anionic materials for Li-ion batteries, $LiMnPO_4$ is receiving a special attention due to its high redox potential (4.1 V vs Li/Li+), which is 0.7 V higher than that of $LiFePO_4$. Difficulties arise due to its poor electronic and ionic Li^+ conductivity[1,2]. To approach the theoretical capacity value (170 mAh/g) small particles and sufficient carbon content are required (~20 nm)[2]. *We report the effects of temperature treatment in the first firing step of our recently invented two-step synthesis on the capacity retention. The materials are characterized by SEM, Raman spectroscopy, and X-ray diffraction characterization.*

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BIO

Bioelectrochemistry and Biomedical Applications

ORAL PRESENTATIONS

BIO-O-01

NEW PROCEDURE IN ELECTROCHEMICAL SYNTHESIS OF SILVER NANOPARTICLES: INSIDE POLY(*N*-VINYL-2-PYRROLIDONE) HYDROGEL

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In order to obtain Ag/poly(*N*-vinyl-2-pyrrolidone) hydrogel nanocomposites (Ag/PVP), biomedically applicable, silver nanoparticles (AgNPs) were incorporated in PVP hydrogel network by the electrochemical reduction of Ag^+ ions within the swollen PVP hydrogel, performed *in situ*, under constant applied voltage. The optimal experimental conditions, examined by varying the applied voltage and implementation time, were determined through analysis of UV-visible spectra. The highest value of the absorbance, corresponding to the highest concentration of AgNPs, was observed for Ag/PVP nanocomposites obtained at 200 V during 4 min. These composites also exhibited lower values of absorbance maximum wavelength and the full width at the half-maximum absorbance, suggesting the smallest diameter of AgNPs. Cyclic voltammetry results suggested the successful entrapment of AgNPs inside PVP network. Silver release kinetics from Ag/PVP nanocomposites was investigated under static conditions. During 28 days of silver release, Ag/PVP nanocomposites still retained about 20 % of the initial silver content, preserving the sterility of the samples.

BIO-O-02

ON THE ROLE OF DIPOLE AND QUADRUPOLE MOMENT OF WATER MOLECULES IN SPATIAL VARIATION OF PERMITTIVITY IN ELECTROLYTE SOLUTION NEAR A HIGHLY CHARGED SURFACE

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The interface electrolyte-charged surface has been captured within the generalized Langevin Poisson-Boltzmann and Langevin-Bikerman models. Here we have modified the latter models to illustrate the importance of the non-zero quadrupole moment of the water molecule within a triangular atomic model. It is shown that in saturation regime the local decrease of relative permittivity of electrolyte solution near the charged surface is further pronounced.

BIO-O-03

STUDIES ON APPLICATION OF METALLOPORPHYRINS AS POTENTIAL PROTEIN LABELS

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Metalloporphyrins by dint of their unique spectroscopic properties and the capability to undergo redox reactions appear to be a very promising tool for molecules of biological origin labeling.

The assumption of presented study was to investigate the properties of metalloporphyrins in terms of their potential usage as proteins markers. For this purpose a number of derivatives of tetraphenylporphyrins and octaethylporphyrins, combined with various metals (Co(III), Cr(III), Fe(III), Mn(III), Sn(IV), Zn) was electrochemically analyzed. The influence of such factors as the material of working electrode, applied solvent and supporting electrolyte was examined. The effect of different counterions (borates, bromides, iodides and perchlorates) on the obtained signals was observed, as various ions interacted differently with porphyrin rings or metal ions contained in their structure.

Subsequently, the protein impact on the derived signals was evaluated (a shift of the potential and the signals intensities). In the role of model proteins bovine serum albumin (BSA) and chicken egg albumin (CEA) were employed. Attention was paid to shift of the potential and the signals intensities.

BIO-O-04

ELECTROCHEMICALLY ASSISTED FORMATION OF HYDROXYAPATITE COATINGS ON NITINOL

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Various surface modifications have been applied to titan)um and titanIum alloys implants tk improve their corrosion resistance and biocompatibility[1]. In thiswork Nhtinol surface was modified witH bioabtive, bone-lika hydropyapatite coatingS(HA), obtained by two deposiTion steps: electrgchemical and chemical. Eabh deposition step has individual formation mechanism and deposited films posseq different protection and biocompatible (bioactive) properties. The kinetics of the first step, nucleation of HA precursor film was studied *in situ* using chronoamperometry (CA) and cyclic voltammetry (CV). The morphology, microstructure and barrier properties of HA coatings were characterized by field emission scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). The chemical composition was examined using energy dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectroscopy (FTIR).

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BIO-O-05

OPTIMIZATION OF TWO PULSE-BASED AMPEROMETRIC DETECTION OF SELECTED BIO-MOLECULES

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Since its introduction in 1924, pulsed potential waveforms (PAD) have been used for hydrocarbon analysis (1). Due to the electrode deactivation in DC mode, the application of alternate potential pulses was found to be most efficient for continuous electrode re-activation. Four-step potential waveform was standardized, but it was found to cause significant electrode dissolution (2). A new two-step potential waveform for PAD of carbohydrates was introduced recently (3).

In the present paper, the optimization of the new two-step potential waveform will be presented with special emphasis on its application for direct determination of selected bioactive molecules (sugars amino acids etc..).

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POSTER PRESENTATIONS

BIO-P-01

IMPROVED BIOSENSOR BY DEGLYCOSYLATION OF PYRANOSE DEHYDROGENASE ISOLATED FROM *AGARICUS MELEAGRIS*

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The deglycosylation effect of pyranose dehydrogenase (PDH), obtained from *Agaricus meleagris* (*Am*) and recombinantly expressed in *Pichia pastoris*, on the glucose detection was investigated. Glycosylated (gPDH) and deglycosylated (dg*Am*PDH) enzymes were immobilized on spectrographic graphite simultaneously with an Os redox polymer (Os-RP). The amperometric responses of G/(Os-RP)-g*Am*PDH and G/(Os-RP)-dg*Am*PDH biosensors to glucose were recorded by using amperometric flow injection measurements and cyclic voltammetry. A significant increase of the maximum catalytic current was observed for G/(Os-RP)-dg*Am*PDH biosensor (10.410 ± 0.001 μA) compared with G/(Os-RP)-g*Am*PDH (5.74 ± 0.13 μA). Additionally, the time decay of the amperometric response to glucose indicates a better short term stability for G/(Os-RP)-dg*Am*PDH biosensor than that observed for G/(Os-RP)-g*Am*PDH biosensor.

BIO-P-02

PHENOLIC BIOSENSOR BASED ON CARBON PASTE ELECTRODE MODIFIED WITH CRUDE TISSUE

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The biosensors based on carbon paste electrode modified with the crude tissues of banana, apple, mushroom, potato, pear plant for quantification of phenolic compounds were studied. The ratio between components (carbon - tissue - paraffin), was investigated to optimize the electrode material with better electro analytical performance: background current, sensitivity and correlation coefficients were obtained when the mixture of 1g graphite powder/ 300 μl paraffin and 0.1 gr tissue was used. Relative response of biosensor modified with crude tissue of banana (CPEB) and apple (CPEA) to different phenolic compounds is studied. The CPEB biosensor shows high sensitivity to hydroquinone (S=3.25mA/ppm) and lowest detection limit (1.02 ppm) to phenol. CPEA biosensor shows better sensitivity for 4-clorphenol (S=1.35mA/ppm) and lowest detection limit (0.13ppm) to phenol substrate.

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BIO-P-03

INFLUENCE OF SURFACE CHARGES IN ALTERING THE PHYSICAL PROPERTIES OF LIPOSOMES

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Positive iron oxide (Fe_2O_3) nanoparticles, neutral and negatively charged cobalt ferrite ($CoFe_2O_4$) NPs were encapsulated in neutral and negatively charged lipids like 1-stearoyl-2-oleoyl-sn-glycero-3-phosphocholine (SOPC) and 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phospho-L-serine (SOPC-POPS). Due to electrostatic attractions, Fe_2O_3 NPs interacted strongly with the negatively charged liposomes which was confirmed by fluidity measurements and also supported by the results of mathematical modeling of nanoparticle-membrane electrostatic interactions[1].

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BIO-P-04

ELECTROCHEMICAL FORMATION OF PURELY IRON COVERINGS

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Biodegradable stents have some advantages to compare with stents which constantly are in an organism (for example further complications doesn't occur and etc.).
In this case as the material for biodegradable stents can be used pure iron. Results of research showed good the biological compatibility, interesting mechanical properties and properties of degradation.
For acceleration of process of a degradation, it is necessary to change structure of pure iron in the course of formation. One of ways of receiving pure iron it is an electrochemical method.
For electro sedimentation we used sulfate of iron ($FeSO_4{\cdot}7H_2O$). Nature of electrode processes and property of a precipitation of pure iron substantially depend on electrolyte's temperature.
At room temperature (20-25°C) process proceeds at sharply expressed cathodic polarization.

BIO-P-05

CORROSION BEHAVIOR OF ANATASE POLYCRYSTALLINE COATINGS ON Ti-BASED BODY IMPLANTS

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Due to the increasing need for bone repair, in the last few decades lot of research has been addressed on surface modifications and optimization of Ti-based body implants. The aim is to improve the beneficial properties of the natural, passivation layer of amorphous titanium dioxide (TiO_2), creating a better protective interlayer between the device and the surrounding tissues and, consequently, enhancing *in vivo* osseointegration. The synthesis of a fully-dense and stable nanocrystalline anatase-TiO_2 coating can be achieved by hydrothermal treatment (HT) on different Ti-alloys substrates. Electron microscopy and corrosion curves by potentiodynamic polarization were used to characterize the morphology and the electrochemical behavior of the obtained anatase coatings. Shape, size and the density of the HT synthesized TiO_2 crystals revealed a great influence on the coating properties; for instance, such homogeneous, fully-packed crystal distribution showed the ability to highly reduce both corrosion potential and corrosion current density. These results give the hope that the HT coated implants would prevent corrosion and immune response *in vivo* by avoiding release of toxic elements from the bulk and, consequently, adverse immune-system reactions from the body.

BIO-P-06

EFFECT OF SURFACE MODIFICATION ON CORROSION RESISTANCE OF Zr-2.5Nb

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Surface modification induced by anodisation in the conditions presented in this work corresponds to a surface design criteria based on the modification of chemical and topological features in the nanometric range with the aim of promote osseointegration of zirconium and Zr2.5Nb as permanent implants. Since an additional requirement of metal implants is the corrosion resistance in body fluids for long periods, the electrochemical in vitro response of anodised samples were studied in order to determine the effect of the surface modification process on the corrosion resistance of these two materials. No significative differences were observed between the pure Zr and the Zr2.5Nb alloy nether as received nor anodised. In the anodised samples, an increase of the total impedance modulus with respect as the as received condition, may be related to the thickening of the surface oxides.

FSM
Electrochemistry of Functional Structures and Materials

ORAL PRESENTATIONS

FSM-O-01

GASES PERMEABILITY STUDY IN DUAL MEMBRANE FUEL CELL

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Gases permeability in a porous mixed (proton and oxide ion) conductive membrane, which is a component of a new high temperature dual membrane fuel cell design is investigated by specially designed testing system based on measurements of the gas flow [ml/min] and pressure P (mmH_2O) when penetrating through porous media. A strong correlation expressed in increase of the permeability with the decrease of the gases molecular weight is registered. The water vapor permeability decreases with the temperature. The results obtained suggest optimal porosity in respect to permeability, mechanical stability and conductivity in the range of 35 - 40%. They confirm the need of optimization concerning not only the pores fraction, but also the pores geometry and distribution, as well as the central membrane geometry and the configuration of the cell. This approach can be applied also for optimization of the electrodes porosity (pores concentration, geometry, distribution etc), especially in cases when gas mixtures (including water vapor) are used or produced.

FSM-O-02

ELECTROCHEMICAL AND MICROSTRUCTURAL INVESTIGATIONS ON Al-Cu-Ni THIN FILMS

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Al-Cu-Ni thin film alloys were deposited by thermal evaporation to generate combinatorial material libraries. Investigations were done to characterize the behavior of thin films in comparison to bulk materials[1].The films were deposited on glass substrates and their microstructural properties and composition were investigated by SEM, EDX and XRD. The electrochemical behavior of the thin films where studied by SKP and cyclic voltammetry was performed by the scanning droplet cell microscope (SDCM). Electrochemical dissolution experiments were performed by a flow cell and the substances were detected with an AAS[2].

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FSM-O-03

RATIONAL DESIGN OF MORPHOLOGICAL PATTERN FOR EFFICIENT ELECTROCATALYTIC GAS EVOLUTION

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Efficiency of the gas evolving reactions (hydrogen, chlorine and oxygen evolution) has been recognized as a major obstacle for sustainability of important industrial processes like chlor-alkali technology, water electrolysis etc. In this work, a methodology is proposed for the rational design of surface morphology of the catalyst layers. Conceptually unique study is based on complementary activity/stability analysis by using SECM and ICP-MS. The obtained results have certainly technical relevance, but also shed light on the fundamental understanding of gas-evolving electrodes.

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FSM-O-04

ADVANCED ELECTROCHEMICAL INTERFACES

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The research effort aimed to fundamental understanding of processes that are relevant for energy conversion and storage will be presented. Fine tuning of the material properties can lead towards unprecedented improvements in functional properties that are relevant for energy conversion and storage [1]. This presentation will address unique research approach that is capable of revealing structure-function relationships in the design of materials for electrochemical systems. The following topics will be discussed: 1) well-defined materials; 2) atomic/molecular insight into electrified interfaces; 3) theoretical modeling of electrochemical systems [2]; 4) identification of the active sites under reaction conditions; 5) insight into chemical bond between the surface atoms, and molecular species in the electrolyte; 6) engineering of advanced materials with desired size, shape and composition profile [3,4].

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FSM-O-05

NEW ELECTROACTIVE POLYANILINE/POLYACRYLAMIDE HYDROGEL COMPOSITES

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New method to prepare the electroactive composite systems consisting of nano-wires of polyaniline (PANI) in the volume of the elastic crosslinked polyacrylamide (PAAm) hydrogel was elaborated. In contrast to widely used approach - in situ polymerization of aniline inside swelled crosslinked polymer matrix, the PANI synthesis in solution of linear polymer – PAAm which was then crosslinked with glutaraldehyde was carried out. The more homogeneous bulk composite systems as compared to standard in situ polymerization were formed by this method. Electrochemical properties of the composites at variation of PANI content were examined by electrochemical impedance, chronoamperometry and voltamperometry. The influence of preparation conditions on the composites structure was investigated by IR-spectroscopy and SEM.

This work was supported by the Program for Basic Research of the Presidium of Russian Acad. Sci. №24 “Fundamentals of Nanostructures and Nanomaterials Technologies” and by the Slovenian-Russian cooperation project BI-RU 12-13-032.

FSM-O-06

COPPER CORROSION IN SALINE/BENTONITE ENVIRONMENT, STUDIED BY COUPLED MULTI ELECTRODE ARRAYS

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Copper is the material chosen for fabrication of nuclear waste disposal containers. Many studies have been revived on copper corrosion in mildly saline and sulphide environment under oxic and unoxic conditions.

Long term exposure of copper in bentonite, saturated with groundwater under oxic conditions showed the uneven corrosion. The study is performed in a bentonite, saturated with saline water. The majority of the investigations up to now was done by using electrochemical impedance spectroscopy, where the average electrode reactions on the exposed surface is measured. However, by the use of coupled multi-electrode arrays (CMEA), corrosion events on each electrode can be detected. The aim of the study is to present the possibility of the use of coupled multi-electrode arrays, made of copper, for detection of localized corrosion by monitoring the spatio-temporal evolution of corrosion and detection of cathodic or anodic sites. Different spectroscopic techniques will be applied at the end of exposure of electrode arrays to identify modes of corrosion and type of corrosion products.

FSM-O-07

GEOMETRY-PERFORMANCE RELATIONSHIP OF ORGANIC ELECTROCHEMICAL TRANSISTORS

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The possibility of simple designed organic electronic devices and logic circuits that are driven at low voltages[1] has increased the attention on organic electrochemical transistors (OECT) during the last years. We report on the evaluation of the assumed geometry-performance relationship of OECTs. Utilizing entirely inkjet-printed devices, we varied several transistor dimensions and monitored the influence on the OECTs output characteristics. In this way, dependence of the on-current I_{on} and of the ratio between I_{on} and the off current I_{off} was observed. These findings allow for the optimization of OECTs for circuitry applications.

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FSM-O-08

THICKNESS AND STRUCTURE OF THIN ANODIC TiO_2 FILMS

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The anodic oxidation of titanium allows the obtaining of an oxide layer with thickness, colour, homogeneity and insulating properties that depend on the process parameters imposed. These thin films have been studied mostly to derive information on the oxidation kinetics of the metal[1]. Still, a deeper understanding of oxide properties is vital to open the way to engineered applications of nanostructured TiO_2 films, such as in the most recent field of memristive devices, where a precise control of oxide thickness and its electrical properties is required.

In this work, titanium was anodised in diluted sulphuric acid, with cell voltage ranging from 0 to 20 V. Oxide thickness was estimated by coulometric and spectrophotometric measurements; these two techniques were then combined with C-AFM to gain a deeper understanding of the oxide coverage of the metal surface and of the presence of crystal domains.

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FSM-O-09

CHARACTERIZATION OF REACTIVELY CO-SPUTTERED Cu-Ni MATERIAL LIBRARIES USING A SCANNING KELVIN PROBE

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The development of new materials is of great interest for finding new property combinations. Thin films offer a wide range of applications, e.g in electronics as well as for optical coatings, benefiting from the special properties due to the preparation method. In this work a combinatorial material library consisting of copper- and nickeloxide is prepared in a smart way by reactive co-sputter deposition using a two-component sectioned target. Thin films are fabricated on glass slides and the composition is analysed by XRF and EDX. The microstructure of the thin films was examined by XRD and AFM. To obtain detailed information on the surface potential, electrochemical characterisation is performed using a Scanning Kelvin Probe [1]. The electrochemical stability of these films in electrolytes was investigated downstream using online AAS [2].

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POSTER PRESENTATIONS

FSM-P-01

FORMATION AND REORGANISATION KINETICS OF SELF-ASSEMBLED CALIXARENE ON GOLD

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Calixarenes possess a remarkable ability to form stable complexes with a variety of metallic ions and organic molecules, exhibiting a pronounced conformational flexibility[1] which can be exploited for preparation of molecular designed electrochemical interfaces. Here is reported the reorganization process observed in the case of a SAM, built up by adsorption of a thioacetylated calix[8]arene derivative (S-Calix) on polycrystalline Au. The kinetics of the S-Calix adsorption and the reorganization processes of the resulted SAM was investigated. Au/S-Calix modified electrode was prepared by immersing a Au wire in an appropriate solution of a new thioacetylated calix[8]arene derivative. Cyclic voltammetry, quartz crystal microbalance Raman and impedance spectroscopy measurements were carried out. The obtained data were corroborated in order to rationalize the kinetics of the S-Calix adsorption, the SAM structure and the kinetics of the reorganization process, undergone by the S-Calix layer formed on the polycrystalline Au surface.

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FSM-P-02

STRUCTURE - ACTIVITY RELATIONSHIPS OF CARBON IN ELECTROCATALYSIS

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Glassy carbon (GC) shows intrinsic changes in electrochemical and morphological properties upon anodization in acid solution. Although the anodization induces a continuous increase in GC capacitance, the structural changes in the material intrinsically fluctuate. While moderate anodizing conditions cause carbon oxidation and formation of highly active defects and carbon functional groups (CFGs) within defects and at the edge planes, higher anodizing potentials produce an abundance of CFGs within a graphene-oxide (GO) layer that, at a first instance, strains the structure of graphitic ribbons. With advanced anodizations, GO interrupts the complete GC structure of graphite bundles and weakens the electrical contact between graphite layers. At this stage, an intensive surface roughening also takes place. Overall GC capacitance increases with intensification of anodization, whereas surface nano-roughness, distance between graphite layers and CFGs content reach the optimal values for electrocatalytic activity of GC electrode to be the highest with the modest anodizing conditions. This relationship between structure and activity is demonstrated for Q/H2Q reaction at GC surface.

FSM-P-03

THE ROLE OF REDUCING AGENT AND MODIFICATION OF A COPPER SURFACE FOR BONDING OF Cu-PPS RESIN

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Various surface modifications has been applied to improve adhesion properties of bivalent metal such as copper and aluminum for electrodes terminal application and sealing for Li ion batteries[1]. In this study, we have investigated the method of forming cupric oxide on the surface of copper. Also, we have tried to find the effective condition on the polymerization of a triazine trithiol on modified copper surfaces. SEM results reveal that the meaningful roughness was formed on the copper surface by chemical oxidation. Therefore, these Cu/polymer assemblies will be beneficial in reducing the process cost and increasing the safety of Li ion batteries

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FSM-P-04

FABRICATION OF 1,3,5-TRIAZINE-2,4,6-TRITHIOL POLYMERIC NANOFILM ON MAGNESIUM SURFACE BY CHEMICAL OXIDATION AND DIRECT ADHESION OF PPS RESIN

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Due to the growing number of the application in the electronics industry, the interest in polymer/metal surface adhesion has greatly increased during the past few years[1,2]. Especially, among these polymers, 1,3,5-triazine-2,4,6-trithiol (TT) is composed of thiol radicals (-SH) with a strong affinity to metals and a hydrophobic alkyl amino group (-R) as a substitution group. In this study, the surface modification using the chemical oxidation to get sufficient surface roughness which enhance the adhesion properties of the polymer film to magnesium has been investigated. As a result, polymer/ magnesium assemblies developed in this study have superior adhesion property. Therefore, these assemblies might be a viable candidate as a sealing technique for Li ion secondary batteries.

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FSM-P-05

ELECTROCHEMICAL STUDIES ON M(Y, Ca)BaCo$_4$O$_7$ IN AQUEOUS SOLUTION

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The paper presents the comparison of YBaCo$_4$O$_7$ and CaBaCo$_4$O$_7$ electrochemical properties in aqueous solution during oxygen insertion/release.The oxygen content of these mixed oxide is depending on the metallic cation included into the oxide structure, which for the nominal valence of Co ions. Oxygen content variations is determining oxygen nonstoechiometry in perovskite structure wich influencing oxygen ion permeability and diffusion, as it is of highly importance to reveal the perovskite structure. Electrochemical behavior has been studied by cyclic voltammetry and electrochemical impedance spectroscopy. In correlation with these techniques the compound morphology was determined by scanning electron microscopy. Based on these results the electrochemical reactions occurring at the interface compound – electrolyte solution have been identified and a mechanism for M(Y,Ca)BaCo$_4$O$_7$ oxidation/reduction in aqueous solution has been proposed.

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FSM-P-06

ELECTROANALYTICAL STUDY OF CYCLODEXTRINS INTERACTIONS WITH SOME PHARMACEUTICAL COMPOUNDS

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Inclusion complexes between cyclodextrins (CDs) and various drug molecules and their applications in pharmaceutical manufacture and analysis is the issue of many papers published in the last decades[1,2,3]. The CDs effect on the electrochemical behavior of some pharmaceuticals by using cyclic voltammetry and square wave voltammetry at carbon paste electrode (CPE) is presented. The oxidation peak of the analytes is shifted to more positive potential values and the current intensity is decreased, by the inclusion complexes formation, confirmed by FTIR spectra. Carbon paste electrodes modified with β-cyclodextrin (β-CD/CPEs) showed enhanced electrochemical responses for ascorbic and uric acid in comparison with the unmodified carbon paste electrode.

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FSM-P-07

NANOSTRUCTURED POLYMERIC FILMS FOR BIOSENSOR DESIGN

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Polymeric nanostructuration of polymeric films by nanosphere lithography is an easy and inexpensive way to improve the performances and the properties of biosensors [1]. The polymeric pattern was created by electrochemical polymerization of pyrrole-nitrilotriacetic acid performed by cyclic voltammetry onto PS beads (100 or 900 nm) previously deposited on the electrode surface. The PS beads were removed by soaking the electrodes in THF [2]. The structure was investigated by laser microscopy, SEM and fluorescent characterization via streptavidin-RPE. Biotinylated polyphenol oxidase and glucose oxidase conjugated with biotin and histidine groups were immobilized by coordination of the biotin groups on the polymerized NTA-Cu^{2+} complex. The enzyme binding was demonstrated by amperometric detection of glucose and catechol.

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FSM-P-08

REVERSE HYDROGEN SPILLOVER IN CARBON-SUPPORTED Pt ELECTROCATALYSTS: A DYNAMIC RESPONSE ANALYSIS OF THE PROMOTED Pt ACTIVITY

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The investigation of the changes in electrochemical and morphological properties of glassy carbon (GC), induced by anodization in acid solution, revealed the particular stages in electrochemical activation of carbonaceous material. These stages were found to affect the activity of Pt supported on electrochemically activated GC. In case of methanol oxidation, it has been supposed that carbon functional groups (CFGs) are able to renew poisoned Pt surface by bi-functional catalysis. In order to evidence the intimate electrocatalytic relationship between Pt and carbon-based supports and its features, Pt black supported on differently activated GC is analysed by electrochemical impedance spectroscopy (EIS) in acid solution. It was found that capacitive properties of Pt black are not affected by GC anodization, whereas clear evidence of the GC (*i.e*, CFGs) influence on the Pt desorption capability toward spiltover hydrogen in the double layer region comes out from both EIS and cyclic voltammetry (CV) measurements. The extent of GC anodization influences in a quite similar way reverse hydrogen spillover desorption parameters, gained EIS and CV, as it did the parameters describing the particular stages of GC electrochemical activation.

FSM-P-09

POLYANILINE DOPED WITH POLY(ACRYLAMIDOMETHYLPROPANESULPHONIC ACID): ELECTROCHEMICAL BEHAVIOUR AND CONDUCTIVE PROPERTIES IN NEUTRAL SOLUTIONS

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Poly(2-acrylamido-2-methyl-1-propanesulphonic acid)(PAMPSA)-doped polyaniline (PANI) layers are synthesised in the presence of sulphuric and perchloric acids. The pH dependence of the electrochemical redox activity and conductivity of the PAMPSA-doped PANI layers are studied depending on the synthesis conditions. Ascorbic acid oxidation is used as a test reaction to investigate the electrocatalytic behaviour of various PAMPSA-doped PANI layers in neutral solution.

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NTM
Nanoscale and Molecular Electrochemistry and Theoretical and Experimental Methods

ORAL PRESENTATIONS

NTM-O-01

POLAROGRAPHIC STUDY OF ANTIOXIDANTS INTERACTIONS WITH Hg(II) AND ITS HYDROXO-PERHYDROXYL COMPLEX

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An antioxidant (AO) assay based on decrease of polarographic anodic current of Hg(II)-perhydroxil-hydroxil complex in the presence of antioxidants (AOs) was developed[1]. Free Hg(II) reduction current, as well as polarographic current (catodic/anodic) of the complex, have been followed. Currents obtained from Clarc & Lubs buffer (pH 9.8) containing free and complexed Hg(II) have been followed by amperometric titration with various AOs as titrants. Reductions of both forms of Hg(II) (free and in complex) have been noticed. Reduction of anodically produced Hg(II)-ion upon mixed complex formation (anodic wave) was proved also. The results obtained by potentiometric titration, under the same experimental conditions as in the amperometric one, supported the above mentioned assumption.

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NTM-O-02

REVERSIBLE ELECTROCHEMICAL CONTACT ANGLE SWITCHING OF HEXAGONAL BORON NITRIDE NANOMESH

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The nanomesh superstructure formed by a monolayer of hexagonal boron nitride (*h*-BN) on Rh(111) holds great promise for supramolecular ordering[1] and other nanoscale phenomena. Here, we have studied the dynamic contact angle at the interface between *h*-BN/Rh(111) and an electrolyte as a function of the electrochemical potential. We observe a strong effect on the contact angle in the potential region where hydrogen adsorption occurs on Rh(111).[2] We propose that this macroscopic effect is caused by nanotexture switching within the 3 nm unit cell of the nanomesh, as hydrogen intercalation flattens the sp^2 hybridized boron nitride layer.[3] The changes in dynamic contact angle of the electrolyte were observed *in situ*, and were fully reversible under electrochemical control. To our knowledge, this system represents one of the first all-inorganic responsive surfaces.

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NTM-O-03

ANODIC TITANIUM NANOTUBES WITH CRYSTALLINITY PREPARED IN ORGANIC ELECTROLYTES

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For many applications, the crystal structure of the formed oxide is crucial for its functionality[1]. Typically, anodization of Ti at moderate voltages in aqueous electrolytes leads to the formation of amorphous films[1]. In the present work, TiO_2 nanotubes were elaborated in viscous organic electrolytes, ethylene glycol (EG) and polyethylene glycol (PEG) with different average molecular weights, via potential step anodization method, at different potentials. In EG, nanotubes are much longer compared with those prepared in PEG, and they are uncovered. For those prepared at higher voltages, spectroscopic measurements on as-anodised samples show anatas peaks, without anealing treatment. From contact angle measurements, Ti substrate was hydrophobic and anodized samples present increased hydrophilic character. Tafel plots and impedance spectra show for anodised samples an increased corrosion resistance compared to Ti substrate.

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NTM-O-04

AMBIGUITIY IN MODELLING AND INTERPRETATION OF IMPEDANCE SPECTRA OF GC ELECTRODES

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Well known problem of ambiguity in modelling and interpretation of the results of electrochemical impedance spectroscopy applied to different electrode systems[1,2], has also been perceived during analysis of impedance spectra of GC electrodes measured within the polarisable region of potentials in H_2SO_4 solution. Presence of more than one relaxation time in IS observed after even mild oxidation/reduction of GC electrode surface, inevitably led to the *so called* solution ambiguity[2]. Here, two possible (duplex or simplex layer) models resulted in two different interpretations going from formation of a passivating layer at the top of the surface[3] to formation of spatially heterogeneous surface with isolated damage centres[4], will be discussed.

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NTM-O-05

CHLORIDE ADSORPTION INVESTIGATION USING COMBINED ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE RADIOTRACER TECHNIQUE

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Chloride adsorption on structural materials can result pitting corrosion in industrial equipments. Our primary aim was to quantify the adsorbed chloride ions on the typical surfaces of a nuclear reactor system. We combined two well-know methods: the Electrochemical Quartz Crystal Microbalance and the Radiotracer technique (foil method). EQCM measure the total mass change (e.g. adsorbed mass), but it is not give any information about the adsorbed species. Using radiotracer technique the quantity of the tracer (radioactive atom) can be determined on the surface, but its chemical form is not. A special glass cell was constructed. The bottom of the cell was a quartz crystal covered with the electrode metal, glued elastically to the glass vessel. A beta detector with plastic scintillator was placed just below the crystal. Using this arrangement adsorption of pure beta emitting nuclides which maximum beta energy larger than 0.5 MeV (e.g. ^{36}Cl) can be investigated.

Chloride adsorption on gold (form perchloric acid solution) and on zirconium (form boric acid solution) was measured.

NTM-O-06

COMBINATION OF NANOGRAVIMETRY AND VISIBLE SPECTROSCOPY: A TOOL FOR THE BETTER UNDERSTANDING OF ELECTROCHEMICAL PROCESSES

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Due to its capability of detecting surface mass changes up to a sensitivity of a few ng/cm^2, the use of the electrochemical quartz crystal nanobalance (EQCN) became an every-day auxiliary technique of electrochemical experiments. By using an EQCN, one can study the changes of the electrode surface mass, and thus, obtain extremely useful quantitative information about an electrode process. Still in some cases neither the QCN frequency change, nor the electrochemical measurements can provide enough qualitative information about the ongoing electrode process. However, especially if the formed products or intermediates are coloured species, the coupling of the EQCN technique with spectroscopic UV-VIS measurements can elucidate the qualitative nature of the electrode process to a great extent and may help in disentangling their constituents. In order to combine the mentioned techniques, a software controlled electrochemical measuring system was constructed in our laboratory. In the present talk we introduce our newly developed hyphenated measurement system and demonstrate its usability.

NTM-O-07

ROTATING RING-DISK ELECTRODE WITH DUAL DYNAMIC POTENTIAL CONTROL: THEORY AND PRACTICE

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The rotating ring-disk electrode (RRDE) is an often used device of investigating the intermediates and side-products of electrode reactions. The application of dual potentiodynamic control to an RRDE has proven to be an especially promising technique of carrying out RRDE experiments with an increased sensitivity.[1]

However, some issues concerning the application of this method may also occur. The "dual dynamic" perturbation of the electrodes can cause cross-talk to appear in the current-potential characteristics of the two working electrodes. The effects arising from collection phenomena and the cross-talk caused by the overlapping potential fields of the two electrodes are not always easy to distinguish without a rigorous theoretical treatment of RRDEs.

In this presentation, numerical simulations (as well as measurements in simple model systems) will be used in order to describe collection phenomena in an RRDE system where *IR* drop effects are also present.

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NTM-O-08

IMPEDANCE INVESTIGATION OF $BaCe_{0.85}Y_{0.15}O_{3-\delta}$ PROPERTIES FOR HYDROGEN CONDUCTOR IN FUEL CELLS

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The influence of the sintering conditions on the electrochemical properties of the proton conducting electrolyte $BaCe_{0.85}Y_{0.15}O_{3-\delta}$ (BCY15) and Ni - based BCY15 cermet anode for application in high temperature proton conducting fuel cell are investigated by electrochemical impedance spectroscopy. The results show that at lower sintering temperatures due to the formation of parasitic Y_2O_3 phase an increase of both the electrolyte and electrode resistances is observed. This effect is strongly reduced by enhancement of the sintering temperature. The obtained BCY15 conductivity ($\sigma = 2.5\text{x}10^{-2}$ S/cm at 700°C) is comparable with that of the best proton conducting materials, while the BCY15-Ni cermet (with ASR = 2.5 Ωcm^2 at 700°C) needs further optimization. The results of impedance investigations of BCY15 as proton conducting electrolyte and cermet anode have been applyed in development of innovative high temperature dual membrane fuel cell.

NTM-O-09

MATHEMATICAL MODELS, DYNAMICAL ANALYSIS AND SYNTHESIS IN FIELDS OF ELECTROCHEMISTRY AND BIOELECTROCHEMISTRY

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In this paper we give mathematical models of objects and processes in electrochemistry and bioelectrochemistry that can be used for dynamical analyse and synthesis that can yield qualitative and quantitative results, controller and stabilizing methods for analyzing and design of processes and objects in electrochemistry and bioelectrochemistry. Based on the main electrochemical and bioelectrochemical processes, we state main assumptions and algorithms for mathematical modeling in general, we propose concrete mathematical models that include standard mathematical models, singular systems, impulsive and hybrid dynamical systems and singularly impulsive dynamical systems. We apply results from system and control theory to the concrete objects or processes in field of electrochemistry and bioelectrochemistry, and we give general framework for mathematical modeling, analysis and synthesis in these fields.

POSTER PRESENTATIONS

NTM-P-01

VOLTAMMETRIC DETERMINATION OF SYNTHETIC FOOD COLOURS TARTRAZINE AND SUNSET YELLOW USING A GLASSY CARBON ELECTRODE

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Differential pulse voltammetry (DPV) was used for the electrochemical determination of Tartrazine and Sunset Yellow, two most commonly found yellow-orange synthetic food dyestuffs in soft drinks. The determination was performed on glassy carbon disk electrode in a conventional three-electrode cell at acidic pHs. The described method presented a linear range up to about 2.5×10^{-4} mol l^{-1} for both colorants, with a detection limit of 1.5×10^{-6} mol l^{-1} for Tartrazine and 2.0×10^{-6} mol l−1 for Sunset Yellow. The proposed method is simple, inexpensive and very sensitive and can be applied to determine both synthetic food dyes in commercial soft drinks. The method was applied in comparison with HPLC method and no significant difference between the results was obtained.

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NTM-P-02

CYCLIC NORMAL PULSE VOLTAMMETRY IN THE STUDY OF *EC* REACTIONS

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In this communication a theory of cyclic normal pulse voltammetry (CNPV) of a simple reversible electron transfer followed by irreversible chemical reaction is presented:

$$Ox + ne^{-} \rightleftarrows Red \overset{k_f}{\rightarrow} POx + ne^{-} \rightleftarrows Red \overset{k_f}{\rightarrow} P$$

where k_f is the rate constant of chemical reaction.
The effect of dimensionless chemical kinetic parameter, $K_c = k_f \cdot t_p$ (where t_p is the pulse duration), on CNP voltammogram was examined. Chemical reaction (i.e. increasing the value of K_c) changes the appearance of forward branch of voltammogram from wave to peak. The relationship between diffusion and maximum reduction current ratio and logarithm of K_c is analysed theoretically and the criterion for recognition of the EC mechanism is given. Experimentally, the value of k_f can be estimated from the linear relationship of i_d/i_{max} on $\log(t_p)$.

NTM-P-03

SPECTROELECTROCHEMICAL BEHAVIOR OF N-METHYL-PHENOTHIAZINYL *MESO*-SUBSTITUTED PORPHYRINS AND THEIR COMPLEXES WITH Ni(II), Cu(II) AND Pd(II)

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The spectroelectrochemical properties of 11 new N-methyl phenothiazinyl *meso*-substituted porphyrins, $H_2Ptz_xPh_{4-x}$Porph (where Ptz stands for N-methyl phenothiazinyl, Ph for phenyl and Porph for porphyrin; x = 0, 1, 2 or 4), and their complexes with Ni(II), Cu(II) and Pd(II) were investigated. The half wave potentials of the redox processes yielding the anion, dianion or p-cation and dication radicals were estimated from SWV measurements. Generally, the newly synthesized compounds exhibit the spectral features characteristic to the porphyrin derivatives[1]. The recorded spectra put on evidence the formation of π-cations in the vicinity of the applied potentials values provided by SWV measurements.

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INVITED LECTURES

SS-IL-01

MECHANISM(S) OF Li-S BATTERIES DERIVED FROM IN-SITU MEASUREMENTS

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In the conventional lithium sulphur (Li-S) battery, lithium metal is used as the negative electrode and it is separated from the positive sulphur based composite electrode by an ion conducting liquid. All three components should be designed with an integrated approach that focuses on the improved cycling stability, cycling efficiency and high sulphur utilization. Among the factors that negatively affect the development of Li-S batteries is also a lack of in-situ techniques. Different mechanism can be obtained by the understanding of the changes in the chemical environment and this is a focus of one work package within European project EUROLIS where we are developing in-situ analytical techniques for Li-S batteries.

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SS-IL-02

MOLECULAR MODELING OF CORROSION INHIBITORS: CAN IT PROVIDE SOME USEFUL INSIGHT?

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A corrosion inhibitor is a substance used in a very small amount that effectively reduces the rate of corrosion. Many efficient inhibitors are also organic compounds. Recently the use of quantum chemical modeling has become of high interest for screening new potential corrosion inhibitors. However, inhibition of corrosion is a very complex phenomenon and it cannot be studied directly by molecular modeling. Although the precise mechanism of how organic corrosion inhibitors work is usually not known, it is generally accepted that the inhibition is achieved through the interaction of corrosion inhibitor molecules with a surface. This assumption is often exploited in the proliferating approach that utilizes quantum chemical modeling and rely solely on the calculation of electronic parameters of isolated inhibitor molecules.[1] This approach will be critically examined and it will be shown that it cannot always explain the corrosion inhibition performance of inhibitors in a sound manner.[2,3] This emphasizes the importance of a rigorous modeling of the interactions between the components of the corrosion system in the molecular modeling studies of corrosion inhibitors. I will present some examples of ours, based on density-functional-theory, aimed toward such rigorous modeling.[3-5]

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SS-IL-03

BISMUTH- AND ANTIMONY-BASED ELECTRODES IN CONTEMPORARY ELECTROANALYSIS

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Electrochemical stripping analysis has been recognized as an extremely powerful tool in modern analytical chemistry, particularly due to its attractive pre-concentration step enabling measurements of numerous metal ions in their trace concentration levels. In the last six decades, mercury has been the most commonly used electrode material in stripping analysis, despite its well-known toxicity and difficulties in its handling and storage. There were several attempts to replace mercury with some other electrode materials, but none of them approached the excellent electroanalytical behavior of mercury-based electrodes. In the year 2000, a bismuth film electrode was presented as a favorable alternative to mercury for measuring selected trace metal ions in combination with anodic stripping voltammetry[1]. This work encouraged many scientists worldwide to study bismuth electrode together with its electroanalytical performance and the ability of detecting additional metal ions. In the year 2007, we reported a successful application of the antimony film electrode in electrochemical stripping analysis[2]. Hitherto, there are many reports about bismuth- and antimony-based electrodes, describing their different configurations and applications for measuring numerous metal and non-metal analytes in combination with advanced electrochemical (stripping) techniques. In this presentation, the latest results of our investigations in the field of bismuth- and antimony-based electrodes for measuring (trace) metal ions and also selected organic compounds, using either electrochemical stripping protocols or direct voltammetry, will be demonstrated. Also critical comparison will be given versus their mercury counterparts.

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SS-IL-04

ON THE ROLE OF DIPOLE AND QUADRUPOLE MOMENT OF WATER MOLECULES IN SPATIAL VARIATION OF PERMITTIVITY IN ELECTROLYTE SOLUTION NEAR A HIGHLY CHARGED SURFACE

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The interface electrolyte-charged surface has been captured within the generalized Langevin Poisson-Boltzmann and Langevin-Bikerman models. Here we have modified the latter models to illustrate the importance of the non-zero quadrupole moment of the water molecule within a triangular atomic model. It is shown that in saturation regime the local decrease of relative permittivity of electrolyte solution near the charged surface is further pronounced.

ORAL PRESENTATIONS

SS-O-01

ELECTRODEPOSITION AND ELECTROCHEMICAL PROPERTIES OF NICKEL OXIDE ELECTRODES

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Nickel oxide is commonly used in the form of nickel(III) oxyhydroxide, NiOOH, as active electrode material in secondary rechargeable batteries. Due to the fast charging/discharging reaction it is increasingly considered as a positive electrode in pseudo-supercapacitors. In this work nickel oxide electrodes of different thicknesses were electrochemically deposited and the mechanisms of electrochemical reactions were studied. The electrodes were prepared from $NiSO_4$ solution onto Au substrate under cathodic (galvanostatic) and anodic (potentiostatic) conditions. Electrochemical behaviour of nickel oxide electrodes was investigated in 0.1 M KOH solution by cyclic voltammetry, electrochemical quartz crystal microbalance, chronoamperometry and XPS measurement. The stability of prepared electrodes was investigated in 6M KOH solution. Results showed that depending on the deposition method two structurally and electrochemically different forms of nickel oxide, α-$Ni(OH)_2$ and β-$Ni(OH)_2$, were obtained. Structural transformation of cathodic α-$Ni(OH)_2$ into anodic β-$Ni(OH)_2$ takes place by ageing of the cathodically prepared layer in 6M KOH solution as demonstrated by CV, EQCM results, chronoamperometry and XPS spectra.

SS-O-02

CHARACTERIZATION OF REACTIVELY CO-SPUTTERED Cu-Ni MATERIAL LIBRARIES USING A SCANNING KELVIN PROBE

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The development of new materials is of great interest for finding new property combinations. Thin films offer a wide range of applications, e.g in electronics as well as for optical coatings, benefiting from the special properties due to the preparation method. In this work a combinatorial material library consisting of copper- and nickeloxide is prepared in a smart way by reactive co-sputter deposition using a two-component sectioned target. Thin films are fabricated on glass slides and the composition is analysed by XRF and EDX. The microstructure of the thin films was examined by XRD and AFM. To obtain detailed information on the surface potential, electrochemical characterisation is performed using a Scanning Kelvin Probe [1]. The electrochemical stability of these films in electrolytes was investigated downstream using online AAS [2].

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SS-O-03

1,2,4,5-TETRAMETHOXYBENZENE AS A REDOX SHUTTLE

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Redox shuttles are compounds used for overcharge protection of commercial Li-ion batteries. They are soluble in electrolyte and are oxidized at high potential to a stable radical cation, which migrates to the opposite electrode, where it is reduced to the initial oxidation state again. The shuttle molecule therefore carries the charging current during overcharge and prevents increase of potential. Most of the redox shuttles are different dimethoxybenzenes and other organic molecules.[1] Recently, we synthesized and characterized a new compound 1,2,4,5-tetramethoxybenzene (MB) with a redox potential 3,65 V vs. lithium. Initial tests in $Li/LiFePO_4$ battery showed good results when we used 3 % (wt.) solution of MB in electrolyte 1 M $LiPF_6$ EC/DEC=1:1.[2]

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SS-O-04

ELECTROCHEMICAL AND MICROSTRUCTURAL INVESTIGATIONS ON Al-Cu-Ni THIN FILMS

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Al-Cu-Ni thin film alloys were deposited by thermal evaporation to generate combinatorial material libraries. Investigations were done to characterize the behavior of thin films in comparison to bulk materials[1].The films were deposited on glass substrates and their microstructural properties and composition were investigated by SEM, EDX and XRD. The electrochemical behavior of the thin films where studied by SKP and cyclic voltammetry was performed by the scanning droplet cell microscope (SDCM). Electrochemical dissolution experiments were performed by a flow cell and the substances were detected with an AAS[2].

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SS-O-05

ELECTROCHEMICAL CHARACTERIZATION OF GLASS LIKE CARBON AND GRAPHITE ELECTRODES: INFLUENCE OF VARYING DEGREE OF OXIDATION IN H_2SO_4 SOLUTION

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Various forms of carbon have widely been used as electrode materials in many different areas. Here, electrochemical properties of polished and electrochemically oxidized (modified) glass-like carbon (GC) and graphite electrodes in H_2SO_4 solution have been characterized using cyclic voltammetry, CV, and electrochemical impedance spectroscopy, EIS. Electrochemical modification with varying degree of oxidation has been performed for both electrodes. It has resulted in increased formation of edge plane surface densities, higher content of surface oxygen containing groups and significant changes in surface morphologies. Impedance spectra of two electrodes, measured within the region of polarisable electrode potentials, have been analysed according to the model that takes into account the effect of pseudocapacitive double-layer charging/discharging at porous surfaces. As was found by CV and EIS experiments, the overall capacitance values increased with degree of activation. However, at the highest level of oxidation, higher capacitance values are obtained for GC what can be explained by exfoliation of graphene sheets from graphite surface.

SS-O-06

COMPARISON OF RESULTS FROM STANDARDIZED CYCLIC CORROSION TESTING AND FLOWING ELECTROLYTE ON THE CORROSION BEHAVIOUR OF HOT DIPPED GALVANIZED STEEL

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Corrosion behaviour of conventionally hot dipped galvanized steel (Z) and Al-Mg-Zn coated steel (ZM) is investigated by standardized cyclic corrosion tests namely VDA 233-1021. The development of flow cells with downstream analytics allow a time resolved investigation of corrosion mechanism in a flowing electrolyte2. In this work results obtained from cyclic corrosion tests and experiments with flowing electrolytes in a flow cell setup are compared. Because of the particular importance in civil engineering and automotive industry, the influences of chloride containing, acidic electrolytes to hot dipped galvanized steel are presented.

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SS-O-07

PROTECTION OF BRONZE WORKS OF ART FROM THE EFFECTS OF POLLUTED URBAN ATMOSPHERES

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Bronze has been widely used in construction of sculptures and other works of art for ages. When bronze is exposed to atmosphere on its surface a layer of corrosion products called patina is formed. This layer is usually blue or green and decorates the piece of art, but also protects it. Due to increased environmental pollution, bronze objects and the patina on their surface dissolve with time. In order to preserve cultural heritage in these conditions it is necessary to apply additional protection from corrosion. The aim of this research is to experimentally determine the impact of polluted urban atmosphere on the corrosion of bronze sculptures, and to explore the possibility of applying a corrosion inhibitor to protect them. A polluted urban atmosphere in the experiments is simulated with a Na_2SO_4 + $NaHCO_3$ solution at pH = 3 and 5. The investigated inhibitor is 2-mercaptobenzimidazole. Electrochemical methods that were used for testing the corrosion process are: Tafel extrapolation method, linear polarization method and electrochemical impedance spectroscopy. The experiments showed that the investigated inhibitor protects bronze and its patina in the conditions of polluted urban atmospheres.

SS-O-08

CORROSION PROTECTION OF COPPER, ZINC AND THEIR ALLOYS WITH CARBOXYLIC ACIDS

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The use of carboxylic acids as a means to modify the surface of Cu, Zn, Cu10Zn and Cu40Zn and thus to increase their corrosion resistance was investigated. The carboxylic acids form by self-assembling a hydrophobic layer[1] on the surface which improves the corrosion resistance of underlying metals.[2] The samples were immersed in ethanol solution of different carboxylic acids: hexanoic, decanoic, myristic and stearic. Their corrosion properties were investigated in artificial rain. The longer the aliphatic tail of carboxylic acid, the better the corrosion resistance. The effect of surface roughness prior the self-assembling process was studied, especially in terms of its effect on the corrosion resistance and degree of hydrophobicity. The increased surface roughness implies better corrosion resistance and higher hydrophobicity.

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SS-O-09

EVALUATION OF THE PERFORMANCE OF CORROSION INHIBITOR FOR MILD STEEL IN CO_2 CONTAINING NaCl SOLUTION

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The objective of this study was to determine the inhibition effect of talloil diethylenetriamine imidazoline (TOFA/DETA imidazoline) as corrosion inhibitor for mild steel in CO_2 environment at different temperatures. For this aim the following techniques were employed: linear sweep voltametry (LSV), electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR), weight loss measurements (WL), quartz crystal microbalance (QCM) measurements and scanning electron microscopy (SEM). The corrosion rate of mild steel in 3 % wt. NaCl, pH 5, was effectively reduced and approached very low values (0.1 mm/y) when 70 ppm_v of TOFA/DETA imidazoline was added. The inhibition efficiency was calculated to be above 85 % while SEM analysis revealed that the damage on the mild steel surface was significantly reduced in the presence of 70 ppm_v of TOFA/DETA imidazoline.

SS-O-10

INVESTIGATION OF CHLORIDE ADSORPTION ON OXIDE COVERED STEEL SAMPLES WITH THE NOVEL ‘THIN GAP’ METHOD

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The in-situ radiotracer ‘thin gap’ method combined with cyclic voltammetry was developed towards the application on rough surfaces. The basic equations of the new model were discussed and validated.

Then, the chloride adsorption on oxide-covered austenitic stainless steel samples was investigated and the following aspects were studied:

Optimization of the parameters for the formation of proper oxide layers

Determination of the extent of chloride adsorption on oxide–covered steel samples

SS-O-11

ENHANCING ELECTROCHEMICAL PERFORMANCE OF TITANIUM OXIDE NANOTUBES-BASED MATERIALS

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Wide use of renewable resources is inseparably connected with energy storage materials that possess both high energy and high power density. Li-ion batteries seem to be the system of choice, but to achieve demanded characteristics we need to nanostructurize battery materials in a highly controlled way. Short transportation paths, good electronic and ionic wiring are crucial parameters to be optimized. Titanium dioxide nanotubes (TONT) are a promising anode material due to their high surface area and good stability [1]. We prepared TONT by hydrothermal method, and added various salts to create spacers that were supposed to prevent aggregation and phase transformation of TONT-derived anatase materials during annealing. We noticed improvement of the electrochemical performance of material when using Rh, especially at high current densities.

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SS-O-12

SPECTROSCOPIC AND ELECTROCHEMICAL SENSING OF LANTHANIDES WITH AZULENE CHROMOPHORES

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The synthesis and electrochemical, optical, and ion-sensing properties of some 1-azulenylmethylenemalonodiamides substituted at the nitrogen atoms with alkyl or hydroxyalkyl groups were studied[1]. They have shown promising molecular recognition properties towards lanthanide cations (Eu^{3+}, Ce^{3+}, Sm^{3+}, Yb^{3+}).

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SS-O-13

VOLTAMMETRIC STUDY FOR THE DETECTION OF FOOD DYESTUFF RED ALLURA AC IN SOFT DRINKS

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Voltammetric methods are becoming more frequently used in the characterization of food dyestuff [1,2]. In this paper, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used for the electrochemical characterization and detection of Allura Red AC, one of the most employed red synthetic food dyestuffs in soft drinks. The voltammetric behaviour was investigated at different pH values (2.0 -7.0) in a three electrode cell with a glassy carbon as working electrode. The influence of concentration, scan rate, pH and scan domain on the peaks currents and potentials was established. The two electrochemical methods are simple, inexpensive and very sensitive and can be applied to determine Alura Red in commercial soft drinks.

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SS-O-14

SEVERE ACCELERATED DEGRADATION OF A THIN FILM PLATINUM BASED CATALYSTS

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The degradation of a polymer electrolyte membrane (PEM) fuel cell catalysts (Pt/C and PtCu/C) has been studied under severe simulated start-stop conditions (50000 cycles from 0.2 V to 1.4 V vs. the reversible hydrogen electrode[1], employing a newly developed identical location scanning electron microscopy technique[2] (IL-SEM). We show that significant platinum particle growth occurs on top of the catalyst film while platinum depletion takes place in the layers beneath. There is a possibility of misleading interpretation of thin film severe degradation experiments, when the catalyst loading and volume of electrolyte are neglected and when the non-identical location electron microscopy pictures are statistically analyzed.

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SS-O-15

THE ELECTROCHEMICAL BEHAVIOUR OF SOME METALLIC MATERIALS USED AS IMPLANTS IN THE PRESENCE OF LACTIC ACID ADDITION IN HUMAN SERUM

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The aim of this study is to evaluate the influence of lactic acid on the electrochemical behavior of three alloys used as prosthetic joints, in simulated physiological conditions. The used alloys were:
SS316, SS316L and CoCrMo. The electrochemical techniques were open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization, as electrolyte being chosen the human serum with different concentrations of lactic acid. Based on experimental data of this investigation we can say that the lactic acid behaves as an inhibitor.

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SS-O-16

CERIUM-CONVERSION COATINGS FOR CORROSION PROTECTION OF ALUMINIUM AND ALUMINIUM ALLOY 7075-T6

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Due to favourable physical and chemical properties aluminium and its alloys are commonly used metals in aerospace, automobile and construction industries. Chromate conversion coatings which have been used for decades for corrosion protection of Al alloys must be replaced due to the restricted use of Cr^{6+}-based compounds in European Union[1]. Rare-earths conversion coatings, especially prepared with cerium salts, have been reported as one of the alternatives[2]. Two types of cerium based conversion coatings were investigated on Al and its alloy 7075-T6: (i) addition of cerium salt solution directly to chloride solution, and (ii) formation of cerium conversion coating prior to immersion to chloride solution. Various cerium salts were tested: nitrate, chloride, acetate and sulphate. Corrosion properties of the modified metal surface were studied in 0.1 M NaCl, while its morphology and composition were analysed by SEM/EDS.

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SS-O-17

SYNTHESIS OF SILVER NANOPARTICLES IN POLY(VINYL ALCOHOL) SOLUTION BY ELECTROCHEMICAL METHOD

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Polyvinyl alcohol (PVA) is one of the most important polymers, especially for pharmaceutical and biomedical applications.[1] Multiple components of bacterial cell metabolism are susceptible to silver, therefore products containing silver have been used as efficient antimicrobial agents.[2] In this work, the electrochemical synthesis of silver nanoparticles in the aqueous solutions of 10 wt. % PVA, containing KNO_3 and $AgNO_3$, was performed by varying the values of the applied current density, ranging from 5 to 50 mA cm^{-2}. The presence of silver nanoparticles was confirmed by UV-vis spectroscopy. TEM analysis shown that the obtained silver nanoparticles were spherically shaped. FTIR spectroscopy indicated the interactions between silver nanoparticles and PVA molecules.

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SS-O-18

PLD DEPOSITED THIN FILMS ON TITANIUM MODIFIED BY TiO_2 NANOTUBES

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Titanium implants still represent golden standards in modern medical treatments of bone replacement surgery. Recent research efforts focus on antibacterial hydroxyapatite coatings on titanium dioxide nanotubes doped with silver. Bactericidal effect of silver is crucial in initial bacterial attachment onto implant surface. We report our latest achievements in hydroxyapatite and silver/hydroxyapatite (Ag/HA) coatings deposited by pulsed laser deposition (PLD) on titanium modified by TiO_2 nanotubes. TiO_2 nanotubes were electrochemically deposited on Ti plate by anodization from fluoride-containing electrolyte. The obtained coatings were characterized by SEM, EDS, ATR-FTIR, XRD and AFM studies. Our goal was to develop surface modification of Ti metal for purpose of improved osteointegration. We successfully obtained uniform coatings of HA and Ag/HA on nanotubular layer with 100 nm tubes in diameter.

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