

5<sup>TH</sup> REGIONAL  
SYMPOSIUM ON  
ELECTROCHEMISTRY  
SOUTH EAST EUROPE

PROGRAM  
BOOK OF ABSTRACTS

5<sup>TH</sup> REGIONAL  
SYMPOSIUM ON ELECTROCHEMISTRY  
SOUTH-EAST EUROPE

PROGRAM & BOOK OF ABSTRACTS

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5<sup>TH</sup> REGIONAL  
SYMPOSIUM ON  
ELECTROCHEMISTRY  
SOUTH EAST EUROPE

June 7-11, 2015  
RIU Pravets | Pravets, Bulgaria

PROGRAM  
BOOK OF ABSTRACTS

Sofia € 2015

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## PREFACE

It is our great pleasure and honor to welcome the participants of the Fifth Regional Symposium on Electrochemistry – South East Europe (RSE-SEE5) to Bulgaria. To follow the 20<sup>th</sup> century traditions of the strong Regional Electrochemical Schools and the excellent networking between them is a challenge and a responsibility, but also a driving force and landmark in the new, dynamic, and quick-paced global environment of the 21<sup>st</sup> century.

The four successful Symposium meetings in Croatia (Red Island, 2008), Serbia (Belgrade, 2010), Romania (Bucharest, 2012) and Slovenia (Ljubliana, 2013) have built a strong and solid base for the fulfillment of the 5<sup>th</sup> edition mission - to contribute to the excellence in electrochemical science as a part of the European Research Area.

We would like to thank the 154 scientists and experts, who represent the best from both research and industry in 24 countries (16 of them from the region), for bringing their extensive knowledge, novel ideas, and boundless enthusiasm to the RIU Pravetz conference venue. During the next few days, we will work together, sharing our recent results, discussing emerging ideas, finding new solutions. Thank you for your interest, valuable contributions, and efforts in preparing 85 oral (6 plenary, 16 key note) and 85 poster presentations.

We encourage your participation in the first RSE-SEE special brokerage session aiming to initialize common projects and wish the successful establishment of new partnerships on an international and interdisciplinary level.

We cheer the active participation of the young scientists and wish them success in the heated competition for the RSE-SEE Young Scientist Awards.

Sincere thanks to the members of the Scientific and Organizing Committees for their continued dedicated support and the commendable decision to incorporate the national event Sofia Electrochemical Days into the Symposium.

We hope that the current Symposium venue, RIU Pravets, with its picturesque scenery and relaxing setting, far away from the hustle and bustle of the big city, will create a warm, friendly, comfortable atmosphere and make RSE-SEE5 an unforgettable gathering from both a professional and a personal point of view.

Thank you for all the ideas and experience you bring to this Conference.

Daria VLADIKOVA



Zdravko STOYNOV



RSE-SEE5 Co-Chairs

Institute of Electrochemistry and Energy Systems

Bulgarian Academy of Sciences

June 2015

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# RSE-SEE5 PROGRAM

## SUNDAY, June 7, 2015

- 16:30-17:00 Bus transportation from IEES (via Sofia Airport) to Pravets, check in  
18:30-19:30 Registration  
19:30-20:30 **"Meet and Greet"**

## MONDAY, June 8, 2015

### 08:30-08:45 Opening ceremony

Welcome address by the Co-Chairs of the Organizing Committee  
Welcome address by Representative of the BAS

### Morning Session / Chairs: Visnja Horvat-Radosevic and Ingrid Milosev

- 08:45-9:30 Nadine Pebere  
**PL1 Contribution of local electrochemical impedance spectroscopy to study corrosion processes**
- 9:30-10:00 D. Rosestolato, S. Ferro, A. De Battisti  
**KN1 On the Complex Mechanism of a "Simple" Electrochemical Reaction: State of the Art and Some New Results on Chlorine Evolution Reaction**
- 10:00-10:30 J. Moskon, M. Gaberscek, R. Dominko  
**KN2 Li ion insertion battery cathodes: determining different transport contributions**
- 10:30-11:00 Magdaléna Hromadová and Lubomír Pospíšil  
**KN3 Electrochemical Oscillation Reactions on Mercury Electrodes**

### 11:00-11:20 Coffee Break

### Session 1 / Hall A

Chairs : Sanjin Gutić and Sotiris Sotiropoulos

- 11:20-11:40 Paolo Piccardo and Roberto Spotorno  
**CPA-O-01 Interaction between differently coated commercial stainless steels and contacting layer (LSCF) aged in air at 800°C**  
Jelena B. Bajat, Ljiljana S. Živković, Bore V. Jegdić, Jovan P. Popić and Vesna B. Mišković-Stanković
- 11:40-12:00 **CPA-O-02 Corrosion stability of cerium modified cathophoretic epoxy coatings on Al6060 alloy**
- 12:00-12:20 Peter Plagemann, Ariane Friedemann  
**CPA-O-03 Investigation of Porous Titanium Dioxide Layers by Plasmaelectrolytic Oxidation**
- 12:20-12:40 András Hushegyi and Ján Tkáč  
**ESD-O-01 Ultrasensitive detection of glycan-protein interactions with electrochemical impedance spectroscopy (EIS)**
- 12:40-13:00 Ľudmila Kluková, Jaroslav Filip and Ján Tkáč  
**ESD-O-01 Graphene-based lectin biosensor as a promising tool for glycans analyses**

### Session 2 / Hall B

Chairs : Jan Tkac and Alain Thorel

- 11:20-11:40 Antonino Arico, Stefania Siracusano, Vincenzo Baglio, Eddy Moukheiber, Luca Merlo  
**ECS-O-02 Advanced electro-catalysts and membranes for proton exchange membrane water electrolysis**
- 11:40-12:00 Svetlozar Ivanov, Codruta Aurelia Vlaic, Ralf Peipmann, Anja Eisenhardt, Marcel Himmerlich, Stefan Krischok and Andreas Bund  
**ECS-O-03 Electrochemical lithiation of thin silicon based layers potentiostatically deposited from an ionic liquid**
- 12:00-12:20 Venko Beschkov, Elena Razkazova-Velkova, Martin Martinov, Nicolae Vaszilcsin, Konstantin Petrov, Dzhamal Uzun  
**ECS-O-04 Production of energy from marine water by sulfide-driven fuel cell**

- 12:20-12:40 Jaroslav Filip, Jana Sefcovicova and Jan Tkac  
**ECS-O-05 Production of energy from marine water by sulfide-driven fuel cell**
- 12:40-13:00 Andraz Pavlisic, Primož Jovanovič, Goran Dražić, Marjan Bele And Miran Gaberšček  
**ECS-O-06 3-D Atomistic Modeling: Dealloying Of Bimetallic Alloys**

**13:00-14:00 Lunch**

**Afternoon Session / Chairs:** Eleonora-Mihaela Ungureanu and Atanaska Trifonova

- 14:00-14:45 N. Wagner, C.A. Cañas, D. Wittmaier and K.A. Friedrich  
**PL-02 Post Li-ion batteries**
- 14:45-15:15 Cecilia Cristea, Mihaela Tertis, Oana Hosu, Luminita Fritea, Robert Sandulescu  
**KN-04 Innovative carbon-based nanoplatfoms for biosensing design**
- 15:15-15:45 Sanjin Gutic  
**KN-05 Electrochemistry of self-doped polyanilines in neutral and alkaline media**
- 15:45-16:00 Jan Tkac, Tomáš Bertók, J. Filip, Ludmila Kluková, András Hushegyi, Dominika Pihíková, Štefan Belický  
**KN-06 Nanoscale-controlled interfaces for construction of ultrasensitive lectin biosensors and effective biofuel cells**

**16:00-16:35 Coffee Break**

**Session 3 / Hall A**

**Chairs :** Achille De Battisti and Jelena Bajat

- 16:35-16:55 Galina Borisov, Stefan Avramov, Evelina Slavcheva, Werner Lehnert  
**ESD-O-04 Stability and durability of gas diffusion ORR electrodes for HT - PEMFC**
- 16:55-17:15 Dimitra Sazou, Kyriaki Saltidou  
**FSP-O-02 The influence of donor density on electrochemical processes taking place across the Ti|TiO<sub>2</sub> interface**
- 17:15-17:35 G.G. Láng, M. Ujvári, S. Vesztergom, K.J. Szekeres, J. Gubicza  
**FSP-O-03 Structural changes during the overoxidation of electrochemically deposited poly(3,4-ethylenedioxythiophene) films**
- 17:35-17:55 A. I.Mintsouli, J.Georgieva, A. Papaderakis, E.Valova, S. Armyanov, K.M.Papazisi, S.Balomenou, D.Tsiplakides, S.Sotiropoulos  
**FSP-O-04 Galvanic replacement as a route for the preparation of multi-metallic Mnoble (M) electrocatalysts**
- 17:55-18:15 Nicoleta Cotoian, Liana-Maria Mureşan, Marjan Bele and Ingrid Milošev  
**FSP-O-05 Synthesis of Ag-TiO<sub>2</sub> coatings on titanium substrate by sol-gel method and their characterization**

**Session 4 / Hall B**

**Chairs :** Raicho Raicheff and Marijana Kraljic Rokovic

- 16:35-16:55 M.P. Carpanese, A. Giuliano, D. Clematis, A. Bertei, C. Nicoletta, M. Delucchi, M. Panizza, R. Botter, A. Barbucci  
**ECS-O-07 Kinetic mechanism that influence the electrochemical behaviour of different type of cathodic materials for intermediate temperature solid oxide fuel cells**
- 16:55-17:15 Katarzyna Lota, Ilona Acznik, Agnieszka Sierczynska, Grzegorz Lota  
**ECS-O-08 Supercapacitors Based on Polypyrrole/Carbon Nanotubes Composites**
- 17:15-17:35 V. Horvat-Radošević, K. Magdić, K. Kvastek  
**ECS-O-10 Impedance aspect of graphite and glassy carbon electrodes in redox electrolyte**
- 17:35-17:55 Roberto Spotorno, Paolo Piccardo, Massimo Viviani, Zdravko Stoynov, Daria Vladikova, Günter Schiller  
**ECS-O-11 Influence of Working Parameters on Anode-Supported Cells studied by Electrochemical Impedance Spectroscopy**
- 17:55-18:15 Sanja Brkić, Zoran Mandić  
**ECS-O-12 Anodic deposition of PBO<sub>2</sub> on Nafion-covered Au electrodes**

**Poster Session 1**

## TUESDAY June 9, 2015

**Morning Session / Chairs:** Paolo Piccardo and Zoran Mandic

- 08:30-9:15 J.C. Grenier, J-M. Bassat, A Flura, F. Mauvy, V. Vibhu, A. Rougier  
**PL-03 Structural features and electrochemical properties of Lanthanide Nickelates as oxygen electrodes for application in SOFC, PCFC and Steam Electrolysers**
- 09:15-9:45 Stefan Freunberger  
**KN-07 Nonaqueous Electrolytes for Post Li-Ion: Materials and Mechanistic Aspects**
- 09:45-10:15 Soma Veszteg, Noémi Kovács, Mária Ujvári and Győző G. Láng  
**KN-08 Generator/Collector Systems under Full Potentiodynamic Control: Aspects of Instrumentation and Modelling**

**10:15-10:40 Coffee Break**

### Session 5 / Hall A

**Chairs:** Magdaléna Hromadová and Venko Beshkov

- 10:40-11:00 Dominika Pihíková, Ján Tkáč  
**BEH-O-01 Fabrication of lectin-based immunosensor with reduced non-specific interactions in favour of early-stage cancer diagnosis**
- 11:00-11:20 I. Milošev, B. Kapun, P. Rodič, J. Iskra, M. Bele, N. Veronovski, M. Rak, A. Cör  
**BEH-O-04 Functionalized hybrid sol-gel coatings deposited on titanium**
- 11:20-11:40 Yolina Hubenova, Mario Mitov  
**BEH-O-05 Mechanisms of electron transfer in eukaryotic biofuel cells**
- 11:40-12:00 Mario Mitov, Yolina Hubenova  
**BEH-O-06 Bioelectrochemical systems as an innovative approach for electrical energy generation, biosynthesis and bioremediation**

### Session 6 / Hall B

**Chairs:** Antonio Barbucci and Vesselin Naydenov

- 10:40-11:00 Yehor Brodnikovskiy  
**ECS-O-13 Zirconia powder for SOFC anode**
- 11:00-11:20 B. Drenchev, M. Dimitrov, V. Boev and A. Aleksandrova  
**ECS-O-14 Absorptive glass mat separator coating and its influence on the heat generation in VRLA battery cell**
- 11:20-11:40 Albena Aleksandrova, Mitko Dimitrov, Detchko Pavlov  
**ECS-O-09 Evaluation of polyethylene separators influence on charge acceptance of negative plates of lead-acid batteries**
- 11:40-12:00 M. Matrakova, M.Foudia, L. Zerroual  
**ECS-O-21 Effect of a mineral additive on the structure and electrical characteristics of the positive active mass of a lead-acid battery**

**12:30 Excursion to Veliko Tarnovo**

## WEDNESDAY June 10, 2015

**Morning Session / Chairs:** Evelina Slavcheva and Győző G. Lang

- 08:30 -9:15 Sylvia Sanchez, Raul Salazar, Cyril Chappaz-Gillot, Solenn Berson, Dmitry Aldakov and Valentina Ivanova  
**PL-04 Electrochemically and Chemically Prepared Materials for Solar Energy Application**
- 09:15-9:45 A. Karantonis, P. Chrysafidis and D. Karaoulanis  
**KN-09 Electrochemical resonance: theoretical and experimental aspects under different modes of operation**
- 09:45-10:15 M. Kraljić Roković, D. Sačer  
**KN-10 Incorporation of graphene oxide into polypyrrole films for supercapacitor application**

10:15-10:45 Burak Esat, Sumeyye Bahceci, Sevda Akay, Anton Momchilov

**KN-11 Organic Electrode Materials in Rechargeable Batteries**

10:45-11:00 Coffee Break

**Session 7 / Hall A**

**Chairs:** Cecilia Cristea and Mario Mitov

11:00-11:20 A. Stoyanova, D. Kovacheva, M. Mladenov, R. Raicheff

**ECS-O-15 Symmetric and hybrid battery-supercapacitor systems for energy storage**

11:20-11:40 N. Hassan, M. Kilicc, E. Okumus, B. Tunaboylu, A.M. Soydan

**ECS-O-16 Experimental determination of optimal clamping torque for Air Breathing PEM Fuel cell**

11:40-12:00 Y. Vlamidis, E. Scavetta, D. Tonelli

**ECS-O-17 Pseudocapacitors based on Layered Double Hydroxides electrodeposited on Pt electrode**

12:00-12:20 Mila N. Krstajić, Sanja I. Stevanović, Vuk V. Radmilović, Jelena R. Rogan, Aleksandra Gavrilović-Wohlmuther, Velimir R. Radmilović, Snežana Lj. Gojković and Vladislava M. Jovanović

**ECS-O-18 Shape controlled, carbon supported Pt anodic catalysts for DFAFC**

**Session 8 / Hall B**

**Chairs:** Tamara Petkova and Ljubomir Arsov

11:00-11:20 Romana Sokolová, Jan Fiedler, Šárka Ramešová, Jacek E. Nycz, Ilaria Degano, Marcin Szala, Viliam Kolivoška and Miroslav Gál

**MOE-O-01 Self-deprotonation in oxidation mechanism of quinoline compounds**

11:20-11:40 Alan Liska, Jiří Ludvík

**MOE-O-02 Stereoelectrochemistry of molecules with multiple redox centres. Influence of structure on electrochemical reduction of isomeric mono- and di-, nitro- or nitrosocalix[4]arenes**

11:40-12:00 Tsutomu Takamura, Junji Suzuki and Kyouchi Sekine

**PEA-O-02 Investigation of Li Mass Transfer in Metal**

12:00-12:20 Kiyoko Takamura, Akira Kotani and Fumiyo Kusu

**PEA-O-03 Quinone-Mediated Electrochemical Detection for the Determination of Total Acid in Food**

12:20-13:40 Lunch & Organizing Committee meeting

**Afternoon Session Chairs:** Norbert Wagner and Tamás Pajkossy

13:40-14:25 Zdravko Stoyanov

**PL-05 Mathematical Fundamentals of Impedance Spectroscopy**

14:25-14:55 Vessela Tsakova

**KN-12 Electrochemical nucleation and growth on foreign substrates – emerging challenges in an old scientific field**

14:55-15:25 Vladimir D. Jović

**KN-13 Electrodeposited coatings as cathodes for hydrogen evolution in industrial chlor-alkali electrolysis**

15:25-16:30 Coffee Break

**Session 9 / Hall A**

**Chairs:** Igor Povar and Konstantin Petrov

16:30-16:40 Ungureanu Eleonora-Mihaela, George-Octavian Buica, Liviu Birzan, Alexandru C. Razus, Cristina, Andreea Amarandei

**PEA-O-01 Concept of new azulene modified electrodes for heavy metal ions analysis**

16:40-16:50 Oxana Spinu

**PEA-O-04 Thermodynamic Approach for Calculating Potential - PH Diagrams in the System Cr –Natural Waters**

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**EMD-O-01 Determination of plant available Mn(II) in soil samples with Voltammetric method after UV-Digestion**
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**EMD-O-02 Some fundamental aspects of EIS data validation**
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**ECS-O-19 Hybrid solutions for high-energy storage systems**
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**ECS-O-20 Carbon additives for advanced lead-acid battery applications**
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- ECS-O-22 Evaluation of glass sealant properties versus thermal ageing simulating switch on and off of an SOFC stack**

**Session Sofia Electrochemical Days 2015 / Hall B**  
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**SED Presentation of the book “Rise of Electrochemistry in the Eastern Europe Countries” to be published by Springer in 2015**
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**SED-O-01 Structure-conductivity correlation of (TiO2)x(V2O5)y(P2O5)100-x-y system for SOFCs application**
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**SED-O-02 Electrochemistry of immobilized multicopper ascorbic oxidase (Cucurbita sp.): a third generation amperometric biosensor for ascorbate**
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**SED-O--03 Investigation and application of pyrolyzed CoTMPP catalysts**
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**SED-O-04 Applications and Trends of Ultrasound Treatment for Activation and Preparation of Perspective Nanosized Materials for Energy Conversion and Storage**
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**SED-O-05 Influence of metal loading on morphology and performance of Co-based Magnelli-phase titania supported electrocatalyst**
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**SED-O-06 Stable and efficient catalyst support for OER in HT-PEMWE**

**Session 10 BROKERAGE**  
 Chair: Antonino Arico

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**Implementing ScSZ electrolyte SOFC for Combined Heat and Power Production**
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**RIGEL, a Reversible and Innovative fuel cell based system for Grid balancing and Energy storage from Large green hydrogen production**
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**Project for Hydrogen Fuel Cell Forklift**
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**FJ K € FÍ K € Poster Session 2**  
**20:00 Closing Banquet**

## THURSDAY 11, June

### Morning Session / Chairs: Dimitra Sazou and Jaroslav Filip

- 08:30-9:15 Iliia Valov  
**PL-06 Atomically scaled systems in action – past and future of memristors**
- 09:15-9:45 Igor Povar, Oxana Spinu  
**KN-14 Thermodynamic evaluation of disproportionation and comproportionation equilibria in heterogeneous systems „solid phase – aqueous solution” under real conditions**
- 09:45-10:15 Irena Mickova, Ljubomir Arsov  
**KN-15 Ellipsometric study of passive and anodic oxide films formed on Nb and Ti substrates**
- 10:15-10:45 O. Vasylyev, Ye. Brodnikovskiy, M. Brychevskiy  
**KN-16 From powder to power: Ukrainian experience**
- 10:45-11:00 Coffee Break

### Session 11 / Hall A

Chairs: Massimo Viviani and Oleksandr Vasylyev

- 11:00-11:20 Antonio Bertei, Cristiano Nicoletta  
**ECS-O-01 Physically-based impedance simulation to decouple convoluted transport and reaction phenomena in SOFC cathodes**
- 11:20-11:40 Borislav Abrashev, Tony Spassov, Sasho Vassilev and Alexander Popov  
**ECS-O-24 Hydrogen sorption and electrochemical properties of TiFe based alloys synthesized by mechanical alloying**
- 11:40-12:00 E. Petkucheva, E. Lefterova, J. Heiss, U. Schnakenberg, E. Slavcheva  
**ECS-O-25 Influence Of The Gold Sublayer To The Catalytic Properties Of Magnetron Sputtered Pt, Ir And Irox Thin Films**
- 12:00-12:20 Daria Vladikova, Dario Montinaro, Ivaylo Genov, Paolo Piccardo, Zdravko Stoynov, Zacharie Wullemin, Roberto Spotorno, Andrea Pecunia, Valeria Bongiorno, Mélanie Rolland, Blagoy Burdin  
**ECS-O-26 In situ impedance monitoring of NiO-YSZ anode behavior during its initial reduction and redox cycling**

### Session 12 / Hall A

Chairs: Tsvetina Dobrovolska and Nicolae Vaszilcsin

- 11:00-11:20 Éva Fekete, Béla Lengyel, Tamás Cserfalvi and Tamás Pajkossy  
**IND-O-01 Electrocoagulation: an electrochemical process for water cleaning**
- 11:20-11:40 Tz. Boiadjieva-Scherzer, H. Kronberger and M. Monev  
**IND-O-02 Zn-Cr electroplating of steel**
- 11:40-12:00 Laszlo Peter, Katalin Neuróhr, Ádám Marsai, Lajos Pogány, Ádám Révész, Bence G. Tóth and Imre Bakonyi  
**IND-O-03 Electrodeposition of nickel and nickel alloys from alcoholic solutions**
- 12:00-12:20 Noura Touabi, Sanja Martinez, Moussa Bounoughaz  
**IND-O-04 Optimization of Electrochemical Copper Recovery Process: Effect of the Steering Speed in Chloride Medium of ph=3**

### 12:20 Closing ceremony

Award Ceremony for Best Young Scientist Presentations  
Closing Remarks

### 13:30 Bus leaves from Pravets for Sofia (Airport and IEES)

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## Contribution of local electrochemical impedance spectroscopy to study corrosion processes

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For a better understanding of processes taking place at local scales, new techniques have been developed during the last decades by using local probes. In electrochemistry, measurements with miniaturized electrodes, allows current and potential distributions to be determined. These local approaches provide significant contribution for the characterization of local electrochemical processes which represent an issue in many domains such as health (cell tissue, DNA chip), energy (fuel cell, electrode material) or the durability of material. The aim of the presentation will be to present local electrochemical techniques which are used and in development in the corrosion domain and more particularly local electrochemical impedance spectroscopy (LEIS) which is particularly applied in this field.

After the description of some local techniques in corrosion science such as microcell, local current measurements by scanning vibrating electrode technique (SVET) and scanning electrochemical microscope (SECM), the principle of the LEIS will be presented [1] and some examples will be discussed:

- Pitting corrosion of stainless steel [2,3],
- Determination of the sensitized zone extension in welded AISI stainless steel [4],
- Corrosion behaviour of aluminium alloys: galvanic coupling between pure Al and pure Cu or pure Mg and pure Al [5-7],
- Corrosion of magnesium alloys [8],
- Corrosion inhibitors for aluminum alloys [9],
- Delamination of organic coatings [10].

### References

- [1] R.S. Lillard, P.J. Moran, H.S. Isaacs, *J. Electrochem. Soc.*, 139 (1992) 1007.
- [2] I. Annergren, M. Keddam, H. Takenouti, D. Thierry, *Electrochim. Acta*, 41, 1121 (1996).
- [3] Annergren, D. Thierry, F. Zou, *J. Electrochem. Soc.*, 144 (1997) 1208.
- [4] P. Lima-Neto, J.P. Farias, L.F. Herculano, H.C. de Miranda, W.S. Araujo, J.B. Jorcin, N. Pébère, *Corros. Sci.*, 50 (2008) 1149.
- [5] J.B. Jorcin, C. Blanc, N. N. Pébère, B. Tribollet, V. Vivier, *J. Electrochem. Soc.*, 155 (2008) C46.
- [6] L. Lacroix, C. Blanc, N. N. Pébère, B. Tribollet, V. Vivier, *J. Electrochem. Soc.*, 156 (2009) C259.
- [7] C. Blanc, M.E. Orazem, N. Pébère, B. Tribollet, V. Vivier, S. Wu, *Electrochimica Acta*, 55 (2010) 6313.
- [8] G. Galicia, N. Pébère, B. Tribollet, V. Vivier, *Corros. Sci.*, 51 (2009) 1789.
- [9] G. Boisier, N. Portail, N. Pébère, *Electrochim. Acta*, 55 (2010) 6182-6189.
- [10] J.B. Jorcin, E. Aragon, C. Merlatti, N. Pébère, *Corros. Sci.*, 48 (2006) 1779.

## Post Li-ion batteries

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In the last decades, the investigation of new secondary cells has been increased considerably, because high energy density rechargeable batteries are supremely demanded for different applications, such as consumer electronic, electro mobility and renewable energy storage. Very promising battery systems are the so called "Post Li-ion batteries" (4. generation batteries) with metal anodes: metal-sulfur and metal-air (oxygen) batteries, in particular Li-sulfur and Li-air batteries.

Li-sulfur battery is a promising system, due to its high theoretical capacity (1675 mAh/g<sub>sulfur</sub>), energy density (2500 Wh/kg), the low cost and non-toxicity of sulfur. Nevertheless, some of the drawbacks of lithium-sulfur batteries are the poor rechargeability and high self-discharge rates. Due to the low electrical conductivity of sulfur, electrical conductive material has to be added in order to encourage the electrochemical reaction. Furthermore, polysulfides of high order (Li<sub>2</sub>S<sub>n</sub> with 2 ≤ n ≤ 8) dissolve in the electrolyte and can diffuse to the anode and react directly with lithium metal. This so-called shuttle mechanism causes irreversible loss of sulfur [1-2]. Moreover, insulating and insoluble polysulfide discharge product (Li<sub>2</sub>S) can precipitate on the surface of electrodes, avoiding further electrochemical reaction.

Metal-oxygen cells exhibit highest theoretical energy densities. Among them, the Li-O<sub>2</sub> system offers highest theoretical gravimetric energy density (11680 Wh/kg) however, anodes of highly abundant elements, such as Al, Si or Zn, offer several advantages over lithium. Apart from the availability, these latter metals are safer and more stable, allowing the battery processing in air. State-of-the-art metal-oxygen cells mainly suffer from severe cyclic aging and low Coulombic efficiency. To overcome these challenges, the underlying complex electrochemical reactions between the electrolyte and the electrocatalyst and the electrodes have to be understood. One of the major challenges is the development of suitable electrolytes and electrocatalysts for the oxygen reduction and gas evolution reactions. One of the major limiting factors on performance and round-trip efficiency is the catalyst used. Today's Lithium-air batteries still suffer from high charge- and discharge overpotentials caused by insufficient catalysts. The major goal is to reduce overpotentials by using bifunctional catalysts catalyzing both the oxygen reduction reaction (ORR) as well as the oxygen evolution reaction (OER). Noble metal catalysts show good performance on both reactions but with increasing prices of noble metals metal oxides have drawn attention recently.

In the presentation new results from the production and characterization of Lithium-sulfur batteries [3-4] and bifunctional cathodes for Li-air batteries [5-6] will be shown.

### References

- [1] Y.V. Mikhaylik, J.R. Akridge, J. Electrochem. Soc., 151 (2004) A1969.
- [2] V.S. Kolosnitsyn, E.V. Karaseva, Russ. J. of Electrochem., 44 (2008) 506–509.
- [3] N.A. Cañas, D.N. Fronczek, N. Wagner, K. A. Friedrich, A. Latz, Journal of Physical Chemistry C, 118 (2014) 12106-121.
- [4] N.A. Cañas, A.L.P. Baltazar, M.A.P. Morais, T.O. Freitag, K.A. Friedrich, N. Wagner, Electrochim. Acta, 157 (2015) 351-358.
- [5] D. Wittmaier, S. Aisenbrey, N. Wagner, K. A. Friedrich, Electrochim. Acta, 149 (2014) 355-363.
- [6] D. Wittmaier, N. Wagner, K. A. Friedrich, H.M.A. Amin, H. Baltruschat, Journal of Power Sources, 265 (2014) 299-308.

## Structural features and electrochemical properties of Lanthanide Nickelates as oxygen electrodes for application in SOFC, PCFC and Steam Electrolysers

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High temperature ceramic solid oxide cells (SOC), based on an ion conducting solid electrolyte are of great interest in many energy conversion systems. These technologies are based on ceramic electrolytes with either oxide ion conductivity (Intermediate Temperature Solid Oxide Fuel cell, ITSOFC, High Temperature Steam Electrolysis (HTSE)) or protonic conductivity (Protonic Ceramic Fuel Cell, SOFC-H+). Nowadays, a lot of work is devoted to the development of such systems operating at intermediate temperatures (550 - 750 °C). One of the main issues is to decrease the high overpotential at the oxygen electrode. Various solutions are considered such as developing new electrocatalyst oxide materials or new designs for single cells or electrodes.

In recent studies carried out at CNRS-ICMCB, the lanthanide nickelates  $\text{Ln}_2\text{NiO}_{4+\delta}$  (Ln = La, Pr or Nd) have been shown to exhibit very good electrochemical properties as oxygen electrode materials [1]. The main features of these compounds is that they show oxygen overstoichiometry leading to an oxide ion conductivity with a 2D character, as well as a mixed valence of the nickel ( $\text{Ni}^{2+}/\text{Ni}^{3+}$ ), which induces Mixed Ionic and Electronic Conducting (MIEC) properties (Fig. 1). Used as SOFC ( $\text{O}^{2-}$  or  $\text{H}^+$ ) cathodes as well as anode material of HTSE, they show excellent electrochemical performances as well as cell tests.

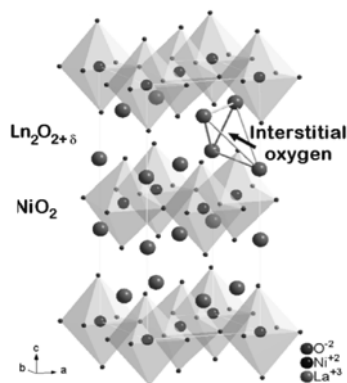


Fig.1 Structure of  $\text{Ln}_2\text{NiO}_{4+\delta}$  compounds showing the  $\text{NiO}_2$  and  $\text{Ln}_2\text{O}_2$  layers

Another key point is the shaping of these electrodes in single cells. Two ways of shaping will be compared:

*i)* the screen printing technique followed by a sintering at high temperature; more especially the role of a barrier layer (GDC (gadolinia doped ceria)) in between the nickelate and the YSZ (Yttria Stabized Zirconia) dense ceramic membrane is emphasized.

*ii)* the infiltration of a nickelate in a porous skeleton of ionic conductor sintered on zirconia electrolyte, followed by a subsequent annealing at moderate temperature ( $T < 900$  °C). Such a process is interesting for the last generation of SOFC single cells, namely Metal Supported Cells, now well known for presenting several advantages.

Comparison based on electrochemical results will be discussed.

### References

- [1] J.C. Grenier, J.M. Bassat, F. Mauvy, "Novel cathodes for solid oxide fuel cells. Functional materials for sustainable energy applications. Eds. J. Kilner and S. Skinner. Oxford Woodhead Pub., (2012) 402-444.

## Electrochemically and Chemically Prepared Materials for Solar Energy Application

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Until recently, investments in photovoltaic (PV) research have been driven by the imminent shortages of fossil fuels and problems related to climate changes, health hazards and political problems. The efficiencies of commercialized solar cells have increased at a slow pace due to the high production costs when compared to well established energy systems. Considerable progress in PV technology is therefore required in order to face the growing energy problems. The new solar cell must not only be highly efficient but also cheap. Among some of the innovations, the third generation solar cells based on nanomaterials was proposed to overcome the hurdles of high production costs. Our research activities are focussed in the preparation of high quality materials for the extremely thin absorber and the hybrid solar cells by low cost deposition methods. With this purpose, the electrodeposition of ZnO and CuSCN thin films and nanowires (NWs) were studied since they play a fundamental role as nanostructured electrodes [1]. Also, wet chemical room temperature deposition by Successive Ionic Layer Adsorption and Reaction (SILAR) technique for the preparation of absorbing materials (CdS, CdTe, CdSe, Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) and CuInS<sub>2</sub> (CIS)) was investigated [2]. The thin films (between 12 and 20 nm) of these absorbers we deposited on the ZnO nanowire arrays. These layers are composed of quantum dots with size less than 10 nm and exhibit good optical and crystalline properties. Only few SILAR cycles are enough to reach full light absorption in the large range of visible solar spectrum.

Electrodeposited ZnO and CuSCN thin films and nanowires have been integrated in organic photovoltaic devices as electron and hole transporting layers, respectively [3]. The n-type or p-type transparent inorganic semiconductors are very interesting due to the physical and chemical stability of these materials compared with that of currently used organic compounds. We consider that a big advantage of the electrodeposited layers is the fact that they exhibit good crystalline quality and could be further used in the polymer solar cells without subsequent annealing process.

### References

- [1] R. Salazar, C. Lévy-Clément, V. Ivanova, *Electrochim. Acta*, 78 (2012) 547. (b) S. Sanchez, C. Lévy-Clément, V. Ivanova, *J. of The Electrochem. Society*, 159 (2012) D705. (c) C. Chappaz-Gillot, R. Salazar, S. Berson, V. Ivanova, *Electrochem. Communications*, 24 (2012) 1. (d) C. Chappaz-Gillot, R. Salazar, S. Berson, V. Ivanova, *Electrochim. Acta*, 110 (2013) 375. (e) D. Aldakov, C. Chappaz-Gillot, R. Salazar, V. Delaye, K. Welsby, V. Ivanova, P. Dunstan, *J. Phys. Chem. C*, 118 (2014) 16095.
- [2] R. Salazar, A. Delamoreanu, C. Lévy-Clément, V. Ivanova, *Energy Procedia*, 10 (2011) 122. (b) S. Sanchez, D. Aldakov, D. Rouchon, L. Rapenne-Homand, A. Delamoreanu, C. Lévy-Clément and V. Ivanova, *J. of Renewable and Sustainable Energy*, 5 (2013) 011207. (c) R. Salazar, A. Delamoreanu, B. Saidi, C. Lévy-Clément, and V. Ivanova, *Phys. Status Solidi A*, 211 (2014) 2115.
- [3] S. Sanchez, S. Berson, S. Guillerez, C. Lévy-Clément, V. Ivanova, *Adv. Energy Mater.*, 2 (2012) 541. (b) C. Chappaz-Gillot, S. Berson, R. Salazar, B. Lechêne, D. Aldakov, V. Delaye, S. Guillerez and V. Ivanova, *Solar Energy Materials and Solar Cells*, 120 (2014) 163.

## Mathematical Fundamentals of Impedance Spectroscopy

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The enlarging application of Electrochemical Impedance Spectroscopy (EIS) for studying of large variety of laboratory and practical objects is aimed to explore the enormous information capabilities of the method. With unbeatable selectivity and precision and a huge frequency range the EIS is the preferred electrochemical method of our days. It worth to remember that the EIS is converting the phenomena taking place in the time-domain into frequency domain images replacing in this way the solution of complicated integro-differential equations by solution of simple algebraic equations with complex numbers.

The kernel of these excellent properties is the mathematics of the Fourier Transform, embedded in every impedance analyzer from the state of the art. Created more then 200 years ago, at present the FT is the basis of many scientific and technological applications in communications, geology, corrosion etc. The application of the FT in electrochemistry has started 100 years ago, converging later in EIS.

The present contribution is aimed to refresh the knowledge about FT and specifically about its form applied in EIS. Many properties of the finite time FT as selectivity, noises and harmonics rejection, efficiency and sufficiency of this estimator will be discussed in details.

The second part of this contribution is devoted to a solution of a general problem – studying non-stationary signals and systems into the frequency domain. The detailed analysis of the errors of the classical FT in a presence of a-periodic additive and multiplicative noise has led us to a creation of new transform, free of those errors. Called Rotating Fourier Transform, the new mathematical tool rejects such noises and provides for effective studies of non-stationary electrochemical objects

## **Atomically scaled systems in action – past and future of memristors**

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Since their re-discovery roughly 20 years ago the resistive switching memories (RRAM) turned out into one of the most exciting, innovative and multidisciplinary scientific field with a greatest potential for application in the nanoelectronics and information technology. Relating these systems to the Leon Chua's missing memristor (memory + resistor) by HP in 2008 and pointing out the possible functionalities pushed this topic to one of the highest priorities not only for the academic research but also for the computer industry.

Resistive switching memories are nanoscale, or in some cases even atomically scaled electrochemical systems fulfilling the demands for low power consumption, high information density, fast read and write speeds and non-volatility. Based on a simple Metal-Insulator-Metal structure these type memories also demonstrate great promise as building units for memristive and neuromorphic operations, paving the way for beyond von Neumann computing.

Control over physicochemical processes at the atomic scale is the key factor for improvement of these devices. However, instrumental but also physical limitations hinder to achieve complete microscopic understandings of the switching mechanism and therefore the ability to finely tune the device characteristics and properties.

The present talk will focus on the thermodynamics and kinetics of nanoscaled memristive devices emphasizing the ability to study and control the device processes at the atomic scale. The interface dynamics, the importance of local charge concentration and distribution, and the generic relevance of the counter charges will be highlighted. The nanobattery effect and its implications on both memristors' theory and device stability and performance will be outlined on theoretical and experimental level.

The topic will be discussed in a more fundamental context of microscopic description of electrochemical processes at the atomic scale.





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## On the Complex Mechanism of a “Simple” Electrochemical Reaction: State of the Art and Some New Results on Chlorine Evolution Reaction

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The anodic oxidation of chloride ions in acidic media (typically below pH 3) has been widely studied, primarily because of the paramount importance of this reaction in chlor-alkali industrial processes but also, from a more fundamental point of view, for its kinetics and mechanism(s). The introduction of stable anode materials, since the middle of the 60's, has allowed the obtainment of quite reliable experimental data, with important connections with the basic principles of catalysis at the surface of solids. Proposed mechanisms of the reaction at RuO<sub>2</sub>-based electrodes were typically the Volmer-Heyrovsky and the Volmer-Tafel mechanisms, which correspond to the Eley-Rideal and Langmuir-Hinshelwood patterns, respectively, well known in heterogeneous catalysis. In spite of the wealth of available data, no univocal mechanism proposition has been achieved so far and a critical literature study is required in order to find out possible coherent data sets and consistent interpretations. In this contribution, a summary of the literature is presented and novel experimental results are also described. Based on a thorough experimental study, the applicability of the Volmer-Heyrovsky mechanism has been proposed, with the electrochemical desorption step as rate determining. In fact, Tafel plots were evidently non-linear and limited linearities with slopes close to 0.040 V could be found only within lower overpotential ranges. It is interesting to observe that in several other papers, although not commented, analogous non-linearity occurrence has been found. On the other hand, as exhaustively proved in the literature, when electrochemical reaction mechanisms involve adsorbed intermediates and the rate-determining-step is the radical desorption, linearity of Tafel plots and “obvious” slopes like 0.030 (Volmer-Tafel) and 0.040 V (Volmer-Heyrovsky mechanism) can be found only if intermediate coverages are low. In cases where coverages reach more significant values, non linearity of Tafel plots is the first consequence. The analysis of our results, with testing of adsorption isotherms of Langmuir and Frumkin, has confirmed that at oxide electrodes chlorine evolution reaction takes place in the presence of high Cl<sup>-</sup> coverages. Analysis of electrochemical reaction orders supports this hypothesis.

### References

- [1] B.V. Tilak and B.E. Conway, *Electrochim. Acta* **37**,51 (1992)

## Li-Ion Insertion Battery Cathodes: Determining Different Transport Contributions

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To prepare powerful and reliable Li batteries it is necessary to optimize the transport of charge and mass between and within the electrodes. We have studied extensively transport processes in cells based on different typical cathode active materials for Li ion batteries: LiCoO<sub>2</sub> (LCO), LiFePO<sub>4</sub> (LFP), LiMnPO<sub>4</sub> (LMP), and comparably on Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO) material. We performed experiments where we were changing the state of the inter-phase contacts in the corresponding electrodes while the intrinsic properties of active material (morphology, crystal structure etc.) were not altered. We used electrochemical impedance spectroscopy (EIS) and found that corresponding EIS spectra of cells based on those different active materials (that differ even in their chemistry and structure) exhibit some main features that are surprisingly common to all the tested active materials. Most evident was the presence of the high-frequency impedance arc (H.F.-arc) with peak frequency of ~1 kHz that was found to be strongly related to the electronic contact resistance of the (current collector)-(electrode composite) interface. Based on those experimental findings we proposed a general equivalent circuit that takes into account the poor inter-phase contacting [1].

We have carried out a detailed analysis of the energy changes in the LFP based cell during galvanostatic charge/discharge in the light of energy efficiency and energy loss of the cell. In this manner we have been able to examine and quantitatively determine the apparent energy loss due to H.F.-arc contribution. We have established that the varying of the condition of the inter-phase contacts is already important at moderate rates (1C) with increasing importance when going to high (10C) and very high current densities (>10C). We have determined the values of the "wiring" parameters of a typical Li ion electrode. We obtained 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 demonstrated how the electrical properties of the "wetted" electrode differ from the one in the starting "dry" state.

As observed experimentally already almost a decade ago a LFP based cell exhibited an effect of reduced total electrode resistance when subjected to an increase of a current driven through the cell [2]. Later on this "activation" phenomenon was confirmed in the work of other groups [3]. Recently in an extensive experimental observation of LFP based electrodes using synchrotron Scanning Transmission X-Ray Microscopy (STXM) Chue et al. [4] have demonstrated that the fraction of the phase-transforming particles depends on C-rate. In the light of the obtained results of our study we proposed that observed decrease of total electrode resistance with increasing current originates from the increase of population of LiFePO<sub>4</sub> particles that simultaneously undergo phase-transition.

### References

- [1] M. Gaberscek, J. Moskon, B. Erjavec, R. Dominko, J. Jamnik, *Electrochem. Solid-State Lett.* 11 (2008) A170.
- [2] M. Gaberscek, M. Kuzma, and J. Jamnik, *Phys. Chem. Chem. Phys.* 9 (2007) 1815.
- [3] C. Fongy, S. Jouanneau, D. Guyomard, J. C. Badot, and B. Lestriez, *J. Electrochem. Soc.* 157 (2010) A1347.
- [4] Y. Li et al., *Nat. Mater.* 13 (2014) 1149.

## Electrochemical Oscillation Reactions on Mercury Electrodes

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Several types of non-linear phenomena (spontaneous oscillations, negative differential resistance NDR, stochastic resonance and chaotic behavior) will be discussed in selected electrochemical redox systems. As a first example we will discuss the indium-thiocyanate oscillator, where the occurrence of spontaneous oscillations of the indium(III) reduction current stems from the catalytic effect of the thiocyanate anions at the hanging mercury drop electrode (HMDE) and their subsequent desorption at more negative potentials.<sup>1</sup> Another type of the electrochemical oscillator is based on the cation-catalyzed reduction of a nitroaromatic radical anion. Described system is a new type of NDR oscillator, in which double-layer effect in connection with cationic catalysis rather than anionic catalysis plays a crucial role in the observation of NDR. At low concentration of tetrahexylammonium hexafluorophosphate the anion radical reduction occurs at extremely negative potentials due to the double layer effect on the negatively charged reactant. An addition of small cations ( $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) to such a system, forming ion pairs with the radical anion, has a remarkable acceleration effect on the electron transfer rate. The double-layer effect ceases to operate in the case of neutral species. At potentials where alkali metal cations are reduced to the corresponding amalgams the acceleration ceases. As a result the current-potential curves show a negative slope. Electrochemical impedance spectroscopy sensitively indicates the presence of the negative differential charge transfer resistance (NDR) or hidden negative differential resistance (HNDR). The addition of an external resistor in series with the electrochemical cell leads to the current oscillations at the stationary mercury electrode and to the current bursts on the dropping mercury electrode.<sup>2,3</sup>

Finally, we will discuss the above-mentioned non-linear phenomena in two oligomers from a series of the extended viologen compounds, which were synthesized to fulfill the function of molecular wires for long-distance transfer of electrons. We will show that such systems obey Feigenbaum universality route from order to chaos.<sup>4-6</sup> Additionally, a selective generation of the odd higher harmonic frequencies in the current domain as a response to small voltage perturbation will be presented. The effect is explained in terms of a theory of the stochastic resonance occurring in the driven oscillating reactions.

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### References

- [1] M. Rudolph, M. Hromadová, R. de Levie, Demystifying an Electrochemical Oscillator. *J. Phys. Chem. A* 102 (1998) 4405.
- [2] M. Hromadová, L. Pospíšil, R. Sokolová, N. Fanelli, New electrochemical oscillator based on the cation-catalyzed reduction of nitroaromatic radical anion. *Electrochim. Acta* 54 (2009) 4991.
- [3] L. Pospíšil, M. Hromadová, R. Sokolová, J. Bulíčková, N. Fanelli, Cationic Catalysis and Hidden Negative Differential Resistance in Reduction of Radical Anion of Nitrobenzene. *Electrochim. Acta* 53 (2008) 4852.
- [4] L. Pospíšil, M. Hromadová, M. Gál, M. Valášek, N. Fanelli, V. Kolivoška, Irregular Polarographic Currents Obey Feigenbaum Universality Route from Order to Chaos. *Collect. Czech. Chem. Commun.* 74 (2009) 1559.
- [5] L. Pospíšil, M. Hromadová, N. Fanelli, M. Valášek, V. Kolivoška, M. Gál, Extended Viologen as a Source of Electric Oscillations. *Phys. Chem. Chem. Phys.* 13 (2011) 4365.
- [6] M. Hromadová, M. Valášek, N. Fanelli, H. N. Randriamahazaka, L. Pospíšil, Stochastic Resonance in Electron Transfer Oscillations of Extended Viologens. *J. Phys. Chem. C* 118 (2014) 9066.

## Innovative Carbon-Based Nanoplatforms for Biosensing Design

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Various types of carbon nanostructures such as carbon nanotubes (CNT) and graphene have recently been used in the development of electrochemical sensors due to their specific structures, properties and their wide application range such as: drug delivery, energy storage and sensing devices [1]. Moreover, their use in the development of electrochemical (bio)sensors offers certain advantages such as: decrease of the overpotentials, increase of the active surface area, improvement of the charge transfer between the (bio)elements and the transducer, all coupled with the possibility of multidetection in complex matrix.

The presentation will focus on the use of CNT and graphene for the design of electrochemical (bio)sensors and immunosensors for the detection of drugs like acetaminophen and dopamine.

The incorporation of single and multi CNTs into layer by layer (LBL) films containing enzymes enhances the electrons diffusion through the films and the electrochemical surface area, increasing the response of the sensor. In the same time, the adsorption of enzymes directly on the CNT reduces the distance between the active site of enzyme and the electrode surface. CNTs provide also a homogeneous porous composite film that facilitates substrate transfer. By using electrochemical impedance spectroscopy (EIS) a comparative study between different types of CNTs for doping polymeric films was achieved [2].

After this study, the optimization of new biosensors with horseradish peroxidase immobilized in carbon nanotubes-polyethyleneimine or polypyrrole nanocomposite film at the surface of two types of transducer was done. The amperometric detection of acetaminophen was carried out at  $-0.2$  V versus Ag/AgCl using carbon based-screen printed electrodes (SPEs) and glassy carbon electrodes (GCEs) as transducers. The electroanalytical parameters of the biosensors are highly dependent on their configuration and on the dimensions of the carbon nanotubes. The best limit of detection obtained for acetaminophen was  $1.36 \pm 0.013$   $\mu\text{M}$  and the linear range  $9.99$ – $79.01$   $\mu\text{M}$  for the HRP-SWCNT/PEI in GCE configuration. Those biosensors were successfully applied for the detection of acetaminophen in several drug formulations [3].

Another platform was developed by combining the enhanced sensibility given by the special properties of graphene and  $\beta$ -cyclodextrin, and the specificity of the enzyme tyrosinase. The nanoplatform was elaborated using the same LBL deposition method on GCEs and various parameters were optimized. Microscopic and spectral techniques (Raman, FTIR, EIS) were used to characterize the modification of electrodes and of the graphene oxide. The biosensor was successfully applied for dopamine detection in pharmaceutical products, human serum and urine with good recoveries.

Carbon based nanomaterials were successfully used also for innovative immunosensors design. By using carbon-based SPEs modified with graphene oxide functionalized with N-hydroxysuccinimide in the presence of 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide hydrochloride a novel immunosensors for selective detection of acetaminophen in synthetic and real samples was developed [4]. The template made by LBL technique provides activated carboxylic groups, which form amidic covalent bonds with the terminal amine groups of antiacetaminophen antibody. The optimization of antibody immobilization and the blocking of the free active groups from graphene template with bovine serum albumin was performed by using EIS, cyclic voltammetry and square wave voltammetry. A limit of detection of  $0.17$   $\mu\text{M}$  was obtained with minimal interference of dosage forms excipients and serum components.

### References

- [1] O.A. Shenderova, V.V. Zhirnov, D.W. Brenner, Carbon Nanostructures, Crit. Rev. Solid State Mater. Sci.27 (2002) 227-356.
- [2] M. Tertis, A. Florea, B. Feier, I.O. Marian, L. Silaghi-Dumitrescu, A. Cristea, R. Săndulescu, C. Cristea, Journal of Nanoscience and Nanotechnology, 15(5) (2015) 3385-3393.
- [3] M. Tertis, O. Hosu, L. Fritea, C. Farcau, A. Cernat, R.Săndulescu, C. Cristea, Electroanalysis, 27(3), (2015) 638-647.
- [4] O. Hosu, M. Tertis, R. Săndulescu, C. Cristea, Farmacia, 63(1) (2015) 140-145.

## **Electrochemistry of Self-Doped Polyanilines in Neutral and Alkaline Media**

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Distinctive features that have marked polyaniline as an interesting material, such as its unique redox properties, easiness of transition from insulating to conducting form, electrochromic and pseudocapacitive properties, are strongly dependent on the pH and are typical for acidic environments. Absence of these features in neutral and alkaline media limits its applications in wide range of electrochemical and biological systems.

Introduction of covalently bound acidic groups on polyaniline backbone leads to the effect known as self-doping, which seems to be responsible for the retention of their electrochemical activity and conductivity in neutral and alkaline environments. Further, functionalization of polymer backbone with different acidic groups opens new possibilities for application in sensors, electrochromic devices, ion exchange materials, energy storage devices, etc.

In this presentation, some synthetic aspects of copolymers of aniline and its derivatives with acidic groups and their electrochemical behaviour as a function of pH in aqueous media is discussed, with some insight into the transport of positive ions in polymers.

## Nanoscale-Controlled Interfaces for Construction of Ultrasensitive Lectin Biosensors and Effective Biofuel Cells

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Preparation of different functional biodevices has to be carefully optimized with the primary focus on the interfacial properties of the surface for effective coupling of biorecognition/biocatalyst elements. An enhanced overall performance and robustness of such devices can be guaranteed in case biorecognition/biocatalyst elements are integrated with nanomaterials. Two different electrochemical-based functional biodevices – biofuel cells and lectin biosensors are presented.

Various concepts applied to increase biocatalyst's loading and an accessibility of the biofuel to the biocatalysts within 3-D structure were tested (1,2). The main objective was to prepare biofuel cells in a cost-effective way implementing cheap sources of carbon nanostructured material including carbon nanotubes and graphene and low-cost biocatalysts of bacterial origin (3,4).

Lectin biosensors working in a label-free mode using an electrochemical detection platform are described (5,6). Moreover, an increase of the device sensitivity using a 3-D configuration based on gold nanoparticles is provided (7). Application of some of these devices in analysis of serum samples from people having various diseases, assay of various cancer cell lines and in cancer diagnostics are provided (8,9).

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### References

- [1] J Filip, J Šefčovičová, P Gemeiner, J Tkac, *Electrochim. Acta* (2013) 87, 366.
- [2] J Filip, R Monosik, J Tkac, *Int. J. Electrochem. Sci* (2014) 9, 2491.
- [3] J Šefčovičová, J Filip, P Gemeiner, A Vikartovská, V Pátoprstý, J Tkac, *Electrochem. Commun.* (2011) 13, 966.
- [4] J Filip, J Tkáč, *Electrochem. Commun.* (2014) 49, 70.
- [5] T Bertok, J Katrlík, P Gemeiner, J Tkac, *Microchim. Acta* (2013) 180, 1.
- [6] E Paleček, J Tkac, M Bartošík, T Bertok, V Ostatná, J Paleček, *Chem. Rev.* (2015), DOI: 10.1021/cr500279h
- [7] T Bertok, A Sediva, J Katrlík, P Gemeiner, M Mikula, M Nosko, J Tkac, *Talanta* (2013) 108, 11.
- [8] Bertok T, Klukova L, Sediva A, Kasák P, Semak V, Micusik M, Omastova M, Chovanová L, Vlček M, Imrich R, Vikartovska A, Tkac J, *Anal. Chem.* (2013) 85, 7324.
- [9] L Klukova, T Bertok, M Petrikova, A Sediva, D Mislovicova, J Katrlík, A Vikartovska, J Filip, P Kasak, A Andicsova-Eckstein, J Mosnáček, J Lukáč, J Rovenský, R Imrich, J Tkac, *Anal. Chim. Acta* (2015) 853, 555.

**Nonaqueous Electrolytes for Post Li-Ion: Materials and Mechanistic Aspects**

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*WITHDRAWN*

## Generator/Collector Systems under Full Potentiodynamic Control: Aspects of Instrumentation and Modelling

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Four-electrode configurations containing two working, a single reference and a single counter electrode in the same electrochemical cell have been routinely used in electrochemistry over the past 50 years. A typical example is the rotating ring–disk electrode (RRDE) introduced by Frumkin et al. in 1959. The RRDE was historically the first generator-collector (GC) system used for studying the intermediates or products formed in electrode processes. The operating principle of RRDEs is the following: when on the generator (disk) electrode some electroactive species are formed as a result of an electrode reaction, these products can be involved in another reaction at the collector (ring), and can thus be detected. In the RRDE system, the transfer of species from one electrode to another occurs by convection due to the rotation of the tip.

Although most GC systems are based on the measurement of steady-state currents, there is a growing interest in the application of transient techniques as well. It was shown for example that the simultaneous potentiodynamic perturbation of the generator and collector electrodes can result in a considerable sensitivity enhancement of RRDEs. The application of transient techniques might also be expedient in the case of other generator/collector systems, such as scanning electrochemical microscopy (SECM) studies, especially when accurate temporal resolution is to be achieved. The simultaneous application of potentiodynamic perturbation to the generator and collector electrodes in such systems can, however, not only yield an increased detection sensitivity (when a charge transfer reaction takes place on both working electrodes), but may also broaden the application range of GC systems. Let us consider as an example the case when an electrochemical reaction taking place on the generator yields only products which are neither reducible nor oxidable on the collector in a reasonable potential range. These products, under steady-state conditions, should not be detectable as they cannot be involved in any charge transfer reaction. This does not mean, however, that the species may not interact with the collector at all: the species can, for example, modify the structure of the electrical double-layer, which can occur by means of specific adsorption, by changing the concentrations in the diffuse double layer, etc. Such effects are, in principle, detectable by measuring the *ac* capacitance of the collector electrode.

In this presentation capacitance measurements are carried out on the ring electrode of an RRDE, and this technique is used to study the counter-ion flux that accompanies the potentiodynamic charging/discharging of conducting polymer films. By taking a poly(3,4-ethylenedioxythiophene) (PEDOT) modified disk electrode in combination with a bare gold ring as a model system, it is shown that the measured ring capacitance correlates with the polarization of the polymer film. The capacitance changes measured in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution are in fair agreement with the results of previous RRDE studies, where the halide counter-ion flux leaving the polymer film was assessable by the standard (faradaic) method of detection. The method of calculating the ring capacitance based on a small-signal sinusoid perturbation is discussed in the presentation, and the most important instrumental limitations are addressed.

In addition, general issues concerning the application of “dual dynamic” perturbation techniques in RRDE systems are discussed. Numerical simulations along with measurements in simple model systems are used to demonstrate the nature of the “electrical cross-talk” in GC configurations that arises due to a shared current route of the two working electrodes, and which often causes severe difficulties in the interpretation of collection phenomena. It is pointed out that in electrochemical systems of a considerable ohmic resistance, the positioning of the reference electrode has a major role in the appearance of the unwanted cross-talk effect. For the case of RRDEs, a practical method is suggested to distinguish between the unwanted cross-talk and the actual collection phenomena.

## Electrochemical Resonance: Theoretical and Experimental Aspects under Different Modes of Operation

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Electric resonance corresponds to a maximum of the total admittance of the system at a specific frequency of a time dependent applied voltage perturbation, Fig. 1(a). This means that at the resonance frequency the amplitude of the current becomes maximum (ideally infinite). Electric antiresonance is observed when the total admittance of the system exhibits a minimum at a specific frequency of the voltage source, Fig. 1(a). At the antiresonance frequency the amplitude of the current becomes minimum (ideally zero). Finally, electrochemical resonance is observed when the electrode potential becomes maximum (ideally infinite) at a specific frequency of the voltage source. The above expressions hold under potentiostatic operation whereas similar definitions are introduced for the galvanostatic case, where the perturbation is the applied current. The importance of these findings lies in the fact that electrochemical systems can be utilized either as band-pass or band-stop devices.

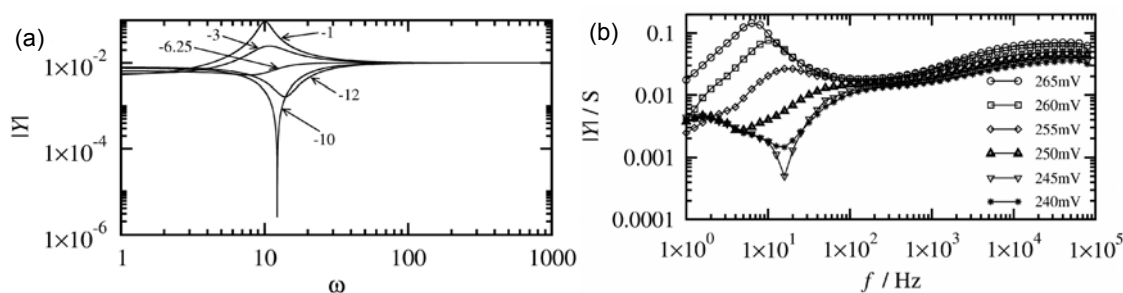


Fig. 1. (a) Theoretical Bode diagram of a system showing resonance and antiresonance around 10 Hz, for different values of the damping parameter, and (b) experimental Bode diagram of the Fe/2M H<sub>2</sub>SO<sub>4</sub> system showing resonance and antiresonance around 10 Hz, for different values of the applied voltage.

In principal, resonance can be observed if the electrochemical system is on a steady state characterized by a natural frequency and damping. Thus, resonance is expected to occur when the system is on a steady state of a stable focus type. The conditions of resonance are derived for potentiostatic and galvanostatic operation. The effect of the system parameters is studied numerically, revealing that it is possible to control the resonance amplitude, as well as the functioning of the interface as a resonator or antiresonator. The theoretical and numerical conclusions are tested experimentally for three different electrochemical systems, namely, the electrodisolution of copper in TFA, of iron in H<sub>2</sub>SO<sub>4</sub> solution and of nickel in H<sub>2</sub>SO<sub>4</sub> solution. It is shown that the theoretical and numerical predictions are observed experimentally, Fig. 1(b), where the system is acting either as a resonator or antiresonator, depending on the value of the applied voltage.

Finally, the effect of non-harmonic (chaotic) perturbations on an electrochemical system that exhibits resonance is studied numerically. Two different types of chaotic signals are applied and it is shown that the electrochemical interface acts as a resonator. As a result, even though the input is chaotic, the output of the electrochemical system is close to harmonic. It is concluded that the electrochemical interface under resonance conditions can control a chaotic signal by transforming it to a harmonic one.

### References

- [1] Karantonis, D. Karaoulanis, *Electrochim. Acta* 56 (2011) 4119.
- [2] Karantonis, D. Karaoulanis, *Electrochim. Acta* 78 (2012) 244.
- [3] Karantonis, E. Bourbos, D. Karaoulanis, *Electrochim. Acta* 87 (2013) 912.
- [4] D. Karaoulanis, P. Chryssafidis, A. Karantonis, *J. Solid State Electrochem.* DOI: 10.1007/s10008-015-2794-y

## Incorporation of Graphene Oxide into Polypyrrole Films for Supercapacitor Application

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Supercapacitors play important role as energy power sources due to fast charging/discharging process that can be utilized in a number of applications such as acceleration of electric vehicle, breaking energy storage, different small electric devices like displays, cameras, mobile phones, toys etc. They can store higher amount of energy compared to the classical capacitors and can achieve much higher power than batteries. Conductive polymers show pseudocapacitive properties due to high electroactivity and reversible redox reaction. They exhibit good stability, easy processability, low cost and could be easily synthesised. Polypyrrole (PPy) is one of the most important candidates among them. Electrochemical properties of PPy depend significantly on the porosity of material that can be improved by adjusting the synthesis parameters or by forming composites with nanostructured materials like carbon nanotubes or graphene [1].

The objective of this work was to prepare PPy by electrochemical synthesis and to provide compensation of positive charge within polymer backbone by graphene oxide (GO) [2]. GO was obtained by chemical oxidation of graphite flakes by Staudenmaiers method. It is oxidized form of graphene containing different oxygen functional groups in basal plane and edges while the size of GO sheet varies in range from 200 nm - 1500 nm. Ppy polymerization was performed from the solution containing 0.3 mg/ml GO and 0.1-0.3 mol dm<sup>-3</sup> pyrrole. During electrochemical synthesis of PPy from GO solution oxidized form of graphene can be intercalated within polymer matrix due to electrostatic forces between negatively charged oxygen functional groups and positively charged PPy backbone. In order to characterize obtained material cyclic voltammetry, electrochemical quartz crystal microbalance and scanning electron microscopy were used. Porous conducting polymer structure was obtained during this procedure. The presence of GO within the PPy influenced morphology and redox reaction properties of the polymer. Obtained layer did not show good electrochemical activity in GO solution, but after transferring it to 0.5 mol dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub> solution activity of the layer has significantly increased and overall properties were improved compared to the properties of PPy prepared from Na<sub>2</sub>SO<sub>4</sub> solution. Resulting material has good pseudocapacitive properties and it is suitable to be used as active material in supercapacitors.

### References

- [1] G. A. Snook, P. Kao, A. S. Best, *Journal of Power Sources* 196 (2011) 1.
- [2] K. Qi, Y. Qiu, X. Guo *Electrochimica Acta* 137 (2014) 685-692.

## Organic Electrode Materials in Rechargeable Batteries

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The ever-increasing demand for high-performing, light weight, economical, and safe power storage for high-tech portable devices and electric vehicles leads to augmented research efforts in the field of organic or organic/hybrid materials to be used as electrodes in energy storage devices [1-13]. There has recently been an increasing number of studies toward the development of novel pure or composite materials containing redox polymers with pendant organic electro-active groups which may be used as cathode- or anode-active material in batteries. These efforts may eventually lead to totally organic batteries [14] with improved properties such as light weight, flexibility, improved environmental safety, low cost of manufacturing. We hereby represent novel polymers and reduced graphene oxide with pendant electro-active groups such as TEMPO, benzimidazole-1-oxyl-3-oxides and quinones used against conventional inorganic cathode or anode materials.

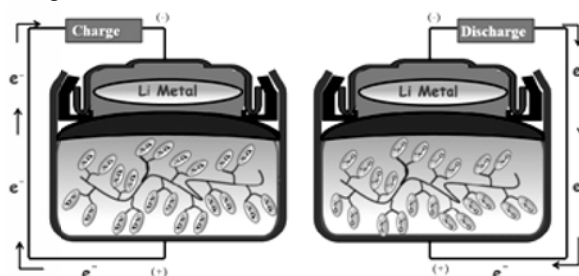


Fig.1 A Nitroxide radical pendant polymer used as a cathode material vs Li.

## References

- [1] Liang, Y.; Tao, Z.; Chen, J. *Adv. Energy Mater.* 2012, 2, 742–769.
- [2] Novák, P.; Müller, K.; Santhanam, K. S. V.; Haas, O. *Chem. Rev.* 1997, 97, 207.
- [3] Cheng, F. Y.; Tang, W.; Li, C. S.; Chen, J.; Liu, H. K.; Shen, P. W.; Dou, S. X. *Chem. Eur. J.* 12, 3082.
- [4] Neves, S.; Polo Fonseca, C. J. *Power Sources* 2002, 107, 13.
- [5] Janoschka, T.; Hager, M. D.; Schubert, U. S. *Adv. Mater.* 2012, 24, 6397–6409
- [6] Sukegawa, T.; Kai, A.; Oyaizu, K.; Nishide, H. *Macromolecules* 2013, 46, 1361–1367
- [7] Choi, W.; Harada, D.; Oyaizu, K.; Nishide, H. *J. Am. Chem. Soc.* 2011, 133, 19839–19843
- [8] Suga T., Ohshiro H., Sugita S., Oyaizu K., Nishide H., *Adv. Mater.* 2009, 21, 1627
- [9] Tang Z. Y., Xu G. X., *Acta Phys. -Chim. Sin.* 2003 19, 307.
- [10] Yao M., Senoh H., Sakai T., Kiyobayashi T., *Int. J. Electrochem. Sci* 2011. 6, 2905.
- [11] Yao M., Senoh H., Sakai T., Kiyobayashi T., *J. Power Sources* 2012, 202, 364.
- [12] Song Z., Zhan H., Zhou Y., *Chem. Commun.* 2009, 448.
- [13] Song Z., Zhan H., Zhou Y., *Angew. Chem. Int. Ed.* 2010, 49, 8444.
- [14] Nishide H., Koshika K., Chikushi N., Sano N., Oyaizu K., *Green Chem.*, 2010, 12, 1573–1575.

## Electrochemical Nucleation and Growth on Foreign Substrates – Emerging Challenges in an Old Scientific Field

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Electrochemical nucleation and growth on foreign substrates is considered from thermodynamic and kinetic points of view [1-4]. Attention is drawn to the decisive role of the substrate for the nucleation process in terms of its surface characteristics. It is demonstrated that the involvement of specific active sites for nucleation in the kinetics of the process depends both on their activity and number.

Limitations of the existing models for the current of nucleation and growth are commented and juxtaposed to the conditions in real systems. Effects due to different types of active sites, parallel electrochemical reactions and availability of porous substrates are addressed. Examples of metal nucleation and growth are given to illustrate the occurrence of these effects. The experimental findings originate from studies on copper and silver (Fig. 1) electrodeposition on conducting polymer substrates [5-11].

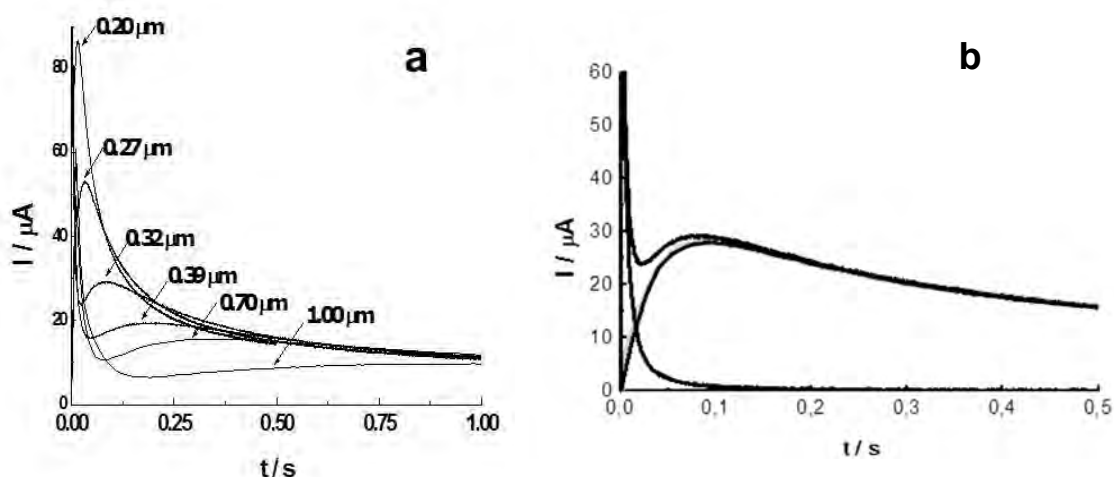


Fig. 1. Reduction current transients measured in the course of silver electrodeposition on polyaniline layers with different thickness (a). Procedure for decoupling silver and polyaniline reduction currents (b).

### References

- [1] Electrochemical Phase Formation and Growth, E. Budevski, G. Staikov, W. Lorenz, VCH, Weinheim, 1996.
- [2] Electrocrystallization, Fundamentals of Nucleation and Growth, A. Milchev, Kluwer Acad. Publ., Dordrecht, 2002
- [3] A. Milchev, Russ. J. Electrochem. 44 (2008) 619.
- [4] Milchev, J. Solid State Electrochem. 15 (2011) 1401.
- [5] V. Tsakova, D. Borissov, B. Rangelov, Ch. Stromberg, J. W. Schultze, Electrochim. Acta, 46 (2001) 4213.
- [6] S. Ivanov, V. Tsakova, Electrochim. Acta, 49 (2004) 913.
- [7] M. Ilieva, V. Tsakova, Electrochim. Acta, 50 (2005) 1669.
- [8] M. Ilieva, A. Stoyanova, V. Tsakova, N. K. Vuchkov, K. A. Temelkov, W. Erfurth, N.V. Sabotinov et al, J. Optoelectronics Adv. Mater. 11(2009) 1444.
- [9] Stoyanova and V. Tsakova, J. Solid State Electrochem., 14 (2010) 1957.
- [10] V. Lyutov, V. Tsakova, J. Electroanal. Chem, 661 (2011) 186.
- [11] V. Lyutov, V. Tsakova, J. Solid State Electrochem., *in press*.

## Electrodeposited Coatings as Cathodes for Hydrogen Evolution in Industrial Chlor-Alkali Electrolysis

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**Composite Ni-MoO<sub>2</sub> coatings:** These coatings were electrodeposited under simulated conditions for industrial production of commercial De Nora's Ni-RuO<sub>2</sub> coatings in the small pilot plant with electrolyte circulation and mixing. They were electrodeposited onto Ni 40 mesh substrates (cathodes dimensions 20x25 cm<sup>2</sup>) from the suspension containing 0.2M NiCl<sub>2</sub> + 2M NH<sub>4</sub>Cl solution and MoO<sub>2</sub> powder. The MoO<sub>2</sub> powder of the particles dimension of 200 nm was used. Depending on the current density and hydrodynamics of coatings deposition it was shown that some cathodes possess lower over-voltage for hydrogen evolution than the commercial one under the conditions of industrial electrolysis in chlor-alkali process (in 32 mas. % NaOH at 90 oC,  $j = -0.3 \text{ A cm}^{-2}$ ). Service life test (SLT), the most important criteria for use in industrial plants, showed that Ni-MoO<sub>2</sub> coatings could be promising replacement for the commercial Ni-RuO<sub>2</sub> cathodes.

**Ni-Sn alloy coatings:** These coatings were electrodeposited from the solution containing 0.6M K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> + 0.3M NH<sub>2</sub>CH<sub>2</sub>COOH + 0.1M SnCl<sub>2</sub> and different concentrations of NiCl<sub>2</sub> onto Ni plates and Ni 40 mesh substrates. It was shown that their chemical and phase composition changes with changing the current density of electrodeposition and that they influence the over-voltage for hydrogen evolution. At the same time, for electrodeposition current densities higher than 10 mA cm<sup>-2</sup>, the morphology of Ni-Sn coatings changed from relatively flat to rough coatings. Catalytic activity for hydrogen evolution was found to be influenced to small extent by the phase composition, while their roughness (high real surface area) mainly caused low over-voltage for hydrogen evolution. EIS measurements performed during the SLT showed that the real values of the  $(R_{ct} + R_p)(r)$ , reflecting intrinsic catalytic activity for the HER, could be obtained (Fig. 1a). Hence, after taking into account the roughness factor, the lowest value of the  $(R_{ct} + R_p)(r)$  is obtained for the DN electrode, confirming that this cathode should possess the highest current density at a given potential (-1.2 V vs. SCE), which is in accordance with the polarization curve measurements. At the same time it could be stated that intrinsic catalytic activity for NiSn(30), NiSn(60) and NiSn(100) are practically insensitive to the number of cycles, as it was the case for the commercial DN cathode. Comparing the values of potential (corrected for the IR drop) recorded at the current density of -0.3 A cm<sup>-2</sup> as a function of the number of cycles (Fig. 1b), it appears that the activity for the HER for all cathodes decreases in a similar way with the number of cycles, being lower for about 20-25 mV after 25 cycles. Hence, it could be concluded that the EIS measurements and polarization curve measurements are in accordance with the SLT measurements and that Ni-Sn coatings could also be promising replacement for the commercial cathodes.

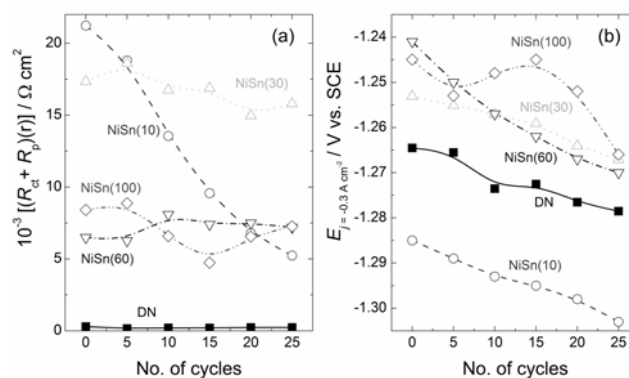


Fig. 1. (a) The values of  $(R_{ct} + R_p)(r)$  as a function of the number of cycles for all investigated electrodes. (b) SLT results, represented as potential (corrected for the IR drop) for the HER at  $j = -0.3 \text{ A cm}^{-2}$  as a function of the number of cycles for all investigated electrodes.

$$\Delta \tilde{G}_f^0(i) = \Delta G_f^0(i) / F$$

$$\Delta \tilde{G}_f^0(i)$$

$$\Delta \tilde{G}_f^0(i)$$

$$\Delta \tilde{G}_f^0(i) = f(n)$$

$$\Delta G_f^0(i)$$

$$\Delta G_f^{0*} = \Delta G_f^0 - x \Delta G_f^0(H_2O)$$

$$\Delta G_f^{0*}$$

$$E^0 = -\Delta G_f^{0*} / n.$$

$$\Delta \tilde{G}_f^0(i)$$

## Ellipsometric Study of Passive and Anodic Oxide Films Formed on Nb and Ti Substrates

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Niobium and titanium metals are very stable in various corrosive media as a result of existence the natural oxide films always present on their surfaces. The thicknesses of these films vary from 1 to 3 nm and it is extremely difficult to remove them from the metal substrates. The corrosion stability of these metals can be considerably enhanced by electrochemical passivation and anodic oxidation.

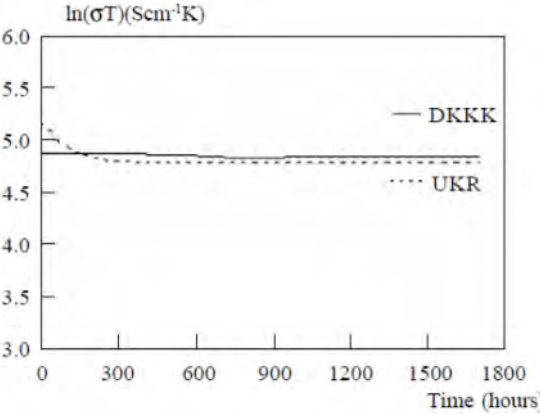
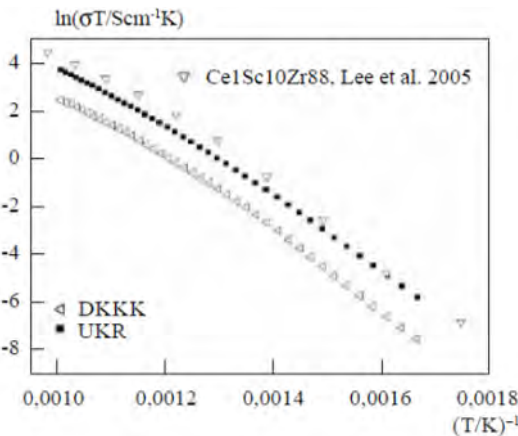
Passive and anodic films formed on the Nb and Ti substrates at different concentrations of  $H_2SO_4$  and KOH solutions (from 0.1 M to 10 M) were studied using cyclic voltammetry, corrosion measurements and ellipsometry [1-4]. Results indicate the strong influence of the concentration and electrolyte nature to the active/passive transitions and stability of passive films. Cyclic voltammetry profiles show that the niobium and titanium easily passivated even at higher concentrations of  $H_2SO_4$  and the KOH solution. By multiple cycle sequences in which the final anodic potential was gradually enlarged, the barrier properties of the passive films were confirmed [5]. For active and passive transition, as well as the reactivation process on Nb surfaces strongly influences the concentration of KOH solution while this effect is insignificant in  $H_2SO_4$ , even at higher concentrations. In contrast, in the process of reactivation with the titanium strongly influences  $H_2SO_4$ , especially in the higher concentrations. The active/passive transition for both electrodes shows the shifts of primary passivation potential towards more positive potentials with increasing the concentrations of  $H_2SO_4$  and shifts to more negative potentials with increasing the concentration of KOH. The films thickness growth on Nb and Ti surfaces and their dissolution in the passive potential range were investigated in specially prepared electrolytic-optical cell adapted for electrochemical and in-situ ellipsometric measurements. Comparing the theoretically computed curves with the experimental ellipsometrical  $\Psi$  vs  $\Delta$  loci, the linear dependence of the applied potentials/voltages with film thickness was determined. In the same time the coefficient of film thickness growth and indexes of refraction of anodic oxide films were also determined. By electrochemical and ellipsometric measurements it was confirmed that with suitably chosen cathode potential, the complete reduction of anodic and passive oxide films as well as partly reduction of natural oxide film is possible for Nb only in KOH solutions, whereas for Ti in  $H_2SO_4$  and KOH solutions [6].

The structure of passive and anodic oxide films were investigated with Raman and micro-Raman spectroscopy. Raman spectroscopy is an alternative technique to the standard X-ray and electron diffraction techniques to study crystal structure. The Raman spectra reveal that the thin passive films for Nb and Ti in all investigated concentrations of  $H_2SO_4$  and KOH solutions are amorphous. At some critical voltages, depending of concentrations of  $H_2SO_4$  and KOH solutions, as well as time of anodization, begin the transformation of the films from amorphous state to the crystalline form.

For Ti the anatase, brookite and rutile have been identified. The micro Raman spectra reveal that brookite is intermediate form of the anodic oxide films. The primarily film formed is composed of an anatase and the final film formed at higher voltage is mainly composed of rutile type  $TiO_2$ . For Nb, the passive films are amorphous, as in case for Ti. At higher voltages, in the beginning of crystallization, the anodic oxide films consist of mixtures of  $NbO_2$  and  $Nb_2O_5$ , while  $NbO_2$  is completely transformed to  $Nb_2O_5$  for thicker and well-crystallized films.

### References

- [1] I. Arsova, Lj. Arsov, N. Hebestreit, A. Anders, W. Plieth, J. Solids State. Electrochem. 11 (2007) 209.
- [2] I. Mickova, Inter. Rev. Chem. Engin. (I.RE.CH.E.), 3 (2011) 550.
- [3] A. Efremova, Lj. Arsov, J. Phys. II, 2 (1992) 1353
- [4] A. Prusi, Lj. Arsov, B. Haran, B. Popov, J. Electrochem. Soc. 149 (2002) B491
- [5] I. Mickova, A. Prusi, T. Grchev, Lj. Arsov, Portugalie Electrochim. Acta 24 (2006) 377
- [6] Lj. Arsov, Electrochim. Acta 30 (1985) 1645



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## Fabrication of Lectin-Based Immunosensor with Reduced Non-Specific Interactions in Favour of Early-Stage Cancer Diagnosis

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Aberrant changes in carbohydrate content of proteins, lipids or on the cell surface are closely related to the pathological processes and disease development in a human body [1]. Thus, better understanding of glycan changes may serve as a reliable diagnostic tool. Such lectin-based biosensors capable to detect a minor glycosylation change of tumour specific glycoproteins can provide additional useful information applicable in diagnostics [2-4].

Herein we present impedimetric biosensor approach based on gold electrode modification with a mixed self-assembly monolayer (SAM). Briefly, SAM was constructed by immersing the pre-treated gold electrodes for 16 h at room temperature in a mixed solution of 11-mercaptoundecanoic acid and 6-mercapto-1-hexanol (in a ratio 1:3). Subsequently, a covalent antibody immobilization was carried out *via* EDC/NHS chemistry with further incubation of the electrode with a blocking agent to avoid non-specific interactions. The following step was attachment of a prostate specific antigen (PSA) with a final incubation of the electrode with various lectins (SNA, MAA, LTA, LCA) to glycoprofile a disease specific glycoprotein. The fabricated lectin-immunosensor was characterized by using electrochemical impedance spectroscopy (EIS).

A crucial event of the assay is minimizing non-specific interactions of biomolecules to biosensor surface [5,6]. Therefore, a comparison with 3 blocking agents (gelatine, carbo-free blocking solution and ethanolamine) was performed. Furthermore, an effect of blocking solution was examined in a human serum with final optimization of serum dilution applied in analysis.

These preliminary results indicate an employment of such a biosensor for biomedical diagnostic purposes with low sample consumption and a sensitive glyco-biomarker detection in patient sample potentially applicable for early-stage cancer diagnosis.

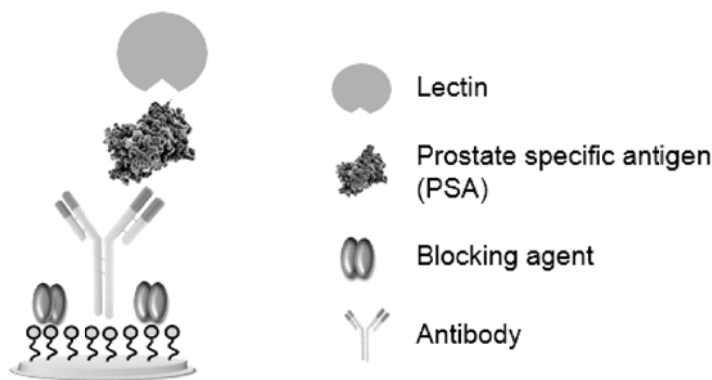


Fig.1. A graphical representation of lectin-based immunosensor.

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### References

- [1] D. Pihíková, P. Kasák, J. Tkáč, *Open Chem.* 13 (2015) 636.
- [2] Hushegyi, J. Tkáč, *Anal. Methods* 6 (2014) 6610.
- [3] L. Klukova, T. Bertok, M. Petrikova A. Sediva, *et al.*, *Anal. Chim. Acta* 853 (2015) 555.
- [4] T. Bertók, J. Katrík, P. Gemeiner, J. Tkáč, *Microchim. Acta* 180 (2013) 1.
- [5] E. Paleček, J. Tkáč, M. Bartošík, T. Bertók, V. Ostatná, J. Paleček, *Chem. Rev.*, DOI: 10.1021/cr500279h (2015).
- [6] T. Bertok, L. Klukova, A. Sediva, P. Kasák, V. Semak, M. Micusik, M. Omastova, L. Chovanová, M. Vlček, R. Imrich, A. Vikartovska, J. Tkáč, *Anal. Chem.* 85 (2013) 7324.

BEH-O-02

**Spectroelectrochemical Investigation of Novel Antitumor Active Platinum(II) Complexes with Pyridine Oxime**

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*WITHDRAWN*

**Electrochemical Behavior of Coated Ti Alloy in Simulated Body Fluid for Biomedical Applications**

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*WITHDRAWN*

## Functionalized Hybrid Sol-Gel Coatings Deposited on Titanium

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Inorganic zirconium-based alkoxide as a completely hydrolysable precursor was combined with organically functionalized silane which is a partially hydrolysable precursor. It gives the hybrid of interesting properties: chelated organic/inorganic network of high density, elasticity and corrosion resistance [1]. Hybrid sol-gel was synthesized as a basis for the preparation of coatings to be used as anticorrosion and antibacterial protection of medical implants. As precursors, zirconium(IV) propoxide and (3-glycidyloxypropyl)trimethoxysilane were used, and acetic acid as a catalyst [2]. The synthesis was followed using in situ Fourier transform infrared spectroscopy. Of special interest was to follow the reaction of the opening of the epoxy ring of GPTMS, both during synthesis and curing at room temperature and at 150 °C without the addition of curing agent. To improve the antibacterial properties of the coatings [3] nano-sized TiO<sub>2</sub> particles were incorporated in the coating. Scanning electron microscopy image reveals a homogeneous coating structure despite the presence of nano-particles (Fig. 1).

To test the corrosion properties of bare titanium samples and samples coated by hybrid coatings electrochemical polarization curves were measured in a simulated physiological solution. Antibacterial activity of prepared coatings was tested by a study of attachment of cells to the surface of the coating. For this purpose bacterial strain *Pseudomonas aeruginosa* was used.

The coating effectively impedes the dissolution of the underlying substrate and offers antimicrobial activity. Therefore, sol-gel treatment combined with the use of nano-technology enabled the functionalization of the surface.

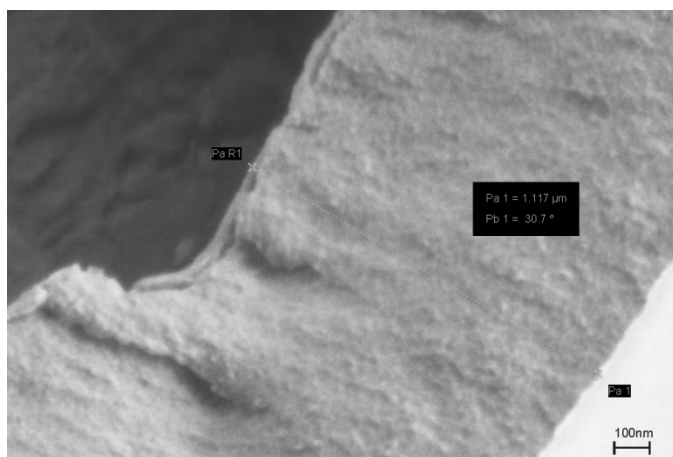


Fig.1. SEM image of cross section of sol-gel hybrid coating deposited on titanium. The coating contains 0.2 % of TiO<sub>2</sub> nanoparticles.

### References

- [1] R.B. Figueira, C.J.R. Silva, E.V. Pereira, J. Coat. Technol. Res. 12 (2015) 1.
- [2] Milošev, B. Kapun, P. Rodič, J. Iskra, J. Sol-Gel Sci. Technol. doi 10.1007/s10971-015-3620-9.
- [3] M. Kulkarni, A. Mazare, E. Gongadze, Š. Perutkova, V. Kralj-Iglič, I. Milošev, P. Schmuki, A. Iglič, M. Mozetič, Nanotechnology, 26 (2015) 062002.

## Mechanisms of Electron Transfer in Eukaryotic Biofuel Cells

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The bioelectrochemical systems (BESs) using whole microorganisms as biocatalysts attract a growing attention in the last decade. Most investigated biocatalysts are bacteria and the mechanisms of electron transfer in these microbial fuel cells (MFCs) are established. In this study we generalize the mechanisms of extracellular electron transfer (EET) of eukaryotic organisms. We discovered that *Candida melibiosica* 2491 yeast strain secrete endogenous mediator of electron transfer as response to the applied conditions and connected load resistance. The intracellular origin of electrons and protons was analyzed by characterization of the redox behavior of intracellular fractions in the presence and absence of specific inhibitors of the mitochondrial electron transfer chains (ETC) and determination of the specific enzyme activities of NADH ubiquinone oxidase (Complex I) and cytochrome c oxidase (Complex III). Contribution of the glycolysis and aerobic respiration to the EET is proposed. We proved that the addition to the culture of electrochemically active substances possessing different potentials modifies EET by changing the cellular metabolic processes and electron exchange with redox molecules with identical and lower potential. The recently synthesized stilbazolium dye 4-[(E)-2-[4-(dimethylamino)naphthalen-1-yl]ethenyl]-1-methylquinolinium iodide monohydrate (DANSQI) increases the generated by the biofuel cell current. Based on the recognized 12 times increased catalase activity of the intracellular fractions, we speculate that the dye enters the cells and provoke peroxisomes retaining for rapid adaptation to the new growth conditions.

## **Bioelectrochemical Systems as an Innovative Approach for Electrical Energy Generation, Biosynthesis and Bioremediation**

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The bioelectrochemical systems (BES), utilizing whole living microorganisms as biocatalysts, have attracted an increasing attention during the last decade as an innovative approach for electricity generation, biosynthesis and bioremediation. BES can produce energy from waste, by converting biodegradable organic matter directly into electricity, hydrogen or other valuable products. Based on the principles of microbial fuel cells (MFCs), in which the ability of specific bacteria to transfer electrons extracellularly to the anode is used, a variety of modifications such as Sediment MFC, Plant MFC, Metallurgical MFC, etc., has been recently developed. While MFCs produce an electric current from the microbial decomposition of organic compounds, microbial electrolysis cells (MECs) partially reverse the process to generate hydrogen, methane or other products by applying an electric current. The use of microorganisms in MEC decreases the overpotential, making easier the electron exchange, as well as the quantity of electricity needed for the conventional electrolysis. This contribution reviews the principles of operation, specificity, advantages and drawbacks as well as potential applications of different BES, based on microbial fuel cells and microbial electrolysis cells. Major results, obtained by our research group with yeast-based biofuel cells, Plant MFCs, Sediment MFCs and MECs, are summarized and discussed.

## Biomedical Composite Silver/Hydroxyapatite/Graphene Coatings

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Novel composite silver/hydroxyapatite/graphene (Ag/HAP/Gr) coatings were produced by electrophoretic deposition (EPD) on titanium to assemble porous bioactive homogenous coatings, with improved corrosion stability in simulated body fluid (SBF). Interesting aspect revealed in related literature showed that EPD is a very attractive technique used to produce single isolated and/or stacked layers of graphene regardless of its orientation and density [1]. Lately, research efforts are devoted to the fabrication of graphene or its derivatives reinforced biocomposites with HAP [2].

Herein, the novel biocomposite Ag/HAP/Gr coatings were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), Fourier transform infrared (FT-IR), thermogravimetric analysis (TGA), Raman spectroscopy, X-ray photoelectron analysis (XPS) and electrochemical impedance spectroscopy (EIS).

The analysis showed improved properties of Ag/HAP/Gr coatings as a consequence of graphene toughness, as opposed to the graphene-free coatings. The surface morphology showed reduced surface cracks, nanoindentation proved better mechanical resistance (hardness and elastic modulus increased by 10% compared to measured values of its counterpart Ag/HAP) and enhanced thermal stability, while the Ca/P ratio was closer to the stoichiometric value.

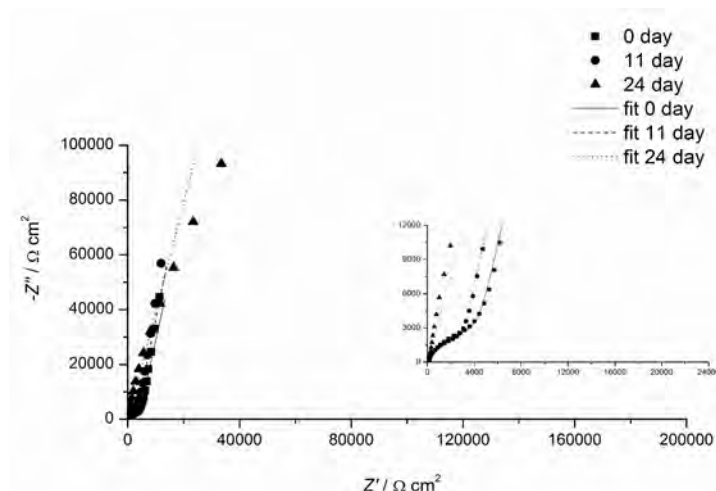


Fig.1. The Nyquist plots of the Ag/HAP/Gr after different immersion times in SBF at 37 °C.

The evidence of good biocompatibility of Ag/HAP/Gr coating was the formation of a new apatite layer, indicating biogrowth of carbonated HAP after only 7 days of immersion in SBF as confirmed by increase of  $R_c$  values, SEM and XRD results. The high value of coating pore resistance after 21 days indicated improved bioactivity of Ag/HAP/Gr coating.

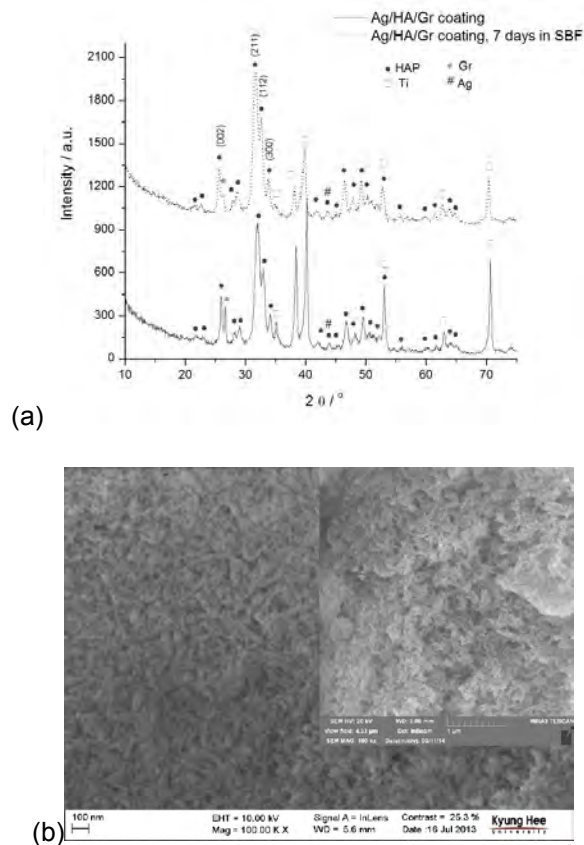


Fig.2. XRD patterns (a) and FE-SEM microphotographs (b) of the Ag/HAP/Gr coating before and after immersion in SBF (inset: Ag/HAP/Gr coating, 7 days in SBF, 37°C).

Ag/HAP/Gr composites were subjected to microbiological testing. Antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* was confirmed after only 3 hours of incubation and noncytotoxicity against healthy peripheral blood mononuclear cells (PBMC) indicate the high potential for biomedical applications

## References

- [1] Janković, S. Eraković, M. Mitrić, I.Z. Matić, Z.D. Juranić, G.C.P. Tsui, C-Y. Tang, V. Mišković-Stanković, K. Yop Rhee, J. Alloy. Compd. 624 (2015) 148.
- [2] Janković, S. Eraković, M. Vukašinić-Sekulić, M. Mitrić, V. Mišković-Stanković, K. Yop Rhee, Prog. Org. Coat. 83 (2015) 1.

## A Novel Graphene/ $\beta$ -Cyclodextrin Biosensor for Dopamine Detection

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Graphene and cyclodextrins have been widely employed for sensors elaboration combining the enhanced sensibility given by the special properties of graphene and cyclodextrins [1, 2]. These sensors were applied for a wide range of biological molecules detection, among which dopamine, an important neurotransmitter, can be mentioned [3, 4].

A graphene/ $\beta$ -cyclodextrin biosensor with tyrosinase was developed for dopamine detection (Fig. 1.).

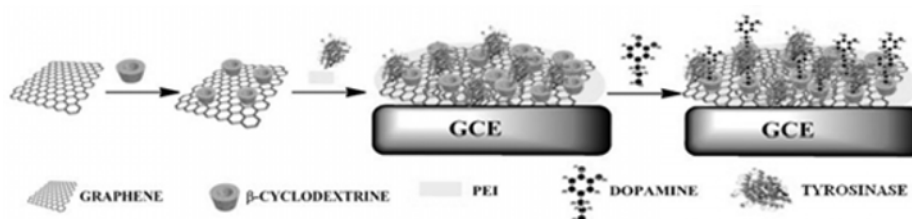


Fig. 1. Schematic representation of the biosensor development

In order to improve the thermal, mechanical and electrical properties, the graphene oxide (GO) was reduced with ascorbic acid, a simple *green method* to avoid the environmentally harmful reducing agents [5]. The glassy carbon electrode was modified with reduced graphene oxide (RGO),  $\beta$ -cyclodextrin ( $\beta$ -CD) and polyethylenimine (PEI) by using layer by layer method (LBL). The obtained nanocomposite was then characterized by Raman and FTIR spectroscopy and optical microscopy. The biosensor elaboration process was studied using electrochemical impedance spectroscopy. The  $\beta$ -CD presence determined the increase of the  $R_{ct}$ , while RGO layer increased the sensor conductivity due to their specific characteristics.

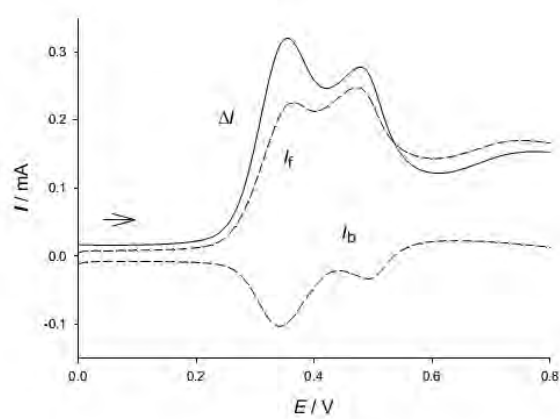
The electrochemical behavior of DA was investigated by electrochemical methods on electrodes modified through multiple possible combinations during the optimization process and the best results were obtained on the electrode modified with 1 layer of RGO, 1 layer of  $\beta$ -CD and 1 layer of PEI. This nanoplatform was used to immobilize the tyrosinase (TYR) obtaining a biosensor applied for the DA determination from pharmaceutical products, serum and urine samples with good recoveries, enhanced sensitivity (LOD of 3.3  $\mu$ M) and good selectivity (tested in the presence of ascorbic acid, uric acid and glucose as interferences).

**ACKNOWLEDGEMENTS:** This paper was published under the frame of European Social Found, Human Resources Development Operational Programme 2007-2013, project no. POSDRU/159/1.5/S/136893 and project no. POSDRU/159/1.5/S/138776.

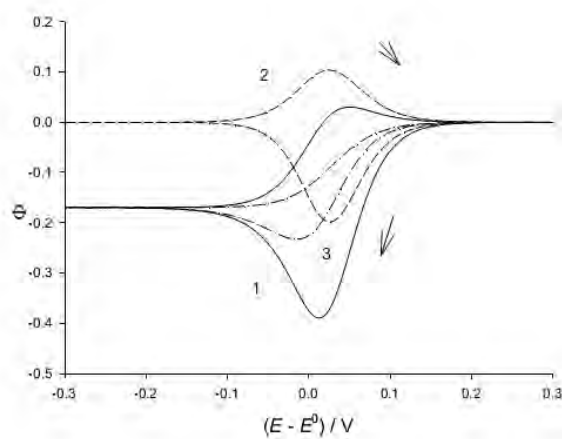
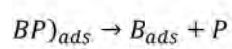
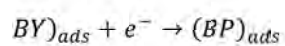
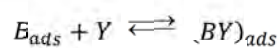
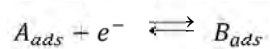
### References

- [1] S. Kochmann, T. Hirsch, O. S. Wolfbeis, TRAC-Trend. Anal. Chem. 39 (2012) 87.
- [2] L. Fritea, M. Terțiș, C. Cristea, S. Cosnier, R. Săndulescu, Anal. Lett. 48 (2015) 89.
- [3] L. Tan, K.-G. Zhou, Y.-H. Zhang, H.-X. Wang, X.-D. Wang, Y.-F. Guo, H.-L. Zhang, Electrochem. Commun. 12 (2010) 557.
- [4] X. Tian, C. Cheng, H. Yuan, J. Du, D. Xiao, S. Xie, M. M.F. Choi, Talanta 93 (2012) 79.
- [5] D. Lu, S. Lin, L. Wang, X. Shi, C. Wang, Y. Zhang, Electrochim. Acta. 85 (2012) 131.

Compound	$E_{p,1} / V$ vs Ag/AgCl	$E_{p,2} / V$ vs Ag/AgCl
delphinidin	0.327	
epigallocatechin gallate	0.365	0.486
epigallocatechin	0.373	
cyanidin	0.403	
myricetin	0.415	
pelargonidin	0.440	
epicatechin gallate		0.480



the linear relationship



cyclic voltammogram,  $\kappa_{cat} = 1$ ,  $\kappa_{dis} = 0.257$ ,  $E_{st} = 0$ ,  $E^0$

$Kc_Y^* = \dots$

## Electrochemical Investigations of Lipase Enzyme Activity on New Pyridinium Ligands

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Enzymes are biocatalysts with a significant capacity to catalyze the conversion of various compounds (enzymatic substrate) to different products. Lipase is one of the most used enzymes in biocatalytic processes. [1-2]. We investigate the mechanism of lipase interaction with new pyridinium ligands derived from 4,4'-bipyridine, which have an essential role in biological systems and are involved in cycloaddition reactions with different dipolarophyls, by biocatalytic way in order to obtain the indolizine core [3].

The new synthesized ligands were N, N' bis (p-bromophenacyl)-4,4'-bipyridinium dibrome (rigid ligand, Lr) and N, N' bis (p-bromophenacyl)-1,2-bis (4-pyridyl) ethane (mobile ligand, Lm). The stability in time of ligands was evaluated by pH and conductivity analysis. Cyclic voltammetry measurements were performed as a useful electroanalytical method to characterize the reduction ability and electrochemical behaviour of new pyridinium ligands which are involved in biocatalyzed cycloaddition by lipase enzymes. To highlight the biocatalytic properties of the lipase, the precursor's behaviour, phenacyl bromide and the dipolarophyle ethyl propionate, involved in biocatalytic process with lipase was evaluated. The precursor and the dipolarphyle are involved in electronic change process for platinum electrode, which is more intense in presence of lipase.

The stability of new ligands in  $\text{KNO}_3$   $10^{-1}$  M as support electrolyte is influenced by the lipase quantity added. The recorded voltammograms showed an intensive electronic transfer in case of Lr interaction with lipase compared with Lm due to mobile groups from its chemical structure (Fig.1).

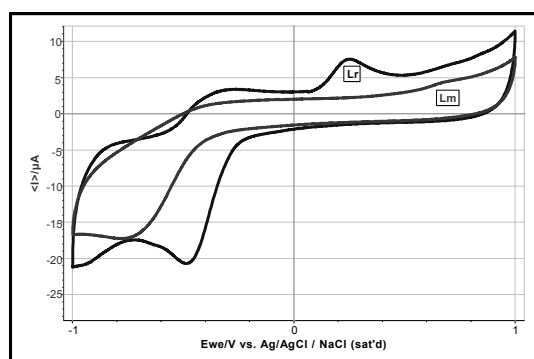


Fig. 1. CVs of Lr and Lm interaction with 10 mg lipase, 500 mV/s; WE-C, CE- Pt; RE- Ag/AgCl

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### References

- [1] T. Ikeda, *Electrochimica Acta* 82 (2012) p. 158.
- [2] K. Gangadhara Reddy, G. Madhavi, B.E. Kumara Swamy, Sathish Reddy, A. Vijaya Bhaskar Reddy, V. Madhavi, *J. of Molecular Liquids* 180 (2013) p. 26.
- [3] R.M. Dinica, F. Marchetti, C. Pettinari, B.W. Skelton, A.H. White, *Inorg Chim Acta* 360 (2007) p. 2609

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## Interaction between Differently Coated Commercial Stainless Steels and Contacting Layer (LSCF) Aged in Air at 800°C

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Two commercial steels currently used as interconnect materials in SOFC stacks (Crofer 22 APU and AISI 441) were aged for 100 hours in near real life working conditions (i.e. 800°C in air flow and with a current flow of 0.5A/cm<sup>2</sup>) after being covered with colloidal LSCF. Such samples are meant to simulate the situation found at the rib of metal plate shaped with channels for gas feeding of the cathode. The ribs of an interconnect are actually in direct contact with the cathode or, in more modern and effective stacks, with the contacting paste used to increase efficiency of electrons distribution between the interconnect and the electrode. LSCF can be used for this purpose thanks to its good conductivity at working temperature and to its complete compatibility with the cathode which is often made of the same material.

The samples are previously prepared according to the nature of the steel. For Crofer 22 APU [1-2], a special ferritic stainless steel designed to be used as interconnect for SOFC stacks, in two differing conditions are used as substrate for the LSCF: as received and after pre-oxidation. The AISI441, a ferritic stainless steel used in high temperature application and already widely used for stacking [3-5], is previously coated with Co<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> spinel oxide and then covered with the LSCF.

The interaction between the LSCF and the metallic substrate is studied with the application of a current flow in the range of the one typically present inside a stack. Despite the short ageing time (i.e. 100h) it was possible to observe the diffusion of elements from the metallic substrate into the LSCF layer and to highlight the effect of the current flow direction on the modification of the layer composition and microstructure

### Acknowledgments

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### References

- [1] R. Hojda, R. Heimann, W.J. Quadackers, ThyssenKrupp Tech- forum, 2003, p. 20
- [2] J. Piron-Abellan, F. Tietz, V. Shemet, A. Gil, T. Ladwein, L. Singheiser, W.J. Quadackers, in: J. Huijsmans (Ed.), Proceedings of the Fifth European Solid Oxide Fuel Cell Forum, Lucerne, Switzerland, 2002, p. 248
- [3] J.-P. Choi, K. S. Weil, Y. M. Chou, J. W. Stevenson, Z. G. Yang, International Journal of Hydrogen Energy 36/7 (2011) 4549
- [4] P. Piccardo, R. Amendola, S. Fontana, S. Chevalier, G. Caboches, P. Gannon, Journal of Applied Electrochemistry 39/4 (2009) 545
- [5] Y.S. Chou, E. C. Thomsen, J. P. Choi, J. W. Stevenson, Journal of Power Sources 197 (2012) 154

## Corrosion Stability of Cerium Modified Cathoretic Epoxy Coatings on Al6060 Alloy

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Protective coatings should provide good barrier to ingress of corrosive species, sufficient adhesion to the substrate as well as good compatibility with additional top coats. The presence of pigments and/or functional agents in the coating composition could be beneficial [1,2] in the corrosion protection.

The doping with rare earth elements, like cerium, has shown to enhance the corrosion stability of organic coatings due to their self-healing properties [3]. In this work cerium doped nanometric epoxy primers were deposited cathoretically with different amounts of cerium nitrate (1, 5 and 10 mM) with the aim of optimizing the cerium content in the epoxy emulsion with respect to adhesion and corrosion stability of deposited primer coating. Cerium-free epoxy coating was also analyzed as a reference. The long term protection was evaluated in the chloride environment (3 wt.%NaCl) using electrochemical impedance spectroscopy (EIS) and polarization measurements. Coatings were also analyzed by scanning electron microscopy (SEM) coupled with EDX, Fourier transform infrared spectroscopy and thermogravimetric measurements. Size and zeta potential of epoxy emulsion were measured by dynamic light scattering and Laser Doppler velocimetry. Adhesion was determined both by a standardized pull-off method and by swelling in *N*-methyl pyrrolidone [4].

The ceria content, as well as its distribution in the epoxy coating, was determined by SEM cross-sectional analysis. The homogeneity of epoxy coatings was evaluated and related to corrosion stability. The results showed that cerium-doping can promote the formation of compact epoxy coatings with enhanced protectiveness in the early stage of immersion in the corrosive media. Increased barrier properties of epoxy primers suggest good compatibility of ceria particles with polymeric epoxy layer. However, zeta potential measurements indicated that higher amounts than 10 mM Ce(NO<sub>3</sub>)<sub>3</sub> added into the epoxy emulsion resulted in unstable emulsion. The water content in the epoxy coatings and their thermal stability were also determined. In addition, a detailed EIS study was undertaken to follow the evolution of corrosion stability of all samples with time of exposure to corrosive media.

It was shown that all examined ceria containing epoxy emulsions resulted with the enhanced adhesion and corrosion stability of epoxy primers. However, the smallest loading of 1 mM showed only improvement during the initial exposure to NaCl solution. EIS and polarization measurements confirmed that higher ceria loadings also provide long term protection in chloride solution. The optimal ceria content in the epoxy emulsion, with respect to adhesion strength, thermal stability and long-term corrosion stability of protective systems was 10 mM.

### References

- [1] M.F. Montemor, Surf. Coat. Technol. 258 (2014) 17.
- [2] J.B. Bajat, O. Dedić, J. Adhesion Sci. Technol. 21 (2007) 819.
- [3] D. Snihirova, S.V. Lamaka, M.F. Montemor, Electrochim. Acta 83 (2012) 439.
- [4] W.J. van Ooij, R.A. Edwards, A. Sabata, J. Yappia, Journal of Adhesion Science Technology 7 (1993) 897.

## Investigation of Porous Titanium Dioxide Layers by Plasma Electrolytic Oxidation

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For titanium there is an ongoing search to improve its beneficial properties. One aspect is to strengthen its applicability by modification of surface characteristics like adhesion and biocompatibility with an adapted chemical surface treatment. Anodization is one of the typical methods to modify the oxide layer on the surface of titanium and its alloys. The plasma electrolytic oxidation (also: micro arc oxidation MAO, plasma chemical oxidation, anodic spark deposition) is a newer type of high-voltage anodic oxidation capable for producing a stable oxide layer on valve metals (Al, Zr, Mg, Ti etc.). It is very suitable as a surface treatment due to the combined adjustment of morphology and chemical composition, while offering the possibility of generating a uniform crystalline surface [1].

In the present study TiO<sub>2</sub>-surfaces were prepared in acidic and alkaline electrolyte and impressing a current in a voltage range between 100 and 300 V on pure titanium plates (grade 1). The voltage was consequently raised into 3 minutes to an assigned value and kept until 15 min and the current was monitored. During the electrochemical process a high amount of characteristic micro discharges on the sample surface occur. These discharges are due to local breakdowns of the growing oxide layer and form a porous structure. The process includes chemical, electrochemical and physical reactions (plasma generation) with a distinct local temperature increase which leads to the formation of a partly crystalline surface. The plasma electrolytic process allows a high layer thickness and surface roughness in comparison to other chemical surface treatments.

### References

- [1] S. Stojadinović, R. Vasili, M. Petkovi, B. Kasalica, I. Belča, A. Zekić, Lj. Zeković; Applied Surface Science 265 (2013) 226–233

## **Role of Metal Impurities in Generation of Defects in Anodic Layers of Nb<sub>2</sub>O<sub>5</sub>**

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Key role in formation of the properties of the anode layers of niobium pentoxide is related to defects of their own or additive nature, while the main defects are oxygen vacancies. The aim of this work – analysis of additive influence in niobium on formation of defects in Nb<sub>2</sub>O<sub>5</sub>.

The object of the study were layers of Nb<sub>2</sub>O<sub>5</sub>, formed by anodic oxidation of the sintered niobium pellets of two types (denoted as A and B), differ by the presence on the surface of A type samples of Mg additive, controlled by X-ray photoelectron spectroscopy (XFES). It shall be noted that XFES - initial analysis of the niobium powder applied at generation of samples of both types, has shown no differences in the composition of additives; presence of Mg has only been detected on the surface of the pellets formed by high-temperature vacuum powder sintering. This fact affirms that additives located in the niobium powder as a result of sintering are concentrated on the pellet's surface probably according to the bulk diffusion mechanism. Anodic oxidation of niobium was similarly carried out in two stages: in a galvanostatic mode, and subsequent aging at a constant voltage. Concentration of charged defects is determined from the current-voltage characteristics (C - V) according to Mott -Schottky equation. The results can be interpreted as follows: at the first (galvanostatic) stage of anodic oxidation of samples part of A atoms displaced from the metal oxide pellets are represented by additive metal atoms (Mg), which behavior in electric field is determined by mechanisms specific for anionic defects. As a result, after galvanostatic stage less quantity of defects as compared to B sample case will be carried out to the oxide / electrolyte border. Further, at the transition to the potentiostatic oxidation mode, Mg<sup>2+</sup> cations along with the basic (anionic) defects are moved to the outer boundary of the oxide layer, which leads to an increase in concentration of the charged defects in the surface layer Nb<sub>2</sub>O<sub>5</sub>.

## Lanthanide and Their Mixtures Conversion Coatings as a Potential Replacement of Chromate Coatings on 7075-T6 Aluminum Alloy

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Aluminium and its alloys are commonly used materials in different applications in industry, especially in aircraft, due to good chemical and physical properties. The mechanical properties of aluminium alloys are improved with addition of metal inclusions, like copper, magnesium, zinc, silicon and others, while the corrosion properties deteriorate, particularly in chloride media. To protect the surface of aluminum alloy against corrosion, chromate conversion coatings have been used for many decades. Today is their used severely restricted, because six-valent form of chromium is very toxic and carcinogenic [1, 2].

To protect aluminum alloys against corrosion, various new solutions, which are more environmentally acceptable are sought today. As an alternative, conversion coatings based on rare earth salts have been identified, especially cerium [3]. Cerium is the most active and the only lanthanide, which can be oxidized in a stable salt with higher oxidization state [4]. Lanthanide compounds are environmentally friendly, they are available in natural sources and also their price is reasonable.

The aim of this work was to investigate various lanthanide compounds as a potential corrosion inhibitors of aluminum alloys and replacement of chromate coatings. To protect aluminium alloy AA7075-T6 against corrosion, conversion coatings based on various lanthanide compounds and their mixtures were investigated [5]. Conversion coatings were prepared using 0.01 M nitrate lanthanide salts, i.e., cerium nitrate, lanthanum nitrate and mixtures of cerium and lanthanum nitrate in ratio 1 : 3 and 3 : 1. Coatings were prepared at different times of immersion in lanthanide solutions with the addition of 30 % hydrogen peroxide at room temperature. The corrosion properties of bare substrate and substrates modified by conversion coatings were studied by electrochemical measurements in 0.1 M NaCl solution. Surface morphology, roughness and composition of the conversion coatings were analyzed. Protection ability of conversion coatings was tested in the salt spray chamber for 24 hours.

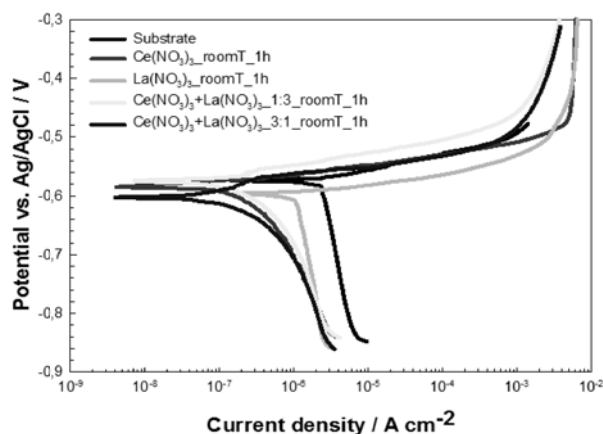


Fig.1. PD curves measured in 0.1 M NaCl for bare substrate and for substrates modified with conversion coatings prepared by immersion for 1 hour at room T.

### References

- [1] M. W. Kendig, R. G. Buchheit, Corrosion 59 (2003) 379.
- [2] R. L. Twite, G. P. Bierwagen, Prog. Org. Coat. 33 (1998) 91.
- [3] D. Zhao, J. Sun, L. Zhang, Y. Tan, J. Li, J. Rare Earths 28 (2010) 371.
- [4] T. G. Harvey, Corros. Eng. Sci. Technol. 48 (2013) 248.
- [5] T. H. Muster, H. Sullivan, et.al, Electrochim. Act. 67 (2012) 95.

## The optimization of cleaning pre-treatment of aluminium alloy AA 7075 and testing of commercial conversion coating

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Aluminum alloys are traditionally used in many industrial applications. The properties which give rise to their widespread use are: lightness, suitability for surface treatments, corrosion resistance, diversity, ease of forming, etc. Aluminum alloys series 7xxx, rich in zinc, are most commonly used in aerospace industry. Despite the fact that aluminum alloys resist corrosion well, they may not be corrosion resistant in specific environmental conditions. Chromate conversion coatings have been effective as aluminum protection against corrosion for many years. Nowadays their use is restricted because of their toxicity. Numerous studies have been focused on the development of technologies alternative to chromates. Before any kind of treatment, cleaning of metal surface to be treated, is necessary to remove inorganic and organic residues from the surface. Cleaning agents can have a role of pickling agents, detergents, degreasing agents or of corrosion inhibitors. The first part of present work aims to study the effect of cleaning of aluminum alloy of series AA 7075 with two different alkaline cleaners, first based on 0.01 M NaOH and 50% HNO<sub>3</sub> (NaOH/HNO<sub>3</sub>), and second supplied by SurTec which is based on phosphates. According to the results obtained by electrochemical method, the cleaner NaOH/HNO<sub>3</sub> causes the passivation of AA 7075, while the potentiodynamic curve of surface cleaned with SurTec is similar to pure aluminum. Results obtained by X-ray photoelectron spectroscopy (XPS) show that both cleaners remove contamination quite effectively. High resolution spectra of Al 2p show that in all samples aluminum is mostly present in its oxide state. Moreover, after both cleaning procedures, using NaOH/HNO<sub>3</sub> and SurTec, the surface of AA 7075 becomes almost superhydrophilic, while the untreated sample is hydrophilic. The concentration of elements as obtained by X-ray photoelectron spectroscopy after various surface treatments, are presented in figure below.

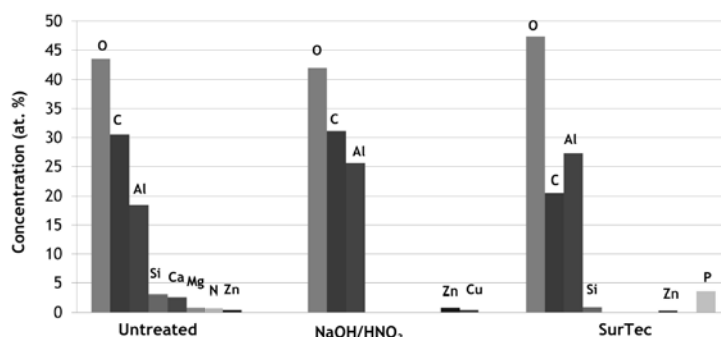


Fig.1. The concentration of elements obtained by XPS after various surface treatments: untreated, exposed to 0.01 M NaOH and HNO<sub>3</sub>, and exposed to SurTec cleaner.

The second part of the present work aims to study the corrosion protection of aluminum alloy AA 7075 by conversion coating that is already commercially used by the industry. Measurements were carried out by electrochemical polarization measurements and electron impedance spectroscopy (EIS). The obtained results will serve as the reference for our further work.

### References

- [1] C. Vargel. Corrosion of aluminum, 1st Edition, The Netherlands (2004)
- [2] S. Joshi, W. G. Fahrenhiltz, M. J. O'Keefe, Appl. Surf. Sci. 257 (2011).
- [3] B. D. Ratner, D. D. Castner, Electron spectroscopy for chemical analysis, 2nd Edition. John Wiley & sons, Ltd (2004)
- [4] E. P. Randviir, C. E. Banks, Anal. Method. 1098 (2013) 5.

## Corrosion of Zn-Mn alloy coating in carbonated concrete solution

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Zinc coating on steel rebars is often used in order to decrease corrosion rate of reinforced steel structures [1]. Being amphoteric metal, zinc is expected to corrode in fresh concrete with alkaline media, but instead, the slightly soluble corrosion product, calcium hydroxyzincate is formed, which is responsible for Zn passivation. However, in concrete exposed to carbonation, where pH is changed to around 9.5, the Zn corrosion is accelerated [2]. Recently, zinc coated steel rebars have been additionally coated with an organic coating [3].

In this work Zn-Mn alloy coating was analyzed as a potential replacement of zinc coated rebar. The aim was to optimize Zn-Mn plating parameters with respect to corrosion stability in alkaline environment, and use it as a sublayer for an organic coating deposition.

The alloy coating was obtained potentiostatically by electrochemical deposition in the range of potentials, starting from -1.6 V vs saturated calomel electrode, i.e. the onset of coating deposition. On the basis of deposition efficiency and coating homogeneity, several deposition potentials were chosen for further study. Surface morphology of freshly prepared and corroded samples was analyzed by SEM, while the alloy crystal structure was examined by XRD. Pure zinc was analyzed as a reference.

The corrosion rates of Zn and Zn-Mn alloy coatings were determined in two carbonated solutions, with different concentrations of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  anions, by electrochemical impedance spectroscopy. Results confirmed that Zn-Mn alloy coating with 16 mass% Mn, deposited at -1.8 V, showed the greatest corrosion stability.

Impedance spectra for both Zn-Mn alloy coating and zinc, in differently carbonated solutions, showed two time constants: one related to corrosion product layer and the second to substrate corrosion. The fitting results of impedance spectra, using appropriate equivalent electrical circuits, indicate that the film resistance and charge transfer resistance are higher for Zn-Mn (16 mass% Mn) coating. EDX analysis revealed that after 48 h in concrete solutions, the Mn amount on Zn-Mn surface decreased from 16 to around 3 mass%.

It can be concluded that a significant dealloying (Mn dissolution) occurs at Zn-Mn coating, but part of Mn ions form Mn oxides [4] in carbonated alkaline solution, thus producing layer of better protective properties as compared to pure Zn. This alloy coating will be further analyzed as a sublayer for organic coating.

### References

- [1] T.Bellezze, M.Malavolia, A.Quaranta, N.Ruffini, G.Roventi, Cement.Concr.Comp. 28 (2006) 246.
- [2] S.Farina, G.Duffo, Electrochim. Acta 52 (2007) 5131.
- [3] R. Selvaraj, M. Selvaraj, S.V.K. Iyer, Prog. Org. Coat. 64 (2009) 454.
- [4] B.Messaoudi, S.Joiret, M.Keddou, H.Takenouti, Electrochim.Acta 46 (2001) 2487.



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## Ultrasensitive Detection of Glycan-Protein Interactions with Electrochemical Impedance Spectroscopy (EIS)

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Glycan biosensors have become a successful tool for the detection of glycan-protein interactions. The structure of biosensors allows us to use label-free detection methods as: electrochemical impedance spectroscopy (EIS), surface plasmon resonance (SPR), atomic force microscopy (AFM), etc. The process of preparation of glycan biosensors has three basic steps: the cleaning of the sensor surface, a surface modification with functional groups contained self-assembled (mono) layers (SAM) and the immobilization of glycans.<sup>1</sup> Most common used surface is a gold, because it can be easily modified with thiol molecules.<sup>2</sup> The length, presence of functional groups and the structure of thiols can define operational features of a biosensor. Shorter thiols are often used for the dilution of SAM, longer thiols with different functional groups can be utilized for different immobilization techniques and functional groups as –OH, ethylene glycol or betain can differently avoid non-specific interactions.<sup>3</sup> Functional groups can also affect the density and the organization of SAM layer. EIS as a sensing method was chosen because it can offer analysis in an ultrasensitive way i.e. single molecule level detection limits can be achieved.<sup>4</sup>

The mixture of 11-mercaptoundecanol and 6-mercapto-1-hexanol was used to create a functional glycan biosensor which is able detect lectins and viral hemagglutinins at aM ( $10^{-18}$  M) level, what is currently the lowest detection limit achieved for EIS-based glycan biosensor. Glycans with terminal sialic acid were immobilized onto surface via amine coupling. EIS, AFM and SPR were used to study interactions between the biosensor and lectins (MAA, DSL) and hemagglutinins from avian and human influenza virus. Moreover, we were able to visualize individual glycan molecules with width of 0.9 nm and length of 1.8 nm by AFM.

### References

- [1] Hushegyi and J. Tkáč, *Anal. Methods* 6 (2014) 6610.
- [2] J. Tkáč, T. Bertók, J. Nahálka and P. Gemeiner, *Methods Mol Biol.* 421 1200 (2014) 421.
- [3] T. Bertók, L. Kluková, A. Sediva, P. Kasák, V. Semak, M. Micusik, M. Omastova, L. Chovanová, M. Vlček, R. Imrich, A. Víkartovska and J. Tkáč, *Anal. Chem.* 85 (2013) 7324.
- [4] E. Paleček, J. Tkáč, M. Bartošík, T. Bertók, V. Ostatná, J. Paleček, *Chem. Rev.* (2015), DOI: 10.1021/cr500279h.

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## Graphene-Based Lectin Biosensor as a Promising Tool for Glycans Analyses

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Graphene is a term used for description of a 2-dimensional (2D), one-atom-thick layer of carbon, consisting of sp<sup>2</sup>-hybridized carbon atoms with regular hexagonal configuration. Its discovery in 2004 caused a revolution in the field of nanotechnology and graphene gained worldwide attention thanks to its unique features. Exceptional electron transfer, thermic, optical and mechanical properties, make graphene a very interesting material for many applications, including lectin biosensors.

It is a well-known fact that various pathophysiological conditions result in an increased concentration of specific substances (biomarkers) in blood or blood serum. Some biomarkers may carry on their surfaces characteristic saccharides (glycans), which may have a different structure comparing to normal (healthy) physiological condition. This means, that glycan profiling can distinguish between healthy and sick individuals, and, in some cases, even determine the stage of the disease.

Lectins are proteins with high affinity towards saccharidic structures, hence they play an important role in profiling of altered glycoform of biomarkers. Moreover, they can be also applied in the process of discovering new (potential) biomarkers

Glycoprofiling of biological samples is relatively demanding and often requires complex instrumentation. Besides this, many of currently used methods involve labelling or fragmentation of target molecules, which can eventually influence whole analysis. Contrary to this, electrochemical methods provide very sensitive, rapid a simple analysis of intact glycoproteins in real samples, without the need of labelling, which makes them an attractive tool for biosensor construction and optimization. Furthermore, in association with unique graphene features and lectin specificity, electrochemical methods bring a promising vision in the field of glycoprofiling.

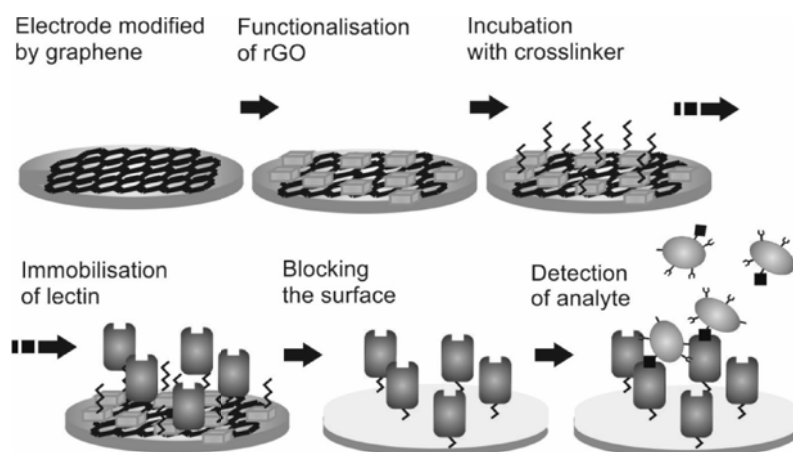


Fig.1. Construction of graphene-based lectin biosensor.

**Acknowledgement:** The financial support from the Slovak research and development agency APVV 0282-11 is acknowledged. The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013)/ERC Grant Agreement No. 311532.

**Gold Nanoparticles-Modified Physically Small Carbon Sensors towards Sensitive and Selective As (III) Detection in Aquatic Samples**

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*WITHDRAWN*

## Stability and durability of gas diffusion ORR electrodes for HT - PEFC

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High temperature polymer electrolyte fuel cells (HT-PEFC) based on phosphoric acid doped polybenzimidazole type membranes are considered as alternative power source for airplanes, trains, ships and other transport and stationary applications, especially when reformat gas is used. On the one hand the high operating temperature (160°C – 200°C) ensures increased tolerance to CO compared to the PEMFC working in the temperature range up to about 80 °C. On the other hand, the more severe working conditions including the highly aggressive phosphoric acid which serves as electrolyte impose the need for increased corrosion resistance in order to reach long term stability of all system components (catalysts, electrodes, current collectors, bipolar plates, etc.). The reliable performance of the HT-PEFC membrane electrode assembly (MEA) requires also a constant amount of phosphoric acid in the MEA which depends to a great extent on the type of gas diffusion electrodes (GDE) used. In the present work anode GDE for HT-PEFC with a catalytic loading of 1 mg cm<sup>-2</sup> were prepared and optimized in regard to porosity, active surface area, and performance through variations in the electrodes sintering regime. The catalyst was a commercial product (Pt/C 20% wt., Johnson Matthey HISPEC 2000). It was mixed with polytetraethylene (Denyon PTFE) emulsion serving as binder and spread over a non-woven GDL with a microporous layer (Freudenberg H2315). The prepared samples were thermally treated in order to change the pore structure and crack size of the catalyst layer influencing the electrochemically active surface area. The electrochemical stability and catalytic utilization were investigated by cyclic voltammetry, polarization curves, and impedance measurements. A series of surface and bulk analysis (XRD, SEM, EDX, TGA, etc.) were performed to characterize the morphology and the electrochemical surface of the electrodes before and after 460 hours operation at a constant current density of 0.2 A.cm<sup>-2</sup>. It was found that in all samples the catalyst particles agglomerate during operation. The GDE treated at 320 °C demonstrated superior catalytic utilization and highest stability without degradation for the whole test duration.

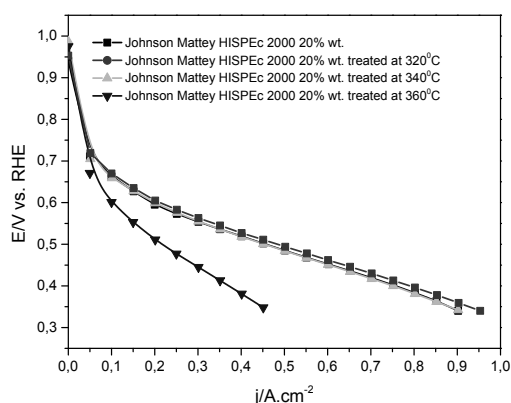


Fig. 1: HT-PEMFC performance of MEA with Pt/C anodes sintered at different regimes; scan rate 1 mV s<sup>-1</sup>; test temperature 160 °C

## Development of a New Amperometric Sensor for L-Cysteine and 2,5-Dimercapto-1,3,4-Thiadiazole Based on Carbon Electrode Modified with Sodium Dichloro-Bis[*N*-Phenyl-5-Bromosalicylideneiminato-*N,O*]Ruthenate(III) Complex

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The thiol residues of L-cysteine and 2,5-dimercapto-1,3,4-thiadiazole and other low molecular mass thiols are readily oxidized in electrochemical reaction on the surface of various thiol sensitive electrodes. For electrochemical detection of thiols the major problem related with high over potential required at most conventional electrode surfaces, thus the use of chemically modified electrodes has been proposed for amperometric detection thiols at low applied potentials.

The aim of this work is to develop a new sensor and optimize the method for determining thiol compounds: L-cysteine and 2,5-dimercapto-1,3,4-thiadiazole in real samples.

A new low-potential amperometric sensor for L-cysteine and 2,5-dimercapto-1,3,4-thiadiazole based on glassy-carbon electrode modified by a water insoluble redox mediator sodium dichloro-bis[*N*-phenyl-5-bromosalicylideneiminato-*N,O*]ruthenate(III) complex. FIA (Flow-Injection Analysis) amperometric measurements for two thiol compounds was performed at the operating potential of 150 mV v.s. Ag/AgCl reference electrode for L-cysteine and 200 mV v.s. Ag/AgCl reference electrode for 2,5-dimercapto-1,3,4-thiadiazole in 0.1 M phosphate buffer, pH 7,4 and 8 with flow rate 0,20 mL/min. The modified electrode shows a fast electric response for L-cysteine and 2,5-dimercapto-1,3,4-thiadiazole oxidation showing good reproducibility and stability. The sensor was tested in the range of 3-9 pH.

Linearity between concentration of L-cysteine (pH 8) and signal exists from 5-125 mg/L, with a correlation coefficient over 0.99. The detection limit ( $3\sigma$ ) for L-cysteine for pH 8 is 0,12 mg/L (or  $9,9 \cdot 10^{-4}$  mmol/L). Linearity between concentration of L-cysteine (pH 7,4) and signal exists from 0,5-100 mg/L, with a correlation coefficient over 0.99. The detection limit ( $3\sigma$ ) for L-cysteine for pH 7,4 is 0,26 mg/L (or  $2,1 \cdot 10^{-3}$  mmol/L).

Linearity between concentration of 2,5-dimercapto-1,3,4-thiadiazole (pH 8) and signal exists from 25-500 mg/L, with a correlation coefficient 0.99. The detection limit ( $3\sigma$ ) for 2,5-dimercapto-1,3,4-thiadiazole for pH 8 is 0,62 mg/L (or  $4,13 \cdot 10^{-3}$  mmol/L). Linearity between concentration of 2,5-dimercapto-1,3,4-thiadiazole (pH 7,4) and signal exists from 20-100 mg/L, with a correlation coefficient 0.98. The detection limit ( $3\sigma$ ) for 2,5-dimercapto-1,3,4-thiadiazole for pH 7,4 is 0,45 mg/L (or  $2,99 \cdot 10^{-3}$  mmol/L).

Nowadays, sensor research, an ever expanding field of analytical chemistry, has been attracting scientists for many related disciplines such as biology, material sciences etc. Chemical sensors are offering alternative solutions, capable of satisfying the increasing demand for precise and fast analytical information through devices that require relatively simple instrumentation.

### References

- [1] Salimi A., Pourbeyram S., *Talanta* 60 (2003), 205-214.
- [2] Drozd R., Naskalski J., Zabek-Adamska A., *Acta Biochimica Polonica*, 54 (2007), 205-212.
- [3] Ferreira Vitoreti A. B., Abrahao O., Silva Gomes R.A., Salazar-Banda G. R., Olivera R. T. S., *Int. J. Electrochem. Sci.*, 9 (2014), 1044-1054.
- [4] Kahrović E., Dehari S., Dehari D., Reci H., Begić S., Ljubijankić N., *Technics Technologies Education Management* 5/4 (2010), 799-803.
- [5] Kahrović E., Turkušić E., Ljubijankić N., Dehari S., Dehari D., Bajsmán A., *Health. MED.*, 2012, 6/2, 699-702.



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## Physically-Based Impedance Simulation to Decouple Convolved Transport and Reaction Phenomena in SOFC Cathodes

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A mechanistic model, based on mass and charge conservation equations [1], is presented for the physically-based simulation of impedance spectra in composite solid oxide fuel cell cathodes, taking into account the complex interaction between transport and reaction phenomena. The impedance simulation, which reproduces the same procedure used in laboratory frequency response analyzers, allows the de-convolution of distinct elementary processes and the identification of a specific double layer chemical capacitance, describing the possible accumulation of adsorbed species and reaction intermediates at the interface between electron-conducting and ion-conducting particles. The satisfactory agreement of simulated spectra with experimental data for different operating conditions and electrode thicknesses reveals that the model is capable to reproduce the transient behavior of composite electrodes by relying on only one fitted parameter. Model simulations show that mass-transfer processes within the electrode produce a resistive contribution in the impedance spectra related to the effect of the local oxygen partial pressure on the reaction kinetics. In addition, the pores act as a buffer for molecular oxygen, leading to a capacitive contribution in the frequency range 102-104Hz, more pronounced at high current densities.

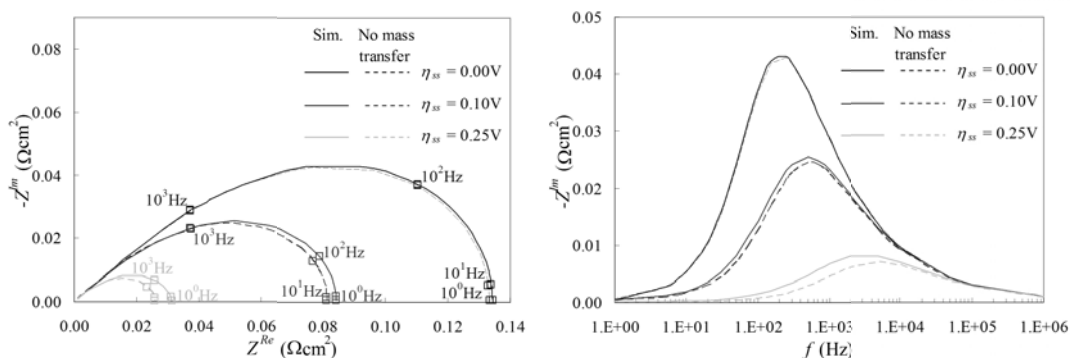


Fig.1. Equivalent circuit and complex-plane impedance diagram of an adsorption model.

### References

- [1] A.Bertei, B. Nucci, C. Nicolella, Chem. Eng. Sci. 101 (2013) 175.

## Advanced Electro-Catalysts and Membranes for Proton Exchange Membrane Water Electrolysis

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The interest in water electrolysis has recently increased with the large diffusion of renewable energy sources and the perspective to produce hydrogen with a very low environmental impact [1-2]. In this regard, hydrogen appears a promising energy carrier that can be produced by cost-effective electrolysis of water using renewable energy sources and it can be used to store energy in grid-balancing services. A challenging problem to the development of such process is the substantial energy loss associated with the oxygen evolution during electrochemical water splitting and ohmic losses. High surface area nanostructured electro-catalysts and highly conductive membranes can substantially reduce such losses allowing to achieve efficient hydrogen production with good perspectives for a wide scale decentralised hydrogen production. IrOx and IrRuOx nanosized materials of similar crystallite size (mean size 5 nm) were prepared for application as oxygen evolution electro-catalysts in solid polymer membrane water electrolyzers (PEMWEs). These materials have been investigated in combination with novel short side chain membranes (Aquivion®).

The physico-chemical properties of the catalysts were characterized by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray (EDX) and X-ray-Photoelectron Spectroscopy (XPS). Particular efforts were addressed to tailor the crystallographic characteristics and the surface properties. The electrochemical properties were investigated in an electrolysis cell, based on Nafion® or Aquivion® perfluorosulfonic membranes and 30% Pt/C as cathode catalyst. Linear sweep voltammetry, electrochemical impedance spectroscopy and Tafel curves were used to assess the membrane-electrode assemblies. The IrRuOx-based electro-catalyst showed a performance better than  $3 \text{ A cm}^{-2}$  at 1.8 V at 90°C in combination with the Aquivion® membrane. The present study indicates that mixed-oxide catalysts in combination with Aquivion® can be very appropriate to enhance the PEM water electrolysis process.

### Acknowledgement

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### References

- [1] S. Siracusano, N. Van Dijk, E. Payne-Johnson, V. Baglio, A.S. Aricò, *Applied Catalysis B: Environmental*, 164 (2015) 488.
- [2] A.S. Aricò, S. Siracusano, N. Briguglio, V. Baglio, A. Di Blasi, V. Antonucci, *Journal of Applied Electrochemistry*, 43 (2013) 107.

## Electrochemical Lithiation of Thin Silicon Based Layers Potentiostatically Deposited from an Ionic Liquid

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The development of thin-film and micro batteries based on Li ion technology established a further main direction for the progress of the electrochemical energy storage. Due to their narrow geometry, a space and shape optimization of the batteries is required. Therefore, deposition of stable and thin layers is a promising approach for attaining simultaneously the required geometry and high energy density [1,2]. In the current work, deposition of thin silicon based layers on copper substrates was performed by potentiostatic electroreduction from 1 M SiCl<sub>4</sub> in 1-butyl-1-methyl-pyrrolidinium bis (trifluoromethyl) sulfonylimide [BMP][TFSI] ionic liquid (IL). The electrodeposition process was investigated by means of voltammetric techniques, coupled with in-situ microgravimetry (quartz crystal microbalance, QCM). Considerable impact of side reactions parallel to the deposition process was indicated by QCM measurements performed under potentiostatic and potentiodynamic conditions. SEM imaging showed a compact and uniform globular morphology of the layers with thickness of about 1 μm. The deposition of silicon-based films was confirmed by energy dispersive X-ray analysis (EDX).

Precise investigations of the chemical composition of the deposit and its elemental distribution were achieved by means of X-ray photoelectron spectroscopy (XPS) depth profiling. The analysis suggests a major contribution of Si, C and O during the electrodeposition process, whereas N and F are present in lower amounts. The distribution of Si, O, C, N and F throughout the film is nearly constant at levels of ~50 at. % for Si, ~20 at. % for O, ~20 at. % for C, ~2 at. % for N and ~1 at. % for F. The absence of [TFSI]<sup>-</sup> anions related signals in the C1s and N1s spectra points to a fragmentation of the [TFSI]<sup>-</sup> anions at the electrode, resulting in incorporation of oxygen, carbon, nitrogen and fluorine into the growing film. The [BMP]<sup>+</sup> cations are more stable and remain accumulated at the surface.

The electrodeposited layers showed stable galvanostatic cycling reaching capacity values of about 1200 mAh g<sup>-1</sup> and 80% capacity retention after 300 cycles in standard Li<sup>+</sup> electrolytes. The specific discharge capacities obtained in a carbonate based electrolyte are comparable [3,4] or even superior [5] to already reported ones. The effective preservation of the structural integrity of the layer during electrochemical cycling can be related to incorporation of side organic products caused by IL decomposition, acting as mechanical buffer against strain accumulation. In ionic liquid media, the material displayed a lower capacity of 500 mAh g<sup>-1</sup>. The galvanostatic discharge transient showed a considerable inhibition of the de-lithiation process, evidenced by a polarization of more than 170 mV. The observed difference in the anodic potential profiles can be related to the influence of the additional passivating products deposited during the charging process and a hindered Li<sup>+</sup> transport into the bulk due to the significant viscosity of the ionic liquid.

### References

- [1] D. Golodnitsky, V. Yufit, M. Nathan, I. Shechtman, T. Ripenbein, E. Strauss, S. Menkin, E. Peled, *Advanced materials for 3D microbattery*, *J. Power Sources* 153 (2006) 281–287;
- [2] M. Nathan, *Microbattery technologies for miniaturized implantable medical devices*, *Curr. Pharm. Biotechnol.* 11 (2010) 404–410.
- [3] R. Epur, M. Ramanathan, F.R. Beck, A. Manivannan, P.N. Kumta, *Electrodeposition of amorphous silicon anode for lithium ion batteries*, *Mater. Sci. Eng. B.* 177 (2012) 1157–1162.
- [4] H. Nara, T. Yokoshima, T. Momma, T. Osaka, *Highly durable SiOC composite anode prepared by electrodeposition for lithium secondary batteries*, *Energy Environ. Sci.* 5 (2012) 6500 – 6505.
- [5] T. Hang, H. Nara, T. Yokoshima, T. Momma, T. Osaka, *Silicon composite thick film electrodeposited on a nickel micro-nanocones hierarchical structured current collector for lithium batteries*, *J. Power Sources.* 222 (2013) 503–509.

## Production of Energy from Marine Water by Sulfide-Driven Fuel Cell

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The present work is directed to two simultaneous goals: first, remediation of the severe environmental situation in the Black Sea waters, and next, to produce “carbon-free” energy. It is based on the opportunity to recover energy from the hydrogen sulfide in the Black Sea deep waters. The thermodynamic analysis shows that the energy recovery of the latter is an energy alternative to the natural gas used in the coastal countries. This technology has a goal the utilization of the energy, conserved in the hydrogen sulfide as well as of other compounds contained in the deep marine water.

It is based on new design of a fuel cell, enabling the oxidation of sulfide to sulfate in order to attain high electromotive force. The proposed technology consists of the following steps: pumping of the water from depths where the sulfide concentration is relatively high; enrichment of the pumped water to attain higher concentrations of sulfide and to enhance the next step: generation of sufficiently high electromotive force (EMF) in a new designed fuel cell operating by catalytic sulfate oxidation by oxygen. This EMF can be employed for hydrogen production by electrolysis.

Experiments with sulfide containing aqueous solutions were carried out. Different factors with impact on the fuel cell performance have been studied: sulfide concentrations (from 10 to 1000 mg m<sup>-3</sup>), pH of the media, operation electrochemical conditions, flow pattern and cell design. Sodium chloride, model saline water as well as genuine Black Sea water pumped from up to 1000 meters depths were used as supporting electrolyte. Different catalysts (cobalt spinel, zirconia) embedded in the electrodes were tested. Carbon electrodes (felt, graphite, etc.) were studied as anodes. Gas diffusion electrodes as well as graphite electrodes operating in saline water blown by air or oxygen were used as cathodes in the new designed fuel cell. Five different ion-exchange membranes were tested. Kinetic studies in batch and continuous stirred tank reactor have been carried out.

The electrochemical processes are sensitive to the sulfide concentrations and the associated pH of the tested solutions. At higher sulfide concentrations the governing reactions are mostly formation of polysulfides, thiosulfate, dithionate, etc. The straightforward oxidation of sulfide to sulfite and sulfate was favored at lower sulfide concentrations and in presence of cobalt spinel and zirconia as catalyst. It was established, that under certain conditions the fuel cell efficiency, based on the created electro-motive force may lead to 80-90% depending on the electrochemical reactions taking place within it. These results were tested and verified in a pilot-scale experiment carried out on a ship in the Black Sea using genuine marine water containing sulfide.

Our future plans are to enhance the current density and the power density to values of importance for practical applications.

**Acknowledgement:** *This work was accomplished within the project HYSULFCEL supported by the program BS-ERA.NET (FP7 of the European Union), Pilot Joint Call 2010/2011 of the Ministry of Education, Youth and Science (contract DNS7RP 01/32/2011), Republic of Bulgaria.*

## Simple Integration of Nanomaterials with Biocatalysts for Clean Electricity Generation

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In recent decade, nanomaterial-based biosensors and biofuel cells (BFCs) have gained significantly increased attention. These devices are based on electron exchange between biocatalysts (purified enzymes or enzymes in whole microbial cells) and the surfaces on which they are immobilized. “Bioelectrodes” fabricated in this way are able to transform chemical energy of substrate(s) relevant for the used biocatalyst(s) into electricity. Application of nanomaterials in these systems does not only promote the rate of these reactions and charge transfers. It also helps to increase an amount of biocatalytic units per geometric area of electrode surface and thus improve significantly the performance of BFCs [1].

Since there are reports on efficient but rather complex methods of preparation nanomaterial/biocatalyst interfaces, we have focused on development of less expensive and more time-saving protocols for integration of either microbial or enzymatic biocatalysts with diverse nanomaterials. Our findings include composites of ethanol-oxidizing *Gluconobacter oxydans* (GbO) cells with diverse nanoparticles prepared by simple mixing of the two components and mild ultrasound treatment. Expensive carbon nanotubes were replaced with much cheaper carbon black with only minor loss of performance of the prepared microbial bioanode [2]. Recent experiments also suggest that graphene oxide (GO) – a “Nobel prize nanomaterial” – can be also employed in the same way. Furthermore, when GO was employed, we observed that bacteria were able to certain rate of exchanging of electrons with electrode surface (via the surrounding nanoparticles) without any electron mediator needed. Influence of GO sheet size and other GO properties and conditions of composite preparation this phenomenon is now under the testing.

Bilirubin oxidase (BOD) is a “multicopper oxidase” enzyme with cuprous active sites where electrons from oxidized substrate or electrode surface are utilized in reduction of dioxygen at high potential [3]. These features make BOD a perfect candidate for biocatalyst securing the final step in electricity generation in BFCs, i.e. passing electrons on the final electron acceptor. Adsorption of BOD on carbon black dispersed in hydrophobic fluorinated polymers, as reported by other scientist, was found to be very effective method of BOD-based biocathode fabrication, but this approach can be modified in more “ecofriendly” and cheaper version by using biopolymers (chitosan or poly(lactic acid)) as dispersing agents. Furthermore, some interesting features of electron exchange between BOD and electrodes were revealed when the enzyme was adsorbed on carbon black dispersed in biopolymers, i.e. electrochemical transformation of all three enzymatic redox sites [4, 5]. Another inexpensive and intriguing way of effective BOD application is its simple adsorption on GO sheets. After collection of the formed composite, deposition on an electrode surface and electrochemical reduction of GO, biocathodes were prepared with current densities as high as 0.28 mA cm<sup>-2</sup> observed in air-bubbled buffer, without any additional stirring or mediator used [6].

Obviously, there is a space for significant simplification of integration of biocatalysts and nanomaterials as well as for employment of cheaper materials. Hopefully, this approach will be another step in development of affordable commercial biofuel cells.

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### References

- [1] J. Filip, J. Tkac, *Electrochim. Acta* 136 (2014) 340.
- [2] J. Šefčovičová, J. Filip, J. Tkac, *Chem. Pap.* 69 (2015) 176.
- [3] S. Shleev, J. Tkac, A. Christenson, T. Ruzgas, A.I. Yaropolov, J.W. Whittaker, L. Gorton, *Biosens. Bioelectron.* 20 (2005) 2517.
- [4] J. Filip, R. Monosik, J. Tkac, *Int. J. Electrochem. Sci.* 9 (2014) 2491.
- [5] J. Filip, J. Tkac, *Bioelectrochem.* 96 (2014) 14.
- [6] J. Filip, J. Tkac, *Electrochem. Commun.* 49 (2014) 70.

### 3-D Atomistic Modeling: Dealloying of Bimetallic Alloys

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Fuel cells have emerged as a very promising substitute for selected conventional energy conversion technologies (e.g. internal combustion engine). To some extent, carbon-supported Pt alloy catalysts have fulfilled the expectation when used in contemporary PEM (proton exchange membrane) 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. In search of deeper understanding of this process we performed atomistic modeling which not only explained degradation behavior but also gave us the answer how to prevent it. Model was verified with many state of the art techniques and was in good agreement with experimental results. Thus, we could also use it to design a new generation of catalysts.

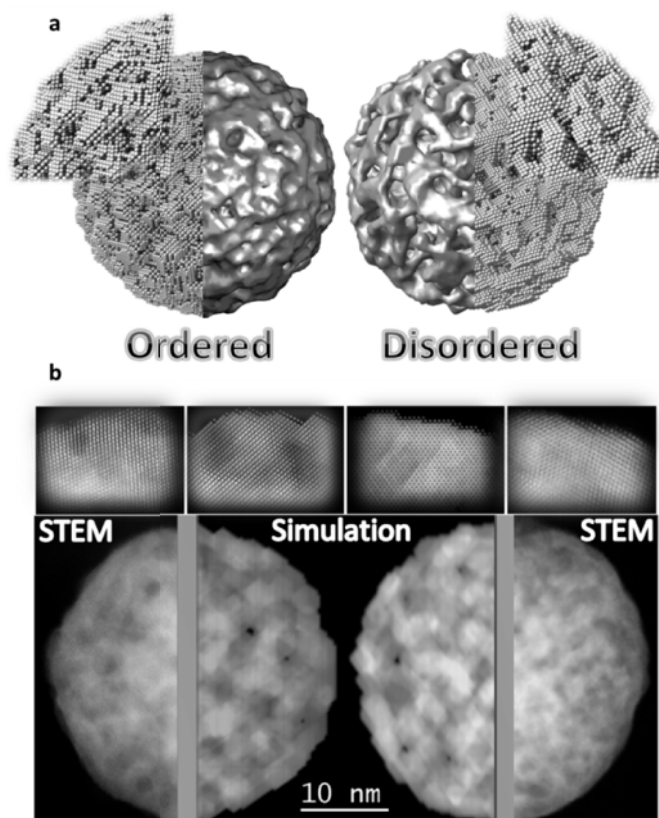


Fig. 1. Disordered ( $Fm\bar{3}m$  crystal structure throughout) and ordered ( $Pm\bar{3}m$ -shell and  $Fm\bar{3}m$ -core crystal structure) particles after acidic treatment: (a) Simulated ordered particles (left) at the tipping point of pore creation and disordered particle (right) with fully developed porosity, taken at the same time. (b) Experimental and simulated HAADF/STEM images of ordered (left) and disordered (right) ~30 nm particles after 12 h in 0.1 M HClO<sub>4</sub> (in the upper row are presented close-up atomic resolution images of below particles edges).

#### References

- [1] J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, Nature, 410 (2001) 450–453.
- [2] McCue, J. Snyder, X. Li, Q. Chen, K. Sieradzki, J. Erlebacher, Phys. Rev. Lett., 108(2012)1-5.
- [3] Pavlišič, P. Jovanovič, V. S. Šelih, M. Šala, N. Hodnik, S. Hočevar, M. Gaberšček, Chem. Commun. (Camb), 50(2014)3732–4.

## Kinetic Mechanism That Influence the Electrochemical Behaviour of Different Type of Cathodic Materials for Intermediate Temperature Solid Oxide Fuel Cells

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Since long time perovskite-type cathodic materials have attracted attention as cathodes for intermediate-temperature solid oxide fuel cells (500-700 °C), because of the high catalytic activity for oxygen reduction reaction.

However, a delicate match between high electrocatalytic activity and long lasting electrochemical and structural properties is still an open issue for good performing SOFCs electrodes and cells.

The study presented in this paper will analyse the results obtained on this field by the authors since several years of research activity considering three types of basic materials ( $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$  –LSM,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  –LSCF, and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  -BSCF) in different electrode configurations; pure materials, composite and impregnated electrode formulations.

The aim of this research is to elucidate how the intrinsic material properties can affect the kinetic rate determining step within the complex overall reaction mechanism of oxygen reduction. The evidence of these phenomena is highlighted through the electrochemical response of the considered systems operating under different conditions determined by applied overpotentials, reactant partial pressures and temperatures.

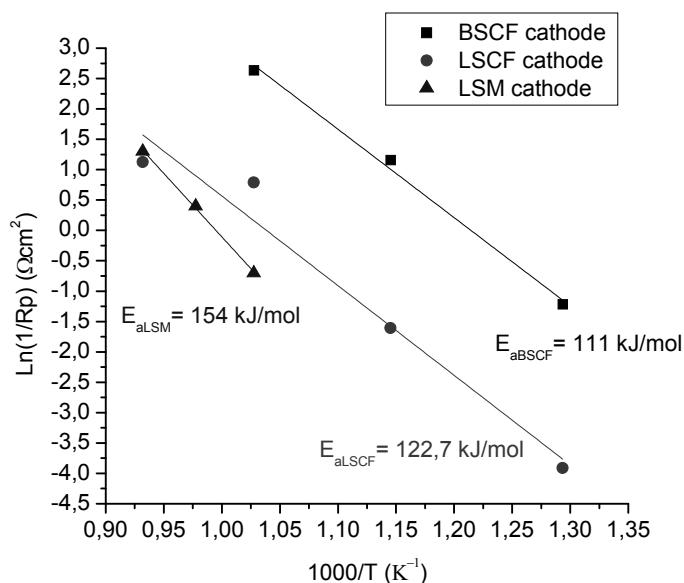


Fig.1. Arrhenius plot, kinetic activity and activation energy of LSM, LSCF and BSCF materials

### References

- [1] Deganello F., Liotta L.F., *Mater Renew Sustain Energy* 2013, 2:8, 2-14
- [2] Ried P., Holtappels P. et al., *J Electroch Soc* 2008, 155:10, B1029-B1035
- [3] S. B. Adler, Factors Governing Oxygen Reduction in Solid Oxide Fuel Cell Cathodes, 2004.

## Supercapacitors Based on Polypyrrole/Carbon Nanotubes Composites

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Electrochemical capacitors have raised great interest because of their high power density, fast charging/discharging rate and excellent long-term cyclability. There is a number of electrode materials being developed for electrochemical capacitors. New trends for supercapacitors development are connected with application of materials such as conducting polymers, with pseudocapacitance properties [1]. However, conducting polymers present some drawbacks (e.g. poor stability during cycling). On the other hand, carbon nanotubes could provide good charge propagation and can be used as a support and an additive for different composite electrode materials [2,3].

The properties of polypyrrole/carbon material composites as electrode materials for supercapacitors are discussed. Composites with different kinds of multi-walled carbon nanotubes (the commercial ones and those obtained by catalytic decomposition of acetylene) and polypyrrole were prepared. The morphology of the composites were observed by SEM and TEM. The electrochemical measurements were carried out using cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy. The composites were tested in 1 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte using two- and three-electrode Swagelok® systems.

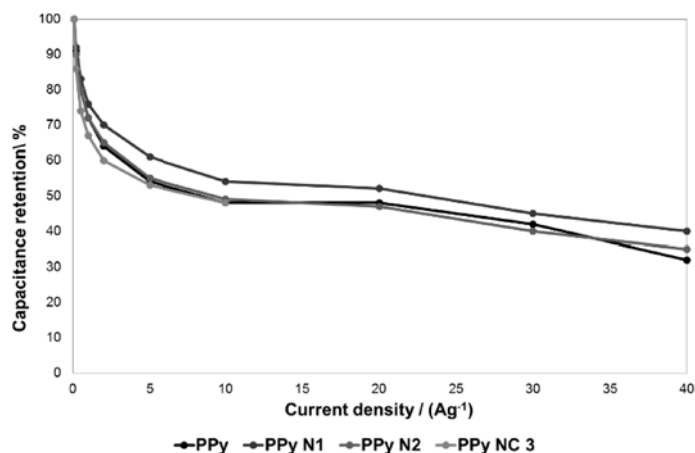


Fig.1. The electrochemical capacitance performances of PPy and PPy composites.

Carbon nanotubes can play a role of conducting support for homogenous distribution of pseudocapacitive components in the composite and can protect conducting polymers from mechanical changes during cyclic charging/discharging. The results showed that addition of only few percent of carbon nanotubes to polypyrrole provided the highest value of capacitance during high current regimes. It could confirm the fact that such amount of carbon additive is optimal to take advantage of both components of the composite, and the latter can be a good solution as a negative electrode in asymmetric configuration.

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### References

- [1] Y. Zhang, H. Feng, X. Wu, L. Wang, A. Zhang, T. Xia, H. Dong, X. Li, L. Zhang, *Int. J. Hydrogen Energy* 34 (2009) 4889.
- [2] H. Pan, J. Li, Y. P. Feng *Nanoscale Res Lett* 5 (2010) 654.
- [3] G. A. Snook, P. Kao, A. S. Best *J. Power Sources* 196 (2011) 1.

## Evaluation of Polyethylene Separators Influence on Charge Acceptance of Negative Plates of Lead-Acid Batteries

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Battery separators are complex multi-component membranes that dictate the mechanical and electrical performance of the battery. A separator is a material that is inserted between the positive and negative plates of the cell to prevent short circuiting. Materials for flooded lead-acid battery separators typically include porous derivatives of cellulose, polyvinyl chloride (PVC), organic rubber and polyolefins.

Microporous polyethylene (PE) lead-acid battery separators are commonly used because of their ultrafine pore size, which inhibits “dendritic” growth of metallic deposits (a short circuit risk), while providing low electrical resistance. Besides, PE separator material is characterized by high puncture strength, good oxidation resistance, and excellent flexibility.

PE separators for lead–acid batteries have traditionally been produced by extrusion and subsequent extraction of a calendered sheet from a multi-component mixture of ultrahigh molecular weight polyethylene (UHMWPE), precipitated silica, process oil, pore formers, surfactants, and anti-oxidant. The chemical composition and the amount of above listed substances can all play a role in the electrical, mechanical and oxidation resistance of the separator. During operation and throughout the service life of a lead-acid battery, the microporous polyethylene separator is exposed to a strong oxidizing environment of concentrated sulfuric acid, oxygen and hydrogen gases, and high temperatures.

A set of organic substances are usually added to the separator to enhance the oxidation stability or to capture metallic ions which may act as hydrogen evolution catalysts.

The aim of present investigation is to evaluate the influence of a new PE separator additive on the charge/discharge performance of the negative plates in a lead acid battery. Two types of separators are investigated, denoted as control (without additive) and new separator with experimental additive, respectively. The basic hypothesis is that some organic species are released from the separator and are slowly adsorbed on the surface on the negative plate aggravating the charge reaction on the lead surface or stabilizing lead sulfate. Therefore, we will try to accelerate the release of the organic substance by raising the temperature and increasing as much as possible the quantity of separator relative to the volume of electrolyte.

The test cell used comprises a flat pure lead working electrode and two symmetrically placed pure lead counter electrodes. All electrodes are enveloped in separators of the respective type, without additive or with additive. The separator to electrolyte ratio is about 3 times higher than that in a real battery. The electrolyte is sulfuric acid artificially enriched with separator leachate.

Linear sweep voltammetry measurements are conducted to characterize the behavior of the Pb electrodes between the hydrogen evolution and oxygen evolution reactions. Potentiostatic reduction experiments are performed to test the reactivity of lead sulfate deposits. X-ray diffraction analysis and scanning electron microscopy are used to characterize the surface of the electrodes.

## Impedance Aspect of Graphite and Glassy Carbon Electrodes in Redox Electrolyte

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Presence of a redox system in electrolyte solution is generally considered valuable in the field of electrochemical capacitors and supercapacitors, where fast redox reaction coupled with already high electrode (pseudo)capacitance is requested for a device with improved charge storage properties [1,2]. Within this area, electrochemical characterization has usually been made by cyclic voltammetry and galvanostatic charging/discharging techniques and in much less extent by electrochemical impedance spectroscopy, EIS. Here, analysis will be presented of some experimental EIS results (Fig. 1) of unmodified graphite, G, and glassy carbon, GC, electrodes in  $\text{H}_2\text{SO}_4$  electrolyte solution and in the same solution containing  $\text{K}_4\text{Fe}(\text{CN})_6$ . In this condition, negatively charged ferro-ferri cyanide complex ions would undergo the one electron redox reaction:  $\text{Fe}(\text{CN})_6^{4-} \leftrightarrow \text{Fe}(\text{CN})_6^{3-} + e^-$ .

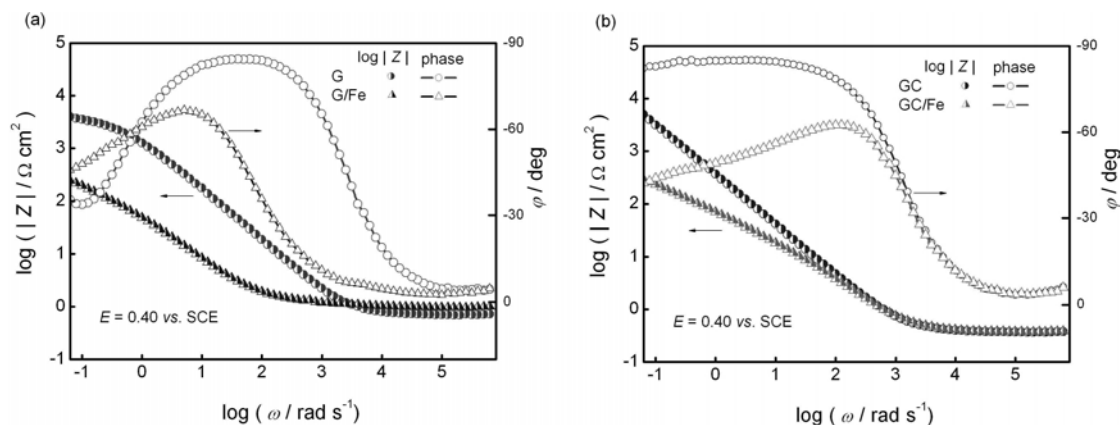


Fig. 1. Bode plots of: (a) graphite and (b) glassy carbon electrodes in  $0.5 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$  and in  $0.5 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4 + 0.5 \times 10^{-3} \text{ mol dm}^{-3} \text{K}_4\text{Fe}(\text{CN})_6$ .  $E = 0.40 \text{ V}_{\text{SCE}} = E^0 [\text{Fe}(\text{CN})_6^{3-/4-}]$ .

Fig. 1 shows that for both electrodes, more (GC) or less (G) expressed capacitive impedance responses, characteristic for blocking electrodes and measured in pure  $\text{H}_2\text{SO}_4$  electrolyte are in presence of  $\text{K}_4\text{Fe}(\text{CN})_6$  in  $\text{H}_2\text{SO}_4$  electrolyte changed to the impedance response characteristic for almost reversible redox reaction with semi-infinite diffusion of electroactive species [3]. Here, difference between G and GC electrode impedance response is perceivable at higher frequencies, where prominent shift of capacitive impedance curve, *i.e.* enhancement of electrode capacitance, is obtained for G vs. GC electrode. This clear pseudo-capacitive contribution of redox reaction can be interpreted as certain extent of electrolyte retention [4] within unmodified and inherently macroporous G surface vs. unmodified and almost flat GC electrode surface [5].

### References

- [1] B.E. Conway, *Electrochemical Supercapacitors: Scientific fundamentals and technological applications*. Kluwer/Plenum Pub., New York. 1999.
- [2] B.Akinwolemiwa, C. Peng, G.Z. Chen, *J. Electrochem. Soc.*, 162 (2015) A5054–A5059.
- [3] M. Sluyters-Rehbach, J.H. Sluyters, *Sine wave methods in the study of electrode processes*. M. Dekker, New York. 1970.
- [4] R. Narayanan, P.R. Bandaru, *J. Electrochem. Soc.*, 162 (2015) A86–A91.
- [5] K. Magdić, V. Horvat-Radošević, K. Kvastek, *Electrochim. Acta*, 117 (2014) 310–321.

## **Influence of Working Parameters on Anode-Supported Cells studied by Electrochemical Impedance Spectroscopy**

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Electrochemical Impedance Spectroscopy (EIS) is one of the most common techniques to characterize Solid Oxide Fuel Cells (SOFCs) during operation and to evaluate the influence on their performances of several working conditions and degradation effects. However the processes overlap in the frequency domain makes difficult to clearly distinguish each cell contribution and to understand the impedance spectra. This becomes even more challenging when complete SOFCs are under investigation.

In this work a state of the art anode-supported cell has been characterized by means of current-voltage curves and EIS under several working conditions. A preliminary investigation consisting in varying the electrodes gases compositions and flows allowed to identify the corresponding processes on the impedance spectra. Afterward, the evolution of such contributions has been studied at the Open Circuit Voltage (OCV) varying the cell working temperature in the range 700-800°C and applying electrical loads up to 1 Acm<sup>2</sup>. Post-experiment analyses have been carried out to support the electrochemical observations.

### **Acknowledgments**

The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) Fuel Cells and Hydrogen Joint Undertaking (FCH-JU-2013-1) under grant agreement No 621207.

## Anodic Deposition of PbO<sub>2</sub> on Nafion-Covered Au Electrodes

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Metal oxides have a great importance in the development of high performance supercapacitors (SC). Lead(IV) oxide shows very promising properties as cathode material due to its high redox potential, high conductivity and facile charge transfer kinetics. However, in order to design SCs of sufficient energy content for practical applications the uniform electrochemical reaction throughout the layer thickness together with negligible slow diffusion-like processes must be ensured.

The aim of this work was to prepare nano-structured PbO<sub>2</sub> electrode by anodic deposition on Nafion-coated gold electrode solutions for the potential utilization as active electrode material in pseudocapacitors. The role of Nafion was to provide a template consisting of nano-channels for Pb(II) ion diffusion resulting in PbO<sub>2</sub> layer which is expected to achieve sufficient porosity to enable fast sulphate ion and proton diffusions.

Nafion coated electrodes were prepared by casting the Nafion solution in iso-propyl alcohol on gold electrode. The thickness of the layer was controlled by varying Nafion concentrations. The electrochemical deposition was carried out by cyclic voltammetry and potentiostatic transient methods from lead(II) nitrate solution. The results showed that electrocrystallization mechanism does not differ considerably from the mechanism taking place on the bare gold electrode. The mechanism, which is well known for these systems, consists of anodic intermediate formation, nucleation and the growth of the resulting layer. However, the obtained results demonstrated that Nafion did not act as an inhibiting layer for the deposition process but, rather surprisingly, facilitated the nucleation and growth rate. Nucleation overpotential was significantly reduced in the presence of Nafion and kinetics of the deposition depended on the Nafion layer thickness (Figure 1).

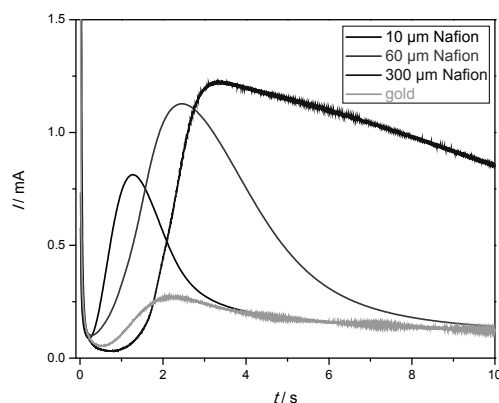


Figure 1. Current transients obtained at 1.6 V vs. Ag/AgCl reference electrode with varying thickness of Nafion coating

XRD results showed the formation of  $\beta$ -PbO<sub>2</sub> phase with the similar structure as the PbO<sub>2</sub> layer obtained in non-covered Au electrode. This confirms the observation that Nafion does not influence the mechanism but kinetics of nucleation process. This is explained by favourable interactions of soluble Pb(III) intermediates with fluorine atoms on Nafion chain as proved by XPS analysis.

## Zirconia Powder for SOFC Anode

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Solid oxide fuel cell (SOFC) is the device for direct transformation of chemical energy of fuel in electricity and heat [1,2]. Its anode is the SOFC's component, which provides passing of main electrochemical reaction and provides mechanical stability of all SOFC as a supporter of SOFC. Therefore, strength is one of the basic requirements for anode. Anode should provide strength not less than 100 MPa and have high porosity (>25%) for venting gases.

The most widespread anode material is a composite on the basis of stabilized in a cube phase zirconia (further  $ZrO_2$ ) and nickel. Usually, anodes are made from mixture of powders of  $ZrO_2$  and NiO. Nickel is reduced at operating condition of SOFC.

Influence of zirconia powder morphology on structure formation of anode NiO- $ZrO_2$  sintered at different temperatures (1300-1450°C) and its mechanical behavior was studied. Type 1 – agglomerated powder with initial nanoparticles; Type 2 – dense plane agglomerates consist of uniform initial particles; Type 3 – practically non-agglomerated powder with uniform initial particles (Fig. 1).

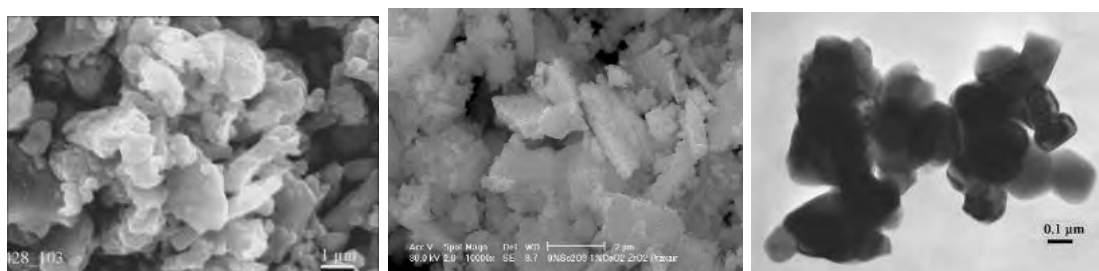


Fig. 1. Structure of different types of  $ZrO_2$  powders: a – type 1, b – type 2, c – type 3.

The size of the initial particles (crystallites) of powders  $ZrO_2$  and NiO were estimated from TEM images of the powder. 20 mm dia, 1.5-2 mm thick disc shaped samples were pressed uniaxially at 20 MPa and then sintered at different temperatures 1300-1450°C for 2h in air. The porosity of the sintered NiO- $ZrO_2$  samples were measured by means of the Archimedes method. The samples were tested for the mechanical strength with biaxial bend test and their fracture surfaces were analysis by means of SEM.

It was found that for formation suitable porosity level (~30 %) and temperature stable structure of anode with strength of 100 MPa, the agglomerated zirconia powder with nanosized initial particles (type 1) is the most suitable.

### References

- [1] S. C. Singhal, K. Kendall (eds.): High-temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications. Elsevier: Oxford, U.K., 2003. (ISBN 13: 978-1-85617-387-2).
- [2] F. Tietz, H.-P. Buchkremer, D. Stover: Components manufacturing for solid oxide fuelcells. Solid State Ionics 152, 153 (2002) 373– 381.

## Absorptive Glass Mat Separator Coating and Its Influence on the Heat Generation in VRLA Battery Cell

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Two types of valve-regulated lead-acid (VRLA) battery cells with uncoated and polymer composite coated absorptive glass mat (AGM) separators were studied. The volt-ampere characteristics of the studied cells, recorded at different ambient temperatures, show that the cells with polymer coated separators have significantly lower overcharge (recombinant and gas) current than the cells with conventional untreated AGM separator. During overcharge, the higher recombinant current in the cells with uncoated separator leads to higher cell temperature than that of the cells with polymer coated AGM separator.

The possibility to avoid thermal runaway (TR) is also illustrated during polarization of the cells at 2.65 V. After 320 h, a conventional cell has C/4 current (trend to TR), while the cell with composite coating sustains low (C/26) constant current for long period of time (at least 650 h). The cycle life test indicates stable operation of the cells with coated separator, while the conventional cell reaches high recombinant current and thus, it is susceptible to thermal runaway phenomena.

SEM images of bare and coated AGM separator are presented in Fig.1. The impact of composite layer on overcharge behavior of the studied AGM lead-acid battery cells is presented in Fig.2 and Fig.3. Cells labeled 01,02&03 are with bare AGM separators. PM labeled cells have coated separators. The percentages on the graphs mark the cell's electrolyte saturation.

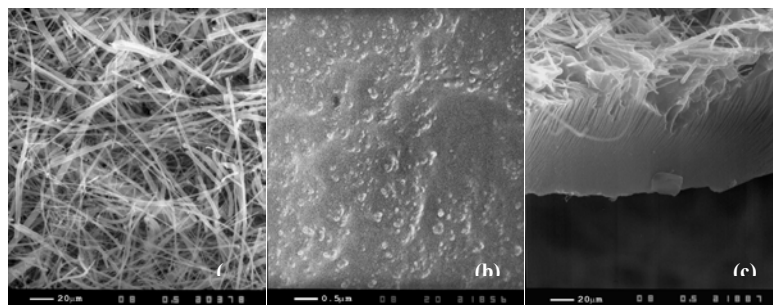


Fig.1 SEM images of bare AGM separator surface before coating (a); polymer coating spread on AGM separator (b) and cross section of the coated separator (c).

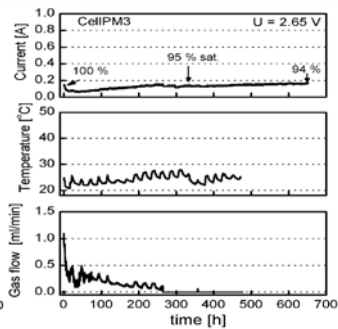
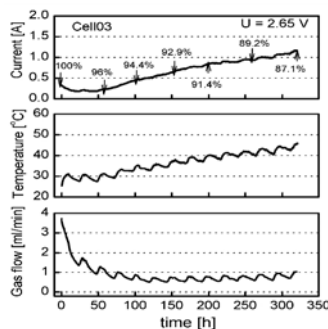
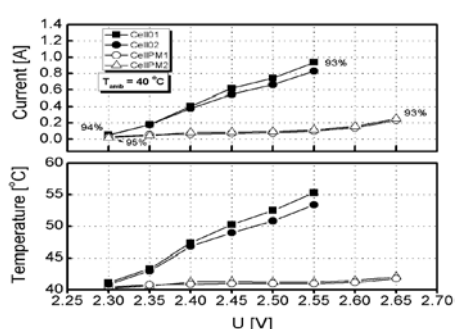


Fig.2 Overcharge current and temperature change during polarization at different constant voltages at 40 °C.

Fig.3 Overcharge current, temperature and gas flow change during polarization at 2.65 V at room temperature.

## Symmetric and Hybrid Battery-Supercapacitor Systems for Energy Storage

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The increased interest to supercapacitor systems is largely determined by the growing needs for new technologies for storage of energy produced by renewable energy sources as solar stations and wind generators, as well as by the remarkable advantages of supercapacitors in comparison to the conventional electrochemical power sources – batteries and fuel cells, such as high power characteristics and practically unlimited cycle life. On the other side, the integration of double layer supercapacitors and batteries in hybrid electrochemical systems gives a possibility to combine the high transient performance of supercapacitors with the high steady-state characteristics of batteries.

In the present paper are reported some results of our research carried out for development of different supercapacitor systems [1-3]. Two types of supercapacitors (SC) are developed:

(i) *Symmetric double-layer SC cells* assembled with two identical electrodes of activated carbon materials and a non-aqueous electrolyte. The nanoporous carbons (specific surface area in the range 700 – 1600 m<sup>2</sup>g<sup>-1</sup>) and various pore structure (partial micropore volume 0,15 – 0,60 cm<sup>3</sup>g<sup>-1</sup>) are produced by carbonization of mixtures of coal tar pitch and furfural (600 °C) with subsequent steam activation at 800 °C. Three types of organic electrolytes are tested: LiPF<sub>6</sub> – DMC/EC (dimethyl carbonate/ethylene carbonate mixture 1:1), Et<sub>4</sub>NBF<sub>4</sub> – PC (propylene carbonate), LiBF<sub>4</sub> – PC;

(ii) *Asymmetric SC cells* – hybrid lithium battery-double layer supercapacitors composed by an electrode of nanosized activated graphitized carbon (1600 g/m<sup>2</sup> specific surface area), a composite electrode with activated carbon matrix and additions of an electrochemically active nanosized oxide (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> or Fe<sub>2</sub>O<sub>3</sub>), and an organic electrolyte (LiPF<sub>6</sub> – DMC/EC 1:1 or LiBF<sub>4</sub> - DMC/EC 1:1). The Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> spinel material is prepared by thermal co-decomposition of oxalates and subsequent thermal treatment (800 °C/1h). The nanosized oxide Fe<sub>2</sub>O<sub>3</sub> is produced by two methods – synthesis by solution-combustion method with subsequent thermal treatment (400 °C/1h) and by thermal treatment (400 °C/2h) of biogenic α-FeOOH, obtained by laboratory cultivated *Leptothrix* bacteria. An asymmetric SC cell composed by an activated nanosized carbon electrode, Ni(OH)<sub>2</sub> electrode an aqueous electrolyte (7M KOH) is also developed. The SC cells are subjected to charge/discharge cycling test under galvanostatic conditions at different current loads.

Both the symmetric and hybrid SC cells demonstrate excellent cycleability, high power capability at discharge (up to 600 mA g<sup>-1</sup>) as well as high current efficiency and stable capacity behavior at prolong cycling. It is proved that the organic electrolyte plays an important role in determining the capacity performance of symmetric SC. It is also shown that the conductivity, pore size distribution and chemical surface properties of the carbon materials contribute greatly on charge storage behavior of the electrodes in the supercapacitor systems.

The capacitance values up to 80 F g<sup>-1</sup> for the symmetric carbon-based SC, depending on the electrolyte and microstructure of the carbon material used, and capacitance up to 2 times higher for the hybrid lithium battery-supercapacitors were obtained.

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### References

- [1] M. Mladenov, N. Petrov, T. Budinova, B. Tsyntsarski, T. Petrov, D. Kovacheva, R. Raicheff, *Bulg. Cheml Commun.* 43 (2011) 125-131
- [2] M. Mladenov, K. Alexandrova, N. Petrov, B. Tsyncarski, D. Kovacheva, N. Saliyski, R. Raicheff, *J. Solid State Electrochem.* 17 (2013), 2101-2108
- [3] B. Tsyntsarski, N. Petrov, S. Veleva, P. Nikolov, M. Mladenov, R. Raicheff "Activated carbon materials for electrochemical supercapacitors and battery applications" *9-th International Conference on Lead-Acid Batteries-LABAT 2014*, Albena (2014), Proceedings (Extended Abstracts), p. 59

## Experimental Determination of Optimal Clamping Torque for Air Breathing PEM Fuel Cell

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Polymer electrolyte Membrane (PEM) fuel cell is an electrochemical device producing electricity by the reaction of Hydrogen and Oxygen without combustion. PEM fuel cell stack is provided with an appropriate clamping torque to prevent leakage of reactant gases and to minimize the contact resistance between gas diffusion media (GDL) and bipolar plates. GDL porous structure and gas permeability is directly affected by the compaction pressure which consequently, drastically change the fuel cell performance. Various efforts have been made to determine the optimal compaction pressure and pressure distributions through simulations and experimentation [1, 4, 5]. Lower compaction pressure results in increase of contact resistance and also chances of leakage. On the other hand, higher compaction pressure decreases the contact resistance but also narrows down the diffusion path for mass transfer from gas channels to the catalyst layers consequently lowering cell performance [2]. The optimal cell performance is related to the gasket thickness and compression pressure on GDL [3]. Every stack has a unique assembly pressure due to differences in fuel cell components material and stack design. Therefore, there is still need to determine the optimal torque value for getting the optimal cell performance. This study was carried out in continuation of development of Air Breathing PEM fuel cell for small UAV applications. Compaction pressure at minimum contact resistance was determined and clamping torque value was calculated accordingly. Single cell performance tests were performed at five different clamping torque values (0.5 Nm, 1.0 Nm, 1.5 Nm, 2.0 Nm & 2.5 Nm) for achieving optimal cell performance. Experimental and theoretical results were compared for making inferences about optimal cell performance. A clamping torque value of 1.5 Nm was determined experimentally to be the best for getting optimal performance for this specific fuel cell (Fig.1).

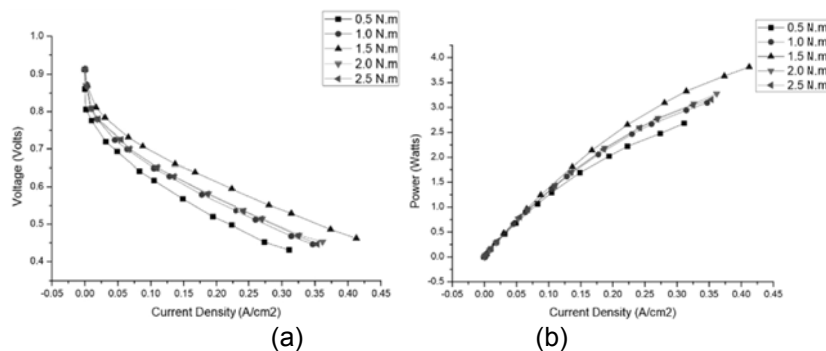


Fig. 1: Fuel Cell performance as a function of clamping torque, (a) Polarization (b) Power

### References

- [1] Alex Bates, Santanu Mukherjee, Sunwook Hwang, Sang C. Lee, Osung Kwon, Gyeong Ho Choi, Sam Park, International Journal of hydrogen energy 38 (2013) 6481e6493.
- [2] W.R. Chang, J.J. Hwang, F.B. Weng, S.H. Chan, Journal of Power Sources 166 (2007) 149–154.
- [3] Woo-kum Lee, Chien-Hsien Ho, J.W. Van Zee, Mahesh Murthy, Journal of Power Sources 84 (1999) 45–51
- [4] Xinting Wang, Ying Song, Bi Zhang, Journal of Power Sources 179 (2008) 305–309
- [5] P. Zhou, C.W. Wu, G.J. Ma, Journal of Power Sources 163 (2007) 874–881

## Pseudocapacitors based on Layered Double Hydroxides electrodeposited on Pt electrode

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Electrochemical capacitors also known as supercapacitors can be divided into two categories, namely, electric double layer capacitors (EDLCs), founded on non-Faradic charge storage process, and pseudocapacitors, which use metal oxides/hydroxides as the main electrodes since their capacitance arises from redox processes occurring at or near the solid electrode surface. Layered double hydroxides (LDHs) especially those containing transition metals are considered as ideal pseudocapacitive materials due to their peculiar properties such as efficient anion exchange capacity and high redox activity[1,2]. LDHs have the general formula  $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[X_q^{x/q-} \cdot nH_2O]$  where M(II) and M(III) are bivalent and trivalent metal cations and X is the charge-balancing interlayer anion.

Electrosynthesis is an efficient method to prepare LDH thin films suitable for sensing applications and in the last few years our group has optimised the one-step electrodeposition, mainly on Pt electrodes, of LDHs based on redox active metals as Ni or Co and Al [3]. The applications of LDH modified electrodes requires the formation of well adherent thin films and this result can be achieved if Pt surface is electrochemically pre-treated in 0.1 M  $H_2SO_4$  [4].

In this work four LDHs containing Co and Ni, as bivalent and Fe and Al as trivalent cations have been synthesized on Pt by electrochemical reduction, at  $-0.90$  V vs SCE for 30 s, of the proper electrolytic solution [5]. All the LDHs have been characterized in basic solution (0.1 and 1 M NaOH) to investigate if they behave as pseudocapacitive materials by using cyclic voltammetry and galvanostatic charge/discharge curves. The calculation of capacitance per gram of material is very important when evaluating materials for this application, so the mass deposited during the synthesis was determined using the electrochemical quartz crystal microbalance. As an example in Fig. 1 a and b the CV and the galvanostatic charge/discharge curves recorded for the LDH containing Al and Co, are shown.

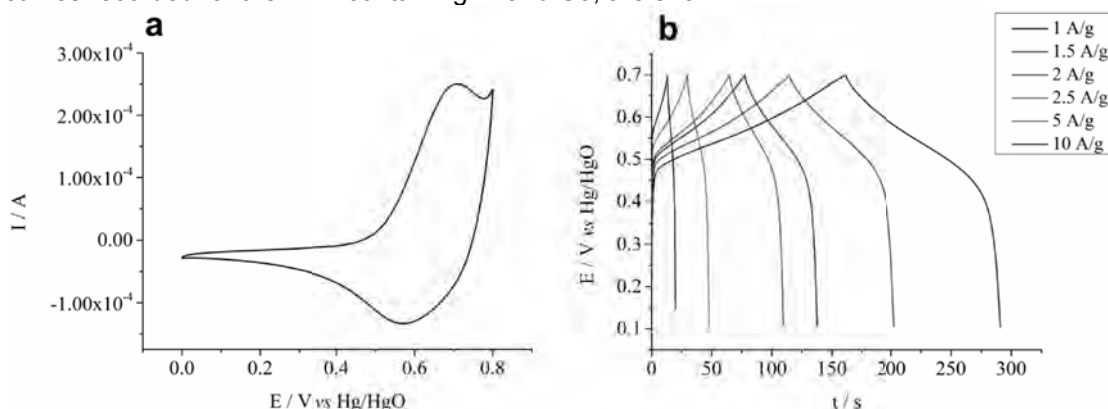


Fig. 1. Characterization CV ( $5^{th}$  cycle) of Co/Al-LDH coated Pt recorded in NaOH 0.1 M at the scan rate of  $0.05$  Vs $^{-1}$  (a) and galvanostatic charge/discharge curves recorded in NaOH 0.1 M (b)

All the LDHs displayed good performances both in terms of specific capacitance and life cycles, as estimated by galvanostatic charge/discharge curves. As conductive support also glassy carbon was investigated in order to fabricate cheaper devices.

### References

- [1] M.F. Shao, F.Y. Ning, Y.F. Zhao, J.W. Zhao, M. Wei, D.G. Evans, X. Duan, Chem. Mater. 24 (2012) 1192.
- [2] B. Wang, Q. Liu, Z. Qian, X. Zhang, J. Wang, Z. Li, H. Yan, Z. Gao, F. Zhao, L. Liu, J. Power Sources 246 (2014) 747.
- [3] E. Scavetta, B. Ballarin, M. Gazzano, D. Tonelli, Electrochim. Acta 54 (2009) 1027.
- [4] E. Scavetta, A. Casagrande, I. Gualandi, D. Tonelli, J. Electroanal. Chem. 722-723 (2014) 15.
- [5] I. Gualandi, A.G. Solito, E. Scavetta, D. Tonelli, Electroanalysis 24 (2012) 857.

## Shape Controlled, Carbon Supported Pt Anodic Catalysts for DFAFC

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Electrocatalytic activity of platinum-based electrocatalysts used in fuel cells has been well recognized. However, significant attention remains on the particle shape and size control of such nanomaterials. Catalytic activity can be enhanced by alloying Pt with another element (e.g. Ru and Sn) [1], or by supporting Pt on metal oxides [2], both of which involve a bifunctional effect. It is also possible to achieve better catalytic characteristics by exposing different Pt crystal facets, which alters chemical and electronic interactions (structural effect) [3].

In order to synthesize Pt nanoparticles of a pre-determined shape, water in oil microemulsion method was used [4], with a few modifications: carbon support (Vulcan XC-72R) was added into the microemulsion itself, just after the completion of the reduction reaction of  $\text{H}_2\text{PtCl}_6$  with  $\text{NaBH}_4$  as the reducing agent and this was crucial for further improvements of the catalyst cleaning procedures. Microemulsion consisted of [n-heptane] / [polyethyleneglycol-dodecyether (BRIJ30)] / [0,1M  $\text{H}_2\text{PtCl}_6$  in 0, 15, 25 and 35% HCl], so four Pt catalyst were formed using different amounts of HCl in the water phase of the microemulsion. In comparison to previously reported applications of the microemulsion method [5], where electrochemical treatment of catalysts before its application was necessary, this alteration of cleaning steps made use of the “as prepared” catalysts possible.

Catalysts A (0% HCl), B (15% HCl), C (25% HCl) and D (35% HCl) were characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD) and transmission electron microscopy (TEM), as well as with electrochemical characterization methods (cyclic voltammetry in supporting electrolyte, CO stripping). Some of the obtained results are given in the following figures.

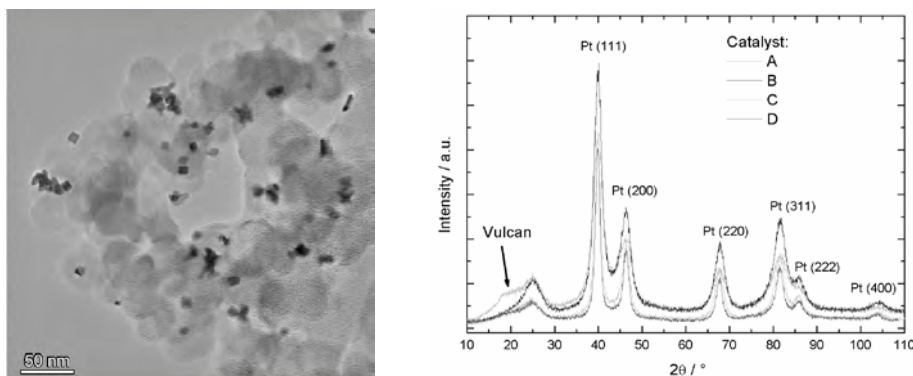


Fig. 1. Left: TEM image of catalyst D; right: XRD patterns of supported Pt catalysts

TEM images confirmed the presence of cubic Pt particles, and indicated their good dispersion on carbon support, while XRD patterns revealed the share of each plane orientation in all investigated catalysts. This acknowledged the influence of HCl in the microemulsion on the shape of Pt particles. Mean particle size was determined both by TEM and XRD investigations, which are in good accordance, and show that average diameters of these four catalysts vary from 3 to 8 nm.

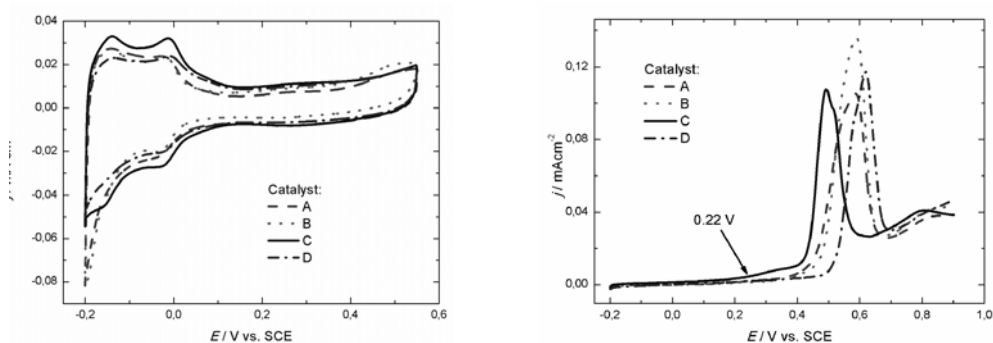


Fig. 2. Left: Basic voltammograms recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub>, scan rate 50 mV/s; right: CO stripping, positive going voltammograms, recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub>, scan rate 50 mV/s

Electrochemical investigations of basic voltammograms and CO stripping voltammograms gave insight into catalyst surface structure, which was further compared to TEM and XRD results. Specific surface area (SSA) was calculated from CO stripping charge, as well as electrochemically active surface area (EASA) that was used for current density calculations.

After characterization of all catalysts by both physical and electrochemical methods, formic acid electrooxidation was carried out. This particular reaction is of great interest for fuel cell technology, because it is one of the anodic reactions for clean fuel production. It takes place in the direct formic acid fuel cells (DFAFC), that use formic acid as a fuel, which is oxidized at the anode surface to CO<sub>2</sub> and water, but CO can also be formed in an indirect mechanism. Surface structure of the anodic catalyst is, therefore, of great influence on the reaction mechanism. A good catalyst must possess high activity towards this reaction, fair stability, and exhibit surface characteristics that would suite the favorable reaction mechanism. HCOOH oxidation voltammograms of four catalysts are shown in Fig. 3.

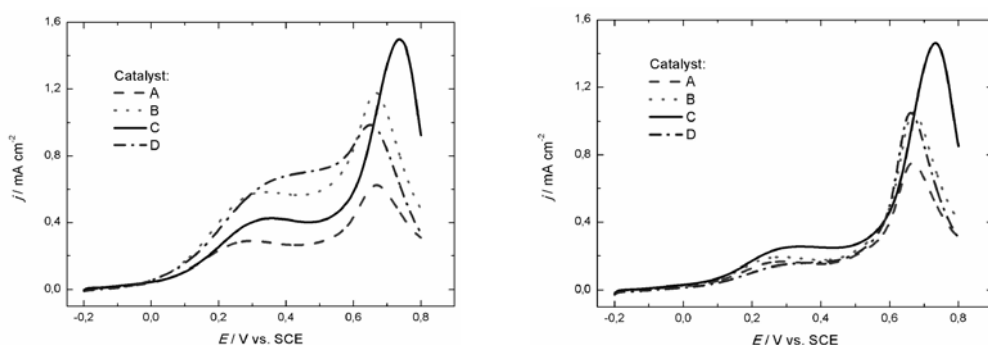


Fig. 3. Formic acid electrooxidation positive going voltammograms, in 0.5 M HCOOH in 0.5M H<sub>2</sub>SO<sub>4</sub>, left: 1<sup>st</sup> cycle; right: 100<sup>th</sup> cycle

Activity and stability during the first 100 cycles of formic acid electrooxidation were investigated for all catalysts, and these results indicated that changes in shape and plane orientation of the particles cause differences in catalysts' activity and stability.

## References

- [1] N. V. Long, Y. Yang, C. M. Thi, N. V. Minh, Y. Cao, M. Nogami, *Nano Energy* **2** (2013) 636-676
- [2] M. N. Krstajić, M. D. Obradović, B. M. Babić, V. R. Radmilović, U. Č. Lačnjevac, N. V. Krstajić, S. Lj. Gojković, *J. Serb. Chem. Soc.* **78** (2013) 1703-1716
- [3] Z. Peng, H. Yang, *Nano Today* **4** (2009) 143-164
- [4] Martinez-Rodriguez, F. J. Vidal-Iglesias, J. Solla-Gullon, C. R. Cabrera, J. M. Feliu, *J. Am. Chem. Soc.* **136** (2014) 1280-1283
- [5] J. Solla-Gullon, V. Montiel, A. Aldaz, J. Clavilier, *J. Electroanal. Chem.* **491** (2000) 69-77

## Hybrid Solutions for High-Energy Storage Systems

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Due to the growing technological advances requirements of energy storage systems incessantly increase. Taking into account power needs for portable devices, the energy storage through electrochemical reactions seems to be a crucial technology. Electrochemical capacitors have attracted great attention as a promising energy storage devices because of their high power density and cycle life noticeably longer than batteries [1, 2]. Recently, extensive work has been focused on several ways enhancing both the energy and power density accompanied by reasonable cost of device production as well as its environment-friendly character.

Asymmetric supercapacitors composed of battery-type electrode and a high surface area carbon electrode [3] merge the advantages and reduces the drawback of redox and capacitive based systems; namely, asymmetric design offers the advantages of supercapacitors (power rate, cycle life) and batteries (energy density) [4].

This work is focused on high-energy electrochemical capacitors utilizing graphite (G) (normally working as an anode in lithium-ion cells) as negative electrode material and activated carbon (AC) with well-developed surface area as positive electrode material. The electrochemical exfoliation of graphite made by reversible intercalation of lithium ions has been chosen as the main method of negative electrode material obtaining. Performed electrochemical measurements i.e., cyclic voltammetry in the range 1 – 100 mV s<sup>-1</sup> and galvanostatic charging/discharging with current regimes from 0.1 to 5 A g<sup>-1</sup>, presented improved energy efficiency compared with results for symmetric cells (i.e. AC/AC capacitor). All measurements were performed in organic electrolyte to provide a wide range of operating voltage.

In the case of the hybrid system energy density has been improved and approaches 100 Wh kg<sup>-1</sup> compared to c.a. 25 Wh kg<sup>-1</sup> for a symmetric systems and are accompanied by good power profile (Fig.1).

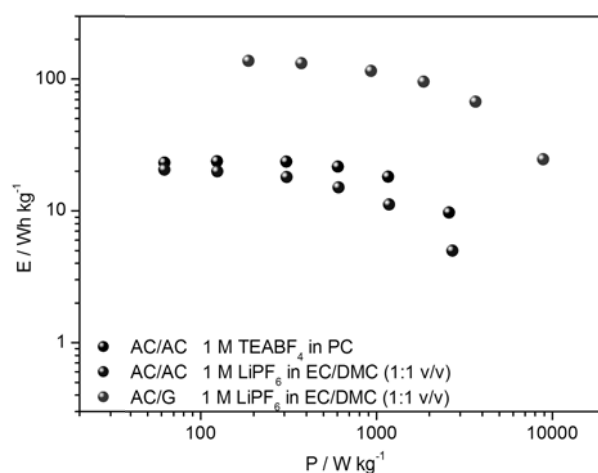


Fig.1. Ragone plot for symmetric capacitors (AC/AC) and hybrid solution (AC/G)

### References

- [1] Burke, J. Power Sources 91 (2000) 37
- [2] P. Simon, Y. Gogotsi, Nat. Mater. 7 (2008) 845
- [3] J.W. Long, D. Belanger, T. Brousse, W. Sugimoto, M.B. Sassin, O. Crosnier, MRS Bull. 36 (2011) 513
- [4] Z.J. Fan, J. Yan, T. Wei, L.J. Zhi, G.Q. Ning, T.Y. Li, F. Wei, Adv. Funct. Mater. 21 (2011) 2366

## Carbon Additives for Advanced Lead-Acid Battery Applications

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New applications such as micro-hybrid cars, remote telecommunications and energy storage for renewables are placing strong demands on lead–acid batteries for improved charge-acceptance and cycleability under partial state-of-charge (PSoC) conditions. Carbon additives to negative active mass (NAM) have a pronounced beneficial effect by reducing negative plate sulfation and significantly improving cycleability and dynamic charge acceptance, both for valve-regulated (VRLA) and enhanced flooded lead–acid batteries.

Unfortunately, other properties such as high-rate discharge and water loss may be impaired by the addition of carbon materials to NAM. When the overall concentration of lignosulfonate in the negative plate paste is appropriately adjusted, the high-rate discharge performance and water loss can be restored to the desired level. Understanding the fundamentals of water loss as a function of carbon properties is critical for identifying conditions under which the beneficial effects of carbon on dynamic charge-acceptance and cycleability are further increased without exacerbating water loss.

Cabot Corp. (USA) has developed several new grades of carbon additives with controlled surface area, morphology and surface properties for the improvement of charge acceptance and cycle life with minimum adverse impact on water maintenance and high-rate discharge.

The present work will describe new test data on how to balance water loss and high rate discharge characteristics for high content carbon lead-acid batteries while preserving the benefits of high charge acceptance and improved cycle life. Test data on the effect of carbon additives to NAM on charge acceptance and cycle life for deep cycling applications will be presented. Relevant applications include motive power and stationary flooded batteries where both increased cycle-life and faster charging capability are desired.

Commercially available carbon black additives (PBX51, PBX09, PBX135, Cabot Corporation) were selected to study the impact of BET surface area and morphology on the electrochemical performance of the negative active material, and the effect of these carbon blacks was compared to those of an activated carbon (PBX101, Cabot Corporation) and an expanded graphite (ABG1010, Superior Graphite). Mixtures of carbon black (PBX135) and activated carbon (PBX101) or expanded graphite (ABG1010) were also evaluated.

## Effect of a Mineral Additive on the Structure and Electrical Characteristics of the Positive Active Mass of a Lead-Acid Battery

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The lead-acid battery has inherent characteristics that make it attractive for many applications. These include high specific power and power density, high volumetric energy density and low initial cost. Compared to the negative plate, the positive plate performance is limited [1-4]. Therefore, extensive research work has been conducted to improve its capacity by the use of positive plate additives [5-8]. It has been concluded that the low coefficient of utilization of the positive active material is a result of pore blockage and reduced pore size caused by PbSO<sub>4</sub> that blocks the diffusion in the pores and leads to lack of electrolyte [9-11].

The present work focuses on the improvement of the capacity of the positive (PbO<sub>2</sub>) electrode of a lead-acid battery. To this end, we add a mineral additive, in various percent concentrations, during the stage of positive paste preparation. Leady oxide (LO) containing different amounts of mineral additive (0-15 wt.% (w/o)) is mixed with water and 1.40 s.g. H<sub>2</sub>SO<sub>4</sub> solution in a H<sub>2</sub>SO<sub>4</sub>/LO ratio equal to 5%. The paste mix is homogenized for 30 min as a result of which 3BS paste is obtained. The paste is filled in a tubular electrode and the latter is set on formation.

Samples of the formed positive active mass are characterized by X-ray diffraction analysis (XRD), thermogravimetry (TG), differential scanning calorimetry (DSC) and scanning electronic microscopy (SEM). The capacity of the different PAM samples is determined by galvanostatic discharge technique.

This study aims to investigate the effect of a mineral additive on the structure and performance of the positive active material in a lead- acid battery. It is found that the addition of mineral additive to the paste before oxidation exerts an influence on the composition and the capacity of the positive active mass after oxidation. We observe a remarkable improvement of the discharge capacity of the positive active mass for additive loading levels ranging between 1 and 5%. This may be explained by the fact that, at this concentration of mineral additive, nanosized PbO<sub>2</sub> particles with amorphous character are obtained. These positive active masses contain more structural water which facilitates the diffusion of the protons through the gel zones. In addition, the mineral additive with its high porosity facilitates the transport of the electrolyte throughout the positive active mass volume.

### References

- [1] S.V. Baker, P.T. Moseley, A.D. Turner, J. Power Sources 27 (1989) 127-143.
- [2] J.E. Manders, N. Bui, D.W.H. Lambert, J. Navarette, R.F. Nelson, E.M. Valeriote, J. Power Sources 73(1998) 152-161.
- [3] S. Wang, B. Xia, G. Yin, P. Shi, J. Power Sources 55 (1995) 47-52.
- [4] M.K. Cartenter, D.M. Bernardi, J.A. Wertz, J. Power Sources 63 (1996) 15-22.
- [5] K. McGregor, J. Power Sources 59 (1996) 31-43.
- [6] H. Dietz, J. Garche, K. Weisener, J. Power Sources 14 (1985) 305-319.
- [7] A. Tokunaga, M. Tsubota, K. Yonezu, K. Ando, J. Electrochem. Soc. 134 (1987) 525-529.
- [8] D.B. Edwards, S. Zhang, J. Power Sources 135 (2004) 297-303.
- [9] D. Simonsson, J. Appl. Electrochem. 3 (1973) 261-270.

## Evaluation of Glass Sealant Properties versus Thermal Ageing Simulating Switch On And Off of an SOFC Stack

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SOFC stack have in prospect to show high reliability and durability working in a temperature range of 650-800°C with degradation rate below 2% of voltage loss for 100 hours.

The state of art fuel cells are expected to grant this behavior for long enough to consider this power source as one of the best solutions for the next future. The recognized bottleneck is currently related to the stacking materials: i.e. metals (frames and interconnects) and sealant.

The investigation on sealing materials is the focus of this communication, with the aim to study a suitable method to evaluate in real time the degradation rate by measuring the capacitance of glass as function of operating parameters.

A commercial glass ceramic sealant is used in connection with ferritic stainless steel AISI 441 and aged at 750°C for 500 h in single atmosphere of laboratory air. Electrochemical results are related to crystallinity and the structural feature of the glass.

### Acknowledgment

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## **Hydrogen sorption and electrochemical properties of TiFe based alloys synthesized by mechanical alloying**

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TiFe alloys with composite nanocrystalline-amorphous structure were obtained mechano-chemically by high-energy ball milling in a planetary type mill. The duration of milling was varied with the aim to produce alloys with defined microstructure. The average size of the powders was reduced from 50 $\mu$ m to <1 $\mu$ m after 30-40 hours of grinding. The synthesized composite material showed relatively high thermal stability. The electrochemical hydrogen charge-discharge behavior of materials with different microstructure was investigated. Increasing the milling time to 40 hours resulted in significant increase in the discharge capacity and cycling stability of the as-prepared hydrogen storage alloys.

*Keywords: TiFe alloys, discharge capacity, hydrogen storage*

## Influence of the Gold Sublayer to the Catalytic Properties of Magnetron Sputtered Pt, Ir and IrO<sub>x</sub> Thin Films

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One of the key goals of catalyst manufacturing for hydrogen energy system is the development of new materials with improved cost efficiency. It is possible to design catalysts with superior properties by alloying two or more metals. Bimetallic catalysts have demonstrated enhanced activity compared to the corresponding monometallic catalysts. Since surface catalyzed reactions are extremely sensitive to the atomic-level details, the choice of the method for preparation of smooth thin layers with good mechanical strength is essential in order to utilize effectively the limited resources of the noble metal elements. Usually the catalysts are powders consisting of metal nanoparticles deposited on catalytic support with high surface area. There are various catalyst preparation techniques such wet chemical reduction, sol-gel, thermal decomposition of metal salts, electrochemical deposition, under-potential deposition, radio frequency and direct current magnetron sputtering (DCMS), and etc. The choice of the method depends on several strict criteria including efficiency, reproducibility, time consumption, cost as well as the technological availability in regard to the application.

Platinum is the best known pure metal catalyst for hydrogen evolution (HER), hydrogen oxidation (HOR), and oxygen reduction (ORR) reactions, while it is not so efficient with respect to the oxygen evolution (OER). The most commonly studied catalysts for OER are Ir, Rh, IrO<sub>x</sub> and RuO<sub>x</sub>. In order to increase the catalytic activity and reduce the cost of catalysis Pt is often alloyed with cheaper metals from the transition series such as Ni, Co, Fe and etc. or with o

ther noble metals (Ru, Ir, Os) which improve not only the efficiency but also the stability of the composite catalysts.

This work concerns: i). the preparation of thin composite catalytic films in which an essential part of the efficient but expensive Pt, Ir and IrO<sub>x</sub> is substituted by dense Au sublayer using the method of magnetron sputtering; ii).characterisation of the surface structure, morphology, and electronic state; and iii).investigation of catalytic performance toward the partial electrode reactions proceeding in the hydrogen energy systems.

The selected single and composite catalytic films (Au, Pt, Ir, IrO<sub>x</sub> and Au-M) are prepared in sequence (layer by layer) using the method of direct current magnetron sputtering on glass substrate upon 25 nm thick Ti-sublayer. The total thickness of all samples is 250 nm. In the bimetallic catalysts 240 nm of the basic functional layer is substituted with Au on the top of which a 10 nm functional layer (M = Pt, Ir, IrO<sub>x</sub>) is sputtered.

The surface structure, morphology and composition of the prepared catalysts are characterized by XRD and XPS analysis. The performance and catalytic efficiency are evaluated in acid aqueous solution (0.5 M H<sub>2</sub>SO<sub>4</sub>) using a standard three electrode cell applying the conventional electrochemical methods of cyclic voltammetry and steady state polarisation curves.

The experimental results in fig.1 show that the intensity of the OER increases in the order Au<IrO<sub>x</sub><Au-IrO<sub>x</sub><Ir<Au-Ir, while for the partial cathodic reaction at low overpotentials Pt still has superior efficiency. In the potential range where hydrogen evolution takes place (HER) the efficiency of Pt and Au-Pt films is nearly the same despite the huge difference in Pt content (250:10 nm, respectively).

The cyclic voltammograms recorded in the water window potential range are compared in fig.2. It is seen that Au-Pt and Au-IrO<sub>x</sub> CVs combine features typical for both single metals.

To evaluate the intrinsic catalytic efficiency (not dependent on the film thickness) the current densities at defined potential are normalised to the thickness of the top functional layer (Pt, Ir or IrO<sub>x</sub>).These data are presented in Table 1.

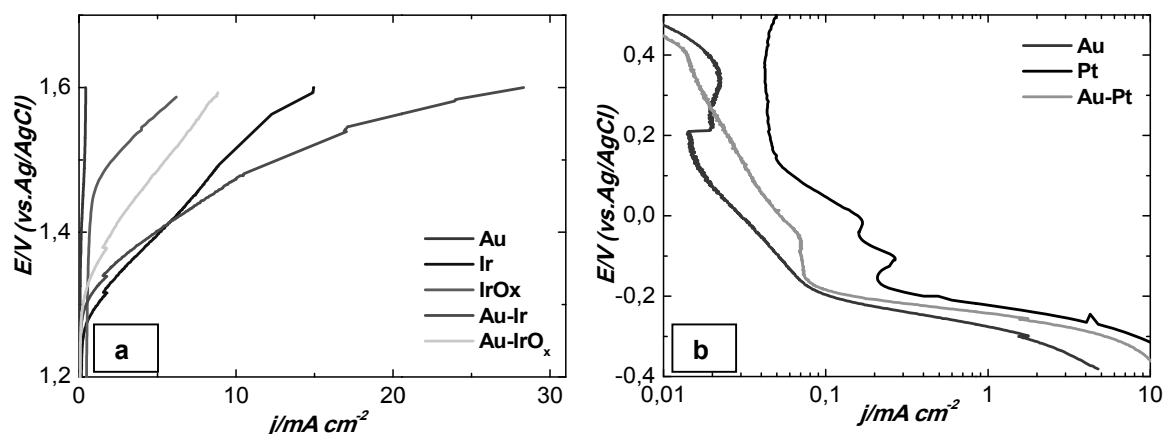


Fig. 1. Steady state polarisation curves a) anodic and b) cathodic, recorded in 0.5M H<sub>2</sub>SO<sub>4</sub> at 22 °C; potential scan rate - 1mV s<sup>-1</sup>

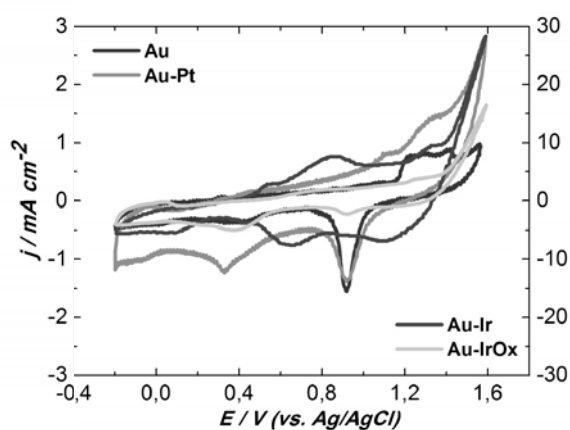


Fig. 2. Cyclic voltammograms of Au and Au-M sputtered films in 0.5M H<sub>2</sub>SO<sub>4</sub> at 22 °C and 100mV.s<sup>-1</sup>; the right y-axis presents the current density of Au-Ir and Au-IrO<sub>x</sub> and left-y Au and Au-Pt respectively

Table 1. Intrinsic catalytic efficiency of the sputtered films

Films	HER	Films	OER
	(E= -0.35V)		(E=1,5V)
	$j/mA.cm^{-2}.nm^{-1} Pt$		$j/mA.cm^{-2}.nm^{-1} Ir \text{ or } IrO_x$
Pt	0.0607	Ir	0.0369
Au-Pt	0.950	IrO <sub>x</sub>	0.0079
		Au-Ir	0.2558
		Au-IrO <sub>x</sub>	0.1104

The results demonstrate the superior performance of Au-Pt for HER and Au-Ir for OER compared to the pure metals (Pt and Ir). The synergistic effect is explained with formation of the interfacial bimetallic layers and electronic interactions, confirmed by the registered shift in the binding of the metallic components. The research proves that the method of DCMS could be used as precise technique for deposition of multilayered catalysts with controlled thickness and tailored synergistic effects between the components.

*Participation of E. Petkucheva in RSE-SSE 5 has been made possible with the financial support of Bulgaria Ministry of Education and Science*

## In Situ Impedance Monitoring Of Nio-YSZ Anode Behavior during Its Initial Reduction and Redox Cycling

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This presentation introduces a new approach for in-situ conductivity measurements of the Ni network's initial formation in NiO-YSZ and its changes during cyclic oxidation and reduction, applying electrochemical impedance spectroscopy. Usually, the electrochemical behavior of the anode reaction is evaluated by impedance measurements carried out on cells. Although impedance is an informative and powerful technique, the data analysis needs the application of equivalent circuit models based on validated preliminary working hypothesis for separation of the anode contribution from the total impedance of the cell. In the present study the testing is performed on single bare anodes. This approach bypasses the complications arising from the impedance data analysis of the cell and ensures more accurate and targeted information regarding the initial stages of the Ni particles electric connectivity in the YSZ matrix and the changes in the Ni percolating network during redox cycling. It opens a new niche for direct observation of the conductivity changes during redox cycling in conditions which can simulate the operating system and thus for the development of strategies for minimization of the degradation effects.

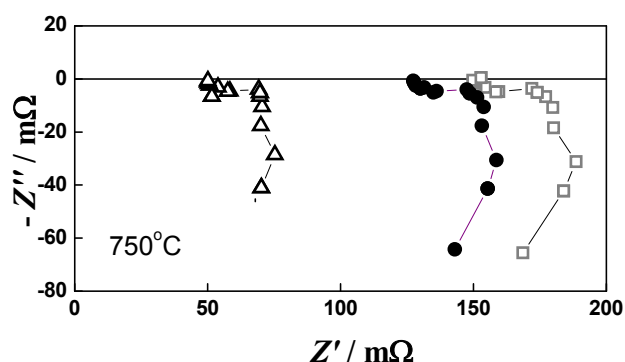


Fig. 1. Complex plane impedance diagrams measured during reduction after 8,5 minutes ( $\circ$ ), after 9,5 minutes ( $\square$ ) and after 10,5 minutes ( $\triangle$ ) from the beginning of the reduction process

For more complete description of the changes in the anode microstructure, gas permeability measurements are also introduced. The obtained results show that impedance can register the changes in the sample's conductivity during anode reduction, as well as during redox cycling performed in mild oxidation conditions. The oxidation rate is much slower than the reduction one. The combination of impedance with gas permeability and microstructural measurements gives new opportunities for anode optimization in respect to the ohmic and concentration polarization.

### Acknowledgements:

The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) Fuel Cells and Hydrogen Joint Undertaking (FCH-JU-2013-1) under grant agreement No 621207.

## Cathodic Hydrogen Evolution Reaction on Copper in Sulphuric Acid Catalyzed by Proton Vectors

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The predicted depletion of fossil fuels, coal, oil and natural gas by 2050 places special emphases on the integration of alternative energy resources, of which energy produced from hydrogen could be predominant primary energy source. Most experts consider that hydrogen can play an important role as energy carrier in the possible scenario for the future. Furthermore, hydrogen has great potential to hold promise as a power source for future, with socio-economic benefits and positive environmental impact [1-3].

In this study, the catalytic effect of several organic amines on hydrogen evolution reaction (HER) was studied on copper electrode. Kinetic parameters were determined from Tafel polarization curves in order to obtain more information about catalytic effect of organic amines. In the case of N,N-dimethylaniline (DMA) the best electrocatalytic effect was reached in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. Molecular parameters of protonated amines were determined by quantum calculation. A larger dipole moment obtained for N,N-dimethylanilinium (DMAH<sup>+</sup>) showed that the orientation of these molecules are more favorable ordered on the electrode surface. In addition, the adsorption behavior of DMA on copper surface follows the Langmuir adsorption isotherm. The low negative values of the standard Gibbs free energy of adsorption  $\Delta G_{ads}$  at different temperature suggested a physisorption. The value of the activation energy obtained for 10<sup>-3</sup> M DMA was 37% higher than that obtained in the absence of DMA.

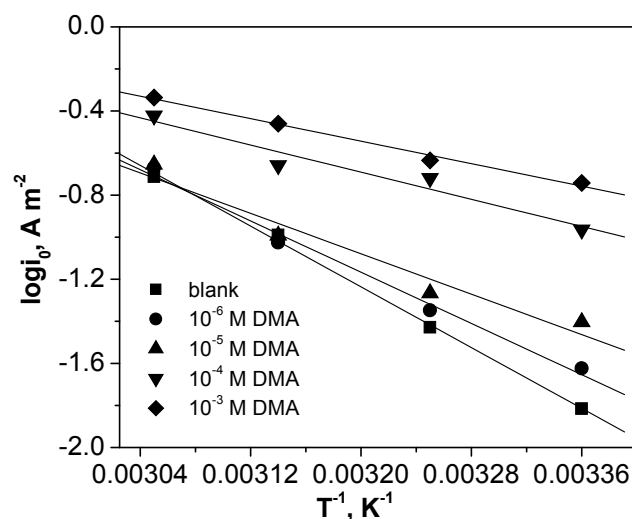


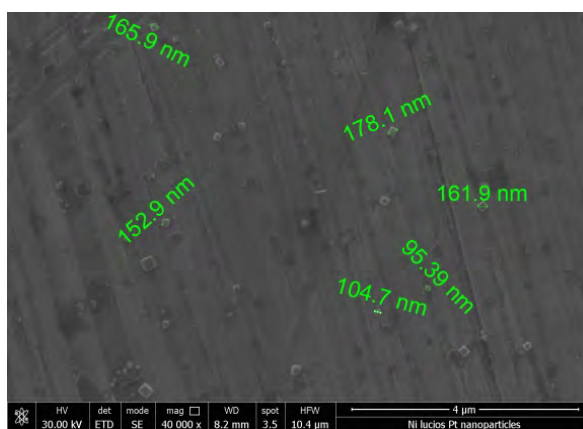
Fig.1. Arrhenius plots for HER in 0.5 M H<sub>2</sub>SO<sub>4</sub> and in the presence of different concentrations of DMA

### References

- [1] Dincer, C. Acar, Int. J. Hydrogen Energy, 2014, p. 1-18.
- [2] S. Sharma, S.K. Ghoshal, Renewable and Sustainable Energy Reviews, 43, 2015, p. 1151-1158.
- [3] M. Wang, Z. Wang, X. Gong, Z. Guo, Renewable and Sustainable Energy Reviews, 29, 2014, p. 573-588.

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## Cyclic voltammetry study of thin-film electrodes from Si-O-Al composites

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Silicon is perspective anode material for lithium-ion batteries due to high theoretical insertion capacity 4210 mAh/g. The films of amorphous Si with thickness less than 1  $\mu\text{m}$  are capable to maintain hundreds cycles without considerable loss of capacity. However, the increase in thickness of such films results in drastic acceleration of degradation at cycling. Recently it was found that layered composites Si-Al possess much higher cycling stability. In the present work, we study multi-layered electrodes made from composite Si-O-Al.

Thin-film layered composite electrodes were prepared by alternate magnetron sputtering pure silicon and mixture of silicon and aluminum onto titanium foil in oxygen-containing environment. The composite under study consisted of 12 layers of plain Si and 12 layers of mixture Si:Al (84:16). Thickness of single layer was ca. 85nm. Cyclic voltammetry tests were carried out in a cell with Li counter and reference electrodes. The electrolyte was 1M LiPF<sub>6</sub> solution in a 1:1:1 (v/v) mixture of ethylene carbonate, dimethyl carbonate and diethyl carbonate. Cyclic voltammograms were registered between 0.0 and 1.0 V at scan rates from 0.1 to 1.0 mV/s by using a cycle tester P30J "Ellins" (Russia).

Cyclic voltammograms registered at low scan rates reveal two cathodic peaks at potentials ca. 0.2 and 0.04 V, and two anodic peaks at potentials 0.35 and 0.5 V. It was shown by special experiments that cathodic peak at 0.04 V unambiguously corresponds to anodic peak at 0.35 V, whereas cathodic peak at 0.2 V corresponds to anodic one at 0.5 V. One can suppose that cathodic peak at 0.2 V reflects the formation of intermetallic compound Li<sub>2</sub>Si, and cathodic peak at 0.04 V could be attributed to formation of more lithium-rich alloys. It is worth noting that the shape of voltammograms at layered composite coincides very well with that of voltammograms at plain silicon, and drastically differ from the shape of cyclic voltammograms at aluminum.

It turns out that the peak currents  $I_p$  are proportional to the square root of the potential scan rate  $v$ . From the slope of  $I_p$  versus  $v^{1/2}$ , we can calculate the apparent diffusion coefficient of Li<sup>+</sup> in the Si-O-Al composite according to modified Ševčík equation with account for non-ideality of Li alloy. The diffusion coefficient happened to be  $5 \cdot 10^{-10}$  cm<sup>2</sup>/s. We underline that the above figure is some effective one, because Li<sup>+</sup> ions can travel through phase bulk as well as along interphase boundaries.

### Acknowledgements

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## Cyclic Behavior of Si-O-Al Composite

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Nowadays the specific capacity of negative graphite electrodes in commercial lithium-ion batteries reached its maximum value, which is close to theoretic value of 372 mAh/g. The only way to increase the specific capacity of battery is the transition to new materials with much higher specific capacity of lithium insertion than carbon materials. The most promising (in terms of specific capacity) is the silicon whose theoretical specific capacity is 4200 mAh/g [1].

We prepared layered Si-O-Al composites by alternate magnetron sputtering pure silicon and mixture of silicon and aluminum in oxygen-containing environment onto titanium foil. The composite thickness was more than 2  $\mu\text{m}$ . The Si-O-Al composite contained about 75,5 at. % silicon, 11 at. % oxygen, and 6.86 at. % aluminum. Such composites were found to have columnar morphology with average pillars' diameter of 50 nm, and inter-pillar distance 1-2 nm. Electrochemical measurements at Si-O-Al-electrodes were carried out in sealed three-electrodes cells of flat-parallel construction. Cells contained one work electrode, two lithium counter and one lithium reference ones. We used 1M LiPF<sub>6</sub> in ethylene carbonate - diethylcarbonate - dimethylcarbonate (1:1:1) mixture as an electrolyte. The cells were assembled in glove-box with humidity about 10 ppm. We used non-woven polypropylene separator. The electrolyte humidity was less than 20 ppm. Cycling of electrochemical cells was performed with computerized cyclers of Buster Co. (St. Petersburg, Russia). Potential limits of cycling were 0.01–2.0 V relatively to lithium reference electrode. Before physical chemical investigations, electrodes were thoroughly rinsed by dimethoxyethane in a glove-box.

The discharge capacity at galvanostatic cycling (C/8) of Si-O-Al electrodes was stable for no less than 100 cycles and was about 2800 mAh/g (1.1 mAh/cm<sup>2</sup>). During the multiple cycles of lithium insertion-extraction the composite thickness increases. Thickness growth happens unequally along the electrode surface. The total thickness of layered composites increases by 10-30-fold after 100-180 cycles. The elemental composition of Si-O-Al films changes during the cycling, specifically, fluorine and phosphorous appears at the surface and in the bulk of the composite. Simultaneously oxygen and carbon contents increase. This suggests the formation of passive film on the pillars' surface, due to electrolyte reduction. Irregularity of thickness growth of Si-O-Al can be a consequence of non-uniform current density distribution, which can be related with different resistance in different areas.

### References

[1] R.A. Sharma and R.N. Seefurth, J. Electrochem. Soc. 123 (1976) 1763-1768.

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## Electrochemical Study of Doped $\text{LiFePO}_4$ as a Cathode Material for Lithium-Ion Battery

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The first report about olivine lithium iron phosphate was made in 1997 by Goodenough and coworkers [1]. Now LFP is the most recent state-of-the-art cathode material.  $\text{LiFePO}_4$  theoretical specific capacity is  $170 \text{ mAh g}^{-1}$  and it has a flat voltage plateau of around 3.45 V (vs.  $\text{Li/Li}^+$ ). Rather low electronic conductivity ( $\sigma \approx 10^{-9} \text{ S cm}^{-1}$ ) should be mentioned as one of the disadvantages of this material. However, electron transfer can be enhanced by a simple carbon coating of the LFP particles in situ during synthesis or ex situ by post-treatment. This leads to significant increase of the achievable specific capacity. Different ways for further enhancement of this active material have been extensively studied for the last few years:

Development of advanced nanostructured LFP-carbon composites

Replacement of carbon by conductive, electrochemically active polymers

Doping of LFP by the ions of transition metals and others

In this paper authors used the last method, Fe ions being partially replaced by the dopant. Sol-gel method was used for synthesis of the samples of different composition:  $\text{LiFe}_{0.99}\text{V}_{0.01}\text{PO}_4/\text{C}$ ,  $\text{LiFe}_{0.97}\text{V}_{0.03}\text{PO}_4/\text{C}$ ,  $\text{LiFe}_{0.95}\text{V}_{0.05}\text{PO}_4/\text{C}$ ,  $\text{LiFe}_{0.9}\text{V}_{0.1}\text{PO}_4/\text{C}$ , and  $\text{LiFe}_{0.7}\text{Mn}_{0.3}\text{PO}_4/\text{C}$ .

The performance of samples was investigated by galvanostatic cycling. Electrodes for electrochemical studies were made by pasting the material (85% active material, 10% carbon black and 5% polyvinylidene fluoride dissolved in anhydrous N-methylpyrrolidone) on a substrate. The electrochemical cell assembled in a glove box with a dry argon atmosphere. The mass of  $\text{LiFePO}_4$  on the substrate was roughly  $6\text{--}10 \text{ mg/cm}^2$ . The current density ranged from 20 to 1600 mA/g. The values of specific capacity obtained at C/8 rate were 130, 117, 96, 128 and 95 mAh/g for  $\text{LiFe}_{0.99}\text{V}_{0.01}\text{PO}_4/\text{C}$ ,  $\text{LiFe}_{0.97}\text{V}_{0.03}\text{PO}_4/\text{C}$ ,  $\text{LiFe}_{0.95}\text{V}_{0.05}\text{PO}_4/\text{C}$ ,  $\text{LiFe}_{0.9}\text{V}_{0.1}\text{PO}_4/\text{C}$  and  $\text{LiFe}_{0.7}\text{Mn}_{0.3}\text{PO}_4/\text{C}$  respectively. Figure 1 shows the comparison of different materials at different cycling rates. As we see  $\text{LiFe}_{0.9}\text{V}_{0.1}\text{PO}_4/\text{C}$  is the most beneficial. However, in the case of  $\text{LiFe}_{0.7}\text{Mn}_{0.3}\text{PO}_4/\text{C}$  an additional plateau at the potential of 4.2 V which increases overall energy density.

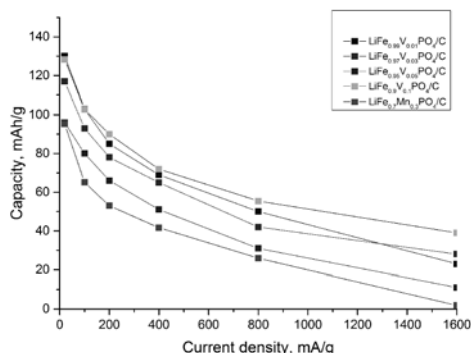


Fig.1 The comparison of different materials at different cycling rates

### References

- [1] Padhi, A.K., 1997. Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. *J. Electrochem. Soc.* 144, 1188.
- [2] The present work is supported by the Russian Foundation for Basic Research (Grant № HK 14-29-04068\14).

## Microwave Synthesis of Unusually-Shaped Crystalline RuO<sub>2</sub> Supercapacitor

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One-step simple temperature-controlled microwave synthesis was applied to prepare nanocrystalline RuO<sub>2</sub> dispersion from aqueous RuCl<sub>3</sub>. RuO<sub>2</sub> dispersion was subjected to dynamic light scattering in order to analyze the synthesized particles, whereas structural and morphological properties of the solid phase are investigated by AFM, SEM, EDAX and XRD techniques. The ordered unusual shape of ca. 100-nm native particles, as well as highly-ordered prismatic agglomerate sheets are observed. Capacitive properties of RuO<sub>2</sub> was investigated by cyclic voltammetry and electrochemical impedance spectroscopy in 1 M H<sub>2</sub>SO<sub>4</sub> and standard three-electrode cell, with ink-type working electrode on glassy carbon substrate. A specific capacitances as high as 750 F/g were obtained, which negligibly depend on sweep rate in 5–500 mV/s range (Fig. 1). These findings are quite unusual for this kind of material consisted of rather large particles [1], and makes it excellent candidate for both low and high power applications. The capacitive response appears stable during prolonged charge/discharge cycling.

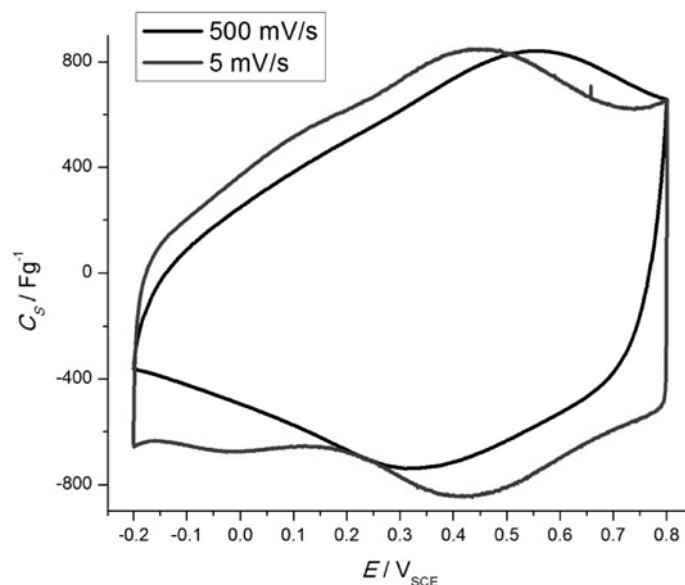


Fig.1. Cyclic voltammograms of nanocrystalline RuO<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub>.

### References

- [1] J. P. Zheng, P. J. Cygan, T.R. Jow, J. Electrochem. Soc. 142 (1995) 2699

## Antraquinone Decorated Reduced Graphene Oxide Nanosheets for Rechargeable Batteries

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Development of low cost and efficient electrode materials is the main target for researchers in Rechargeable Lithium Ion Battery (LIB) Technology. In order to achieve fast electron transfer and thus high power capability, graphene carbon network has attracted a great deal of attention due to its high electrical conductivity and easy modification by electron donating and deficient organic/inorganic compounds, which can tune its chemical and electrochemical behavior. In the light of these feedbacks, reduced graphene oxide (RGO) samples were chemically synthesized by using graphene oxide (GO) precursor in accordance with literature procedures. Then obtained carbon nanosheets were modified by electroactive anthraquinone (AQ) moieties in different ratios by using azide chemistry. In this way, the main solubility problem of electroactive organic compounds (or polymers) faced during charge-discharge cycling is precluded. Thus, electrode integrity was protected and capacity losses during repeated charging/discharging was minimized. Sheet resistance of partially reduced graphene sample increased from 5.175 to 13.83, 16.83, 21.11ohm/sq depending on loading level of AQ groups on RGO, 50%, 200% and 500% by mass as compared to RGO weight respectively. The electrodes were prepared by spreading of active mass (85% AQ modified graphene samples (RGO-AQ) and 15% TAB (Teflonized conductive carbon)) on Al and Cu foils with mass loading of 1-2mg/cm<sup>2</sup>. The electrodes were tested in 1M LiClO<sub>4</sub> in PC and 1 M LiPF<sub>6</sub> in EC:DMC by cyclic voltammetry and galvanostatic cycling. The obtained AQ modified graphene nanosheets show good cycleability with a voltage plateau at about 2.5V vs. Li metal.

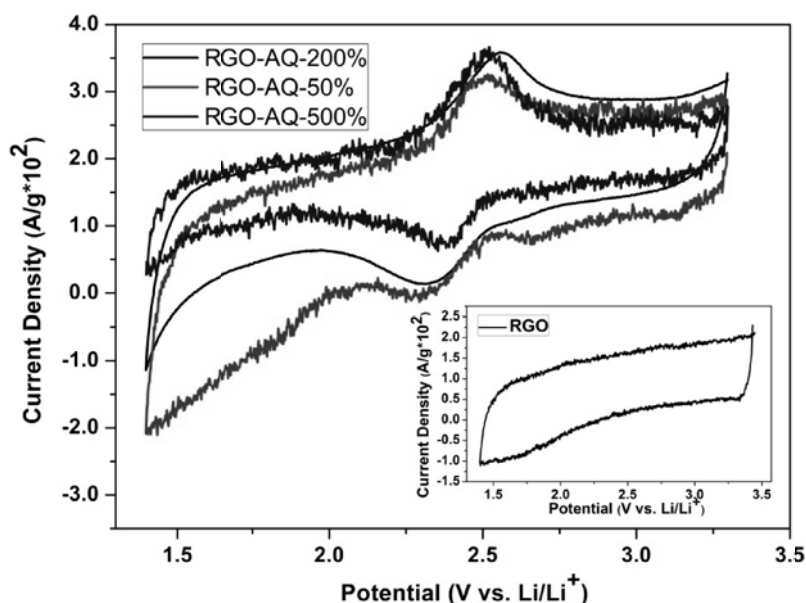


Fig.1. Cyclic Voltammetry (CV) of reduced graphene oxide (RGO) and AQ modified graphene (RGO-AQ) samples vs. Li metal at scan rate of 0.07mV/s.

### References

- [1] R. S. Robinson, Kent Sternitzke, Mark T. McDermott and Richard L. McCreery, J. Electrochem. Soc. 138, 1991, p. 2412.
- [2] L. Qu, Y. Liu, J.B. Beak, L. Dai, ACS Nano 4, 2010, p. 1321.
- [3] L. Tang, Y. Wang, Y. Li, H. Feng, J. Lu, J. Li, Adv. Funct. Mater. 19, 2009, p. 2782.
- [4] Ayrat M. Dimiev, Lawrence B. Alemany, and James M. Tour, ACS Nano 7, 1, 2013, p. 576–588.

## Structural and Electrical Properties of Ternary Oxides in the $\text{CeO}_2\text{-Sm}_2\text{O}_3$ System

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Doped  $\text{CeO}_2$  is widely considered as the only feasible alternative to YSZ as electrolyte material in SOFC. In fact, ionic conductivity of RE-doped  $\text{CeO}_2$  can exceed 0.01 S/cm already at 600 °C, which would allow a decrease in the standard operating temperature of cells.

Thanks to the fluorite structure, ionic conduction mechanism relies on oxygen vacancies which are formed to compensate charge unbalance due to the incorporation of  $\text{RE}^{3+}$  ions at  $\text{Ce}^{4+}$  sites and their equilibrium concentration can be extrinsically modified just by changing the amount of doping agent. However, increasing dopant concentration beyond a certain threshold reduces ionic conductivity, due to defect clustering and structural modifications.

In order to investigate the correlation between structure and electrical conduction at different doping levels, a detailed structural-electrical study was carried out in the system  $\text{CeO}_2\text{-Sm}_2\text{O}_3$ .

Ternary oxides of nominal composition  $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-x/2}$  with  $0.1 \leq x \leq 0.9$  were prepared by co-precipitation of mixed oxalates and subsequent thermal treatment in air at 1200, 900, or 800 °C; the structure was then analyzed at room temperature both by synchrotron X-ray diffraction and  $\mu$ -Raman spectroscopy, while conductivity was studied in the temperature range 300 – 800 °C by electrochemical impedance spectroscopy (Fig. 1) on samples sintered in air at 1400 °C.

Results show that for  $x < 0.3$  a solid solution exists, and conductivity increases with  $x$ , while for  $0.3 \leq x \leq 0.9$  a hybrid structure, intermediate between the  $\text{CeO}_2$  and the  $\text{Sm}_2\text{O}_3$  cubic structure, becomes stable; within this compositional range a gradual change of structural parameters sensitive to the fluorite  $\rightarrow$  cubic  $\text{Sm}_2\text{O}_3$  transition can be observed. Correspondingly, conductivity decreases with increasing  $x$ .

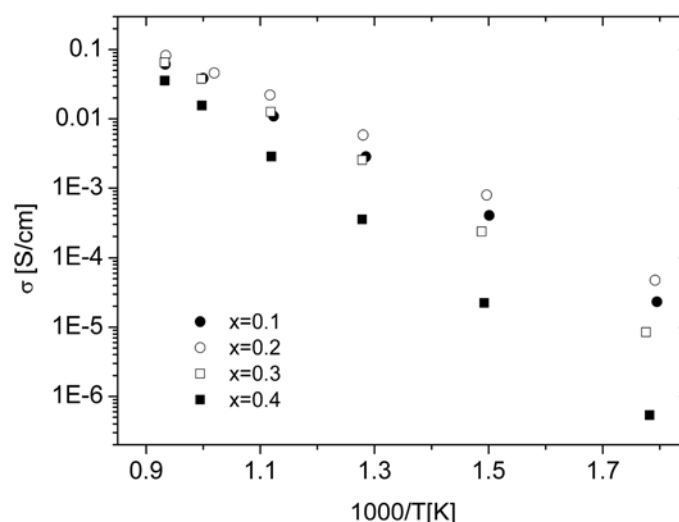


Fig. 1. Arrhenius plot of total conductivity at different Sm-concentrations.

## Enhanced ionic conductivity in borate ester plasticized Polyacrylonitrile electrolytes for lithium battery application

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Lithium ion batteries have acquired great importance in the last several decades as the energy storage of portables devices, such as cell phones and laptop computers [1]. However most lithium ion batteries containing liquid electrolytes have potential safety problems, due to the presence of large amount of organic solvents. In order to solve the safety problems, polymer electrolytes have attracted attention [1]. Solid polymer electrolytes as well as gel polymer electrolytes have been reported by many groups [2]. Solid polymer electrolytes have advantages like high specific energy, high energy density, leak proof, high ionic conductivity, wide electrochemical stability windows, light, solvent free and easy processability [2]. The interest in using of borate esters as additives have increased as they can lead to higher conductivities by trapping the anions due to their Lewis acidic nature, in spite of a very low solvent dielectric constant. They are non-volatile and also have high flash points [3]. Many borate esters have been recently synthesized and studied both as additives [4] and as solvents [5] in salt-in-polymer electrolytes. It is therefore of interest to analyze their influence on conduction of PAN-based electrolytes. The effect of low molecular weight borate ester on the ionic conductivity of polyacrylonitrile (PAN) was systematically investigated by means of measuring conductivity using the impedance technique. Gel polymer electrolyte (SPE) films consisting of PAN as host polymer, LiCF<sub>3</sub>SO<sub>3</sub> and LiBF<sub>4</sub> as ionic salts, and poly (ethylene glycol) borate ester (PEGB), ethylene carbonate/propylene carbonate (EC/PC) as plasticizers were prepared by physical blending method. All measurements were performed on electrolyte samples with various contents. Fourier transform infrared spectroscopy (FT-IR) gave evidence of the interactions among PAN, plasticizers and lithium salt. The surface morphology of the electrolytes was investigated by scanning electron microscopy (SEM). Thermal properties of these materials were searched with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Conductivity studies of these blend polymer electrolytes were carried out in the temperature range 20–100 °C. The maximum ionic conductivity values of  $1.8 \times 10^{-3}$  and  $1.4 \times 10^{-4}$  S.cm<sup>-1</sup> were measured for the film containing 4PAN-10EC/PC-4LiBF<sub>4</sub> and 4PAN-10PEGB-4LiCF<sub>3</sub>SO<sub>3</sub>, respectively, at room temperature. These films have a good conductivity, better dimensional stability and wide electrochemical stability window. These unique properties make the composite gel membranes suitable for application as electrolyte in rechargeable Li-ion batteries.

### References

- [1] Y.S. Zhu, X.J. Wang, Y.Y. Hou, X.W. Gao, L.L. Liu, Y.P. Wu, M. Shimizu, A new single-ion polymer electrolyte based on polyvinyl alcohol for lithium ion batteries, *Electrochimica Acta* 87 (2013) 113–118.
- [2] R. Prasanth, V. Aravindan, M. Srinivasan, Novel polymer electrolyte based on cob-web electrospun multi component polymer blend of polyacrylonitrile/poly(methyl methacrylate)/polystyrene for lithium ion batteries-Preparation and electrochemical characterization, *Journal of Power Sources* 202 (2012) 299–307.
- [3] Y. Kato, K. Hasumi, S. Yokoyama, T. Yabe, H. Ikuta, Y. Uchimoto, M. Wakihara, Polymer electrolyte plasticized with PEG-borate ester having high ionic conductivity and thermal stability, *Solid State Ionics* 150 (2002) 355–361.
- [4] W. Xu, X. G. Sun, C. A. Angell, Anion-trapping and polyanion electrolytes based on acid-in-chain borate polymers, *Electrochimica Acta* 48 (2003) 2255–2266.
- [5] S. Tabata, T. Hirakimoto, H. Tokuda, M. A. B. H. Susan, M. Watanabe, Effects of Novel Boric Acid Esters on Ion Transport Properties of Lithium Salts in Nonaqueous Electrolyte Solutions and Polymer Electrolytes, *Journal of Physical Chemistry B* 108 (2004) 19518–19526.

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## Gas Permeability Studies of Ni-YSZ Cermet Anodes for SOFCs

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Nickel - yttria stabilized zirconia (Ni/YSZ) cermet is the most common anode material in solid oxide fuel cells (SOFC). The high catalytic activity of Ni for the H-H bond breaking and relatively low cost justify its application. In addition the anode should ensure good permeability for the input of the fuel and the output of the exhaust water, which requires percolating porous structure combined with highly conducting Ni network needed for reduction of the ohmic losses. Usually the quality of the porous anode microstructure is evaluated by a combination of microscopic observations and electrochemical testing of the concentration polarization [1-5]. This work proposes a new approach - direct measurement of gas permeability in the porous anode media.

The experiments were performed on bare anode samples with different porosity obtained by variation of the graphite pore former (15-40 vol% for NiO/YSZ samples; 20-55 vol% for Ni/YSZ samples). The granules of NiO-YSZ mixture were compacted and uniaxially pressed into pellets with 1,5 mm in thickness and 25 mm in diameter and then sintered at 1350°C in air. The reduction of NiO/YSZ cermet to Ni/YSZ was performed at 725°C in gas mixture of Ar and H<sub>2</sub> in ratio 3:1. For evaluation of the Ni network the resistivity of the reduced samples was measured at room temperature applying advanced DC four points method.

For the performance of the permeability studies a new testing system was especially designed. It is based on measurements of the gas flow  $q_{\text{flow}}$  [ml/min] and pressure  $P$  (mm H<sub>2</sub>O) when penetrating through media with different porosity. A new characteristic parameter, named permeability resistance  $R_p$  was introduced [6]:

$$R_p = P/q_{\text{flow}}, \quad (1)$$

The permeability measurements were carried out at room temperature with different gases: air, O<sub>2</sub>, N<sub>2</sub>, Ar, dry and humidified H<sub>2</sub>.

Gas permeability is sensitive to gasses pathway tortuosity in the porous structure which may not correlate with the porosity volume. Thus the combination of porosity and gas permeability measurements opens additional opportunities for optimization of the anode.

The permeability measurements were carried out with different gasses at room temperature and constant conditions (set-up configuration and porosity) (Fig.1).

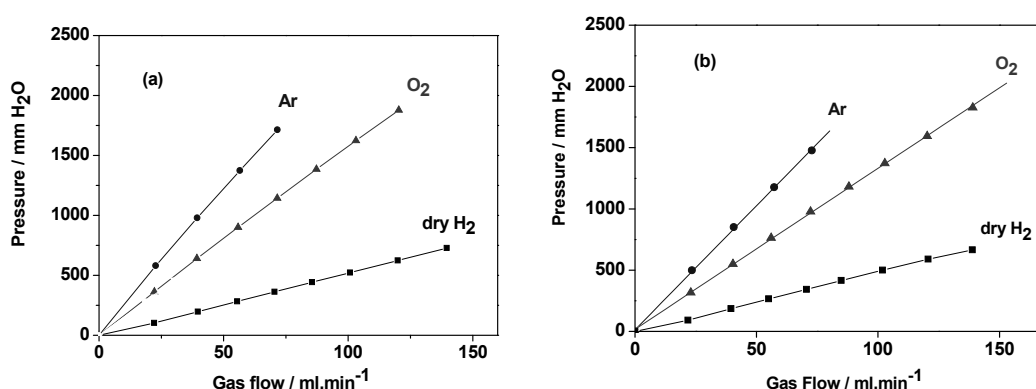


Fig.1. Gas pressure as a function of the gas flow: a) sample before reduction (NiO/YSZ); b) same sample after reduction (Ni/YSZ).

An increase of the permeability with the decrease of the molecular weight was registered for all the samples before, and after reduction. This tendency is valid also for gas mixtures.

The results show that an anode with a given porous structure should have different permeability in respect to the fuel and the exhaust water. Since  $H_2$  is diluted in operation conditions with the heavier inert gas ( $N_2$  or Ar), the permeability decreases with the increase of its concentration. The effect is stronger for Ar. For humidified  $H_2$  the permeability decreases in respect to dry  $H_2$ .

It is interesting to check the dependence between  $R_p$  and the molecular weight. Since the samples have different height  $h$ ,  $R_p$  was replaced with the resistivity  $\rho_p$ :

$$\rho_p = R_p \cdot s / l, \quad (2)$$

where  $s$  is the surface of the pipe line input. The results are presented in Fig. 2.

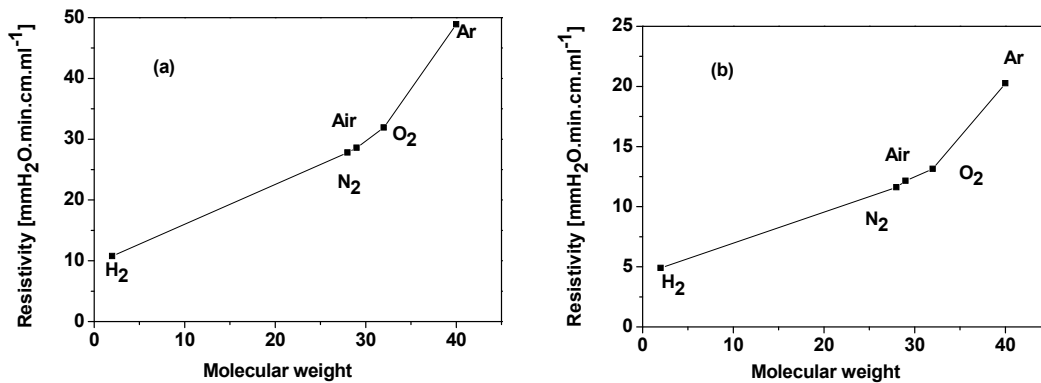


Fig.2. Dependence between permeability resistivity  $\rho_p$  and the gas molecular weight for the anode sample from Fig.1: a) before reduction (NiO/YSZ); b) after reduction (Ni/YSZ).

The observed dependence shows a kink in the vicinity of molecular weights about 28-30 (nitrogen/air). For higher molecular weight (as that of Argon) the resistivity increases faster. This experimental fact needs further studies for its explanation.

The resistivity of the reduced samples (Ni/YSZ) was evaluated by DC resistivity measurements. The results show that although the samples are reduced, those with lower porosity (about 20%) have no conductivity, i.e. there is no Ni percolation to ensure electron transport through the anode. We suppose that the loss of electron conductivity could be connected with Ni evaporation/deposition, which we have observed during reduction (Ni deposition on the sample's holder). Very probably for denser samples that process occurs inside the porous structure, causing Ni coarsening and thus, preventing the formation of the Ni network.

#### Acknowledgements:

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#### References

- [1] T. Talebi, M.H. Sarrafi, M. Haji, B. Raissi, A. Maghsoudipour, *Internat. J. Hydrogen Economy*, 35 (2010) 9440.
- [2] W.K. Yoshito, J.R. Matos, V. Ussui, D.R.R. Lazar, J.O.A. Paschoal, *J. Therm Anal. Calorim.*, 97 (2009) 303.
- [3] M.H. Pihlatie, A. Kaiser, M. Mogensen, M. Chen, *Solid State Ionics.*, 189 (2011) 82.
- A. Satikaya, V. Petrovsky, F. Dogan, *Internat. J. Hydrogen Economy*, 37 (2012) 11370.
- [4] Liu, Y. Zhang, B. Tu, Y. Dong, M. Cheng, *J. Power Sources*, 165 (2007) 114.
- [5] E. Mladenova, D. Vladikova, Z. Stoynov, A. Chesnaud, A. Thorel, M. Krapchanska, *Bulg. Chem. Commun.*, 45 (2013) 366.

## Structural Dependence of 1Ce10ScSZ Electrolyte Strength

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The influence of structure on mechanical behavior of 1Ce10ScSZ (1-mol. % CeO<sub>2</sub>, 10-mol. % Sc<sub>2</sub>O<sub>3</sub>, 89-mol. % ZrO<sub>2</sub>) electrolyte ceramics made of powders of various types was studied. Assuming that consolidation of powders and refinement of ceramic structure with sintering are thermally activated processes, the analytical equations, which are describing the relationships between strength, structural sizes, porosity and quality of interfaces are invented.

Strength of ceramics  $\sigma$  is dependent on the sintering temperature  $T_s$  too and might be described as some complex function of structural components, primary porosity  $P$ , effective size of structural elements  $d$  and some effective surface energy  $\gamma$ , which describes quality of boundaries between all structural components and depends on amount and state of impurities.

Generally, the named dependence might be expressed as some complex function  $\sigma(T_s)=f\{d(T_s), P(T_s), \gamma(T_s)\}$ . It requires numerous structural parameters. Traditional ones, like grain size, porosity, are obtained easily. Parameter describing state of inner interfaces might be obtained from fractography, e.g., as strong or weak boundaries resulting in transgranular or intergranular failures, which reflect cleavage and intergranular fracture micromechanisms.

The detailed study of structure and mechanical behavior shows that the fullest set of structural parameters suitable for a sophisticated analysis might be obtained from structural and fractographical data on ceramics made of three different types of zirconia powders, which differ by properties of initial particles and their agglomerates [1]. The data show dramatical difference of structure that is dependent on both the powder type and sintering temperature (Fig. 1).

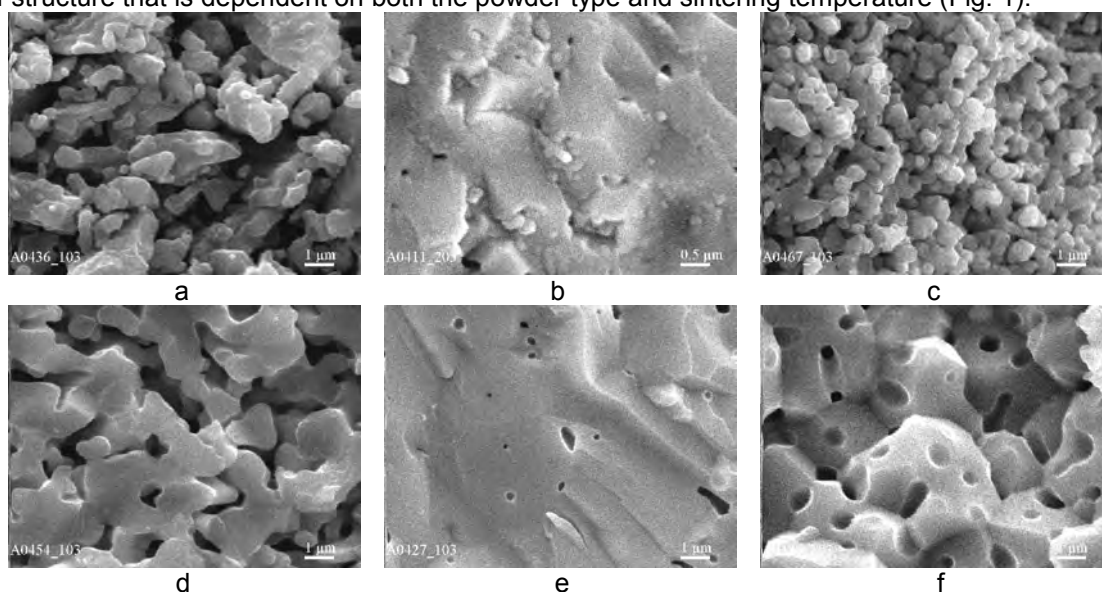


Fig. 1. Fracture surfaces revealed with scanning electron microscopy of 1Ce10ScSZ ceramics made of I - III powder types and sintered at 1350 and 1550 °C, respectively: I - a and d; II - b and e; III - c and f.

Finally, for intergranular and cleavage fracture micromechanisms, ceramic strength is described in above mentioned terms as

$$\sigma = (\sigma_0 + kd^{-1/2}) \cdot (1 - P)^n \cdot \gamma, \quad (1)$$

where  $\gamma$  - the normalized coefficient that determines the boundary quality.

### References

- [1] M. Brychevskiy, O. Vasylyev, Ye. Brodnikovskiy et al. Electron microscopy and strength of materials. Vol. 19, Proceedings of IPMS NAS of Ukraine, Kyiv, 2013, p. 169-183.



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## Determination of Plant Available Mn<sup>2+</sup> in Soil Samples with Voltammetric Method after UV-Digestion

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Plant available Mn (II) can be determined with flame atomic absorption spectroscopy (FAAS) and also by inductively coupled plasma optical emission spectrometry (ICP-OES) after DTPA extraction. These techniques are time-consuming and expensive due to the reagents used in analytical procedures [1]. For these reasons, electroanalytical methods can be used due to high sensitivity, portable instrumentation and low cost.

Homemade UV digestion system has been used to breakdown the organic matter (DTPA-Mn complex) prior to electrochemical determination of available Mn in soil samples. After the UV digestion and anodic polarization, a cathodic peak has appeared at 0.50 V resulting from reduction of MnO<sub>2</sub> to Mn<sup>2+</sup>. Differential pulse cathodic stripping voltammetry (DPCSV) was used as electroanalytical method with disposable pencil graphite electrode. Electrochemical parameters affecting the determination of Mn (II) such as supporting electrolyte, accumulation time, accumulation potential and stirring rate have been deeply investigated. UV digestion parameters were also optimized. Analytical variables such as linear working range, detection limit, etc., have been determined for Mn (II). Then, the resulting electroanalytical method has been tested on environmental samples.

### References

- [1] R.A. De Toledo, M. L. Simoes, W.T.L. Da Silva, L.M.-Netto, C. P. Vas, Intern. J. Environ. Anal. Chem. 89 (2009) 1099-1111

## Some Fundamental Aspects of EIS Data Validation

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For immittance data validation electrochemist generally use the consistency test based on the Kramers-Kronig transformation. In spite of the extensive discussion in the literature, a few fundamental questions were simply omitted, namely:

What is the mathematical idea behind the Kramers-Kronig transformation?

The transformation in the present form comes from optics: Is an optical system completely analogous to an electrochemical system? Can Kramers-Kronig transformation be directly applied to electrochemical systems in the same way as in the case of optical systems?

Does the KK compliance of the impedance data imply the compliance of the corresponding admittance data and vice versa? Is it enough to test only the impedance data, or should a complete validation procedure involve the testing of both the impedance and corresponding admittance?

From mathematical point of view the KK transformation can be explained in a very simple way based on the corresponding  $w(t)$  weight function of the system. Whenever  $w(t) = 0$  for each  $t \leq 0$  and the Fourier integral is convergent for  $w(t)$ , the corresponding impedance data will obey the KK test - better saying, such an impedance is KK transformation invariant. However, KK transformation will never fail on an impedance data set involving a time delay. That is a main difference between optical systems and impedance. An electrochemical cell is basically an electrical two-pole, not allowing the presence of a time delay between voltage and current signals in any direction. In contrast, an optical system is analogous to an electrical four-pole permitting the presence of a time delay between the input and output signals. Thus, unlike in optics, it is not sufficient to test only the impedance or the admittance for KK invariance, a complete consistency test should involve the test of both the impedance and admittance.

A regularization based algorithm will also be shown for the calculation of KK transformation.

## Dissolved Hydrogen Voltammetric Sensor and Its Application for Bacterial Photosintetic Hydrogen Production Evaluation R. Zlatev<sup>1\*</sup>, C. Iniguez<sup>2</sup>, M. Stoytcheva<sup>1</sup>, J-P Magnin<sup>3</sup>, E. Rodríguez<sup>4</sup>, Benjamin Valdez<sup>1</sup>, G. Montero<sup>1</sup>

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The hydrogen being the only carbon-free fuel is of particular interest as a future energy source because of its renewability and absence of polluting emissions during its direct combustion or application in fuel cells. Unfortunately the high cost of hydrogen and the atmosphere contamination during its production limits its application – only 4% are produced by the application of clean industrial technologies. The use of green biological methods however can significantly reduce the cost of hydrogen production using industrial wastes as substrate and sun light as an energy source [1]. The photosynthetic bacterium *Rhodobacter capsulatus* is one of the strains able to produce H<sub>2</sub> at anaerobic conditions with a high efficiency with the participation of the enzyme nitrogenase, which in absence of alternative substrates reduces protons to hydrogen gas at presence of light. The optimization of the experimental conditions of this process to obtain maximal hydrogen production efficiency requires a great number of experiments, respectively a great amount of reagents and a long duration of the experiments to collect a volume of hydrogen able to be measured precisely.

The application of small volume photosynthetic reactors may reduce the quantity of the reagents but it must be combined with a real time *in-situ* method for dissolved hydrogen concentration measurement. Recently the authors developed a potentiometric sensor [2] based on Reversible Hydrogen Electrode (RHE) which drawback however was the altering of the calibration curve with the changes of the bacterial medium composition, mainly pH. This drawback was overcome by the development of a voltammetric sensor, subject of the present work where the electrodes and the electrolyte are separated from the bacterial media by a membrane. This sensor is based on the hydrogen electrochemical oxidation occurring in accordance with the equations:  $H_2 + 2OH^- = 2H_2O + 2e^-$  in alkaline media and  $H_2 = 2H^+ + 2e^-$  in acidic media respectively. Since in both cases electrolyte acidification occurs a concentrated HCl was applied as supporting electrolyte. The low hydrogen solubility in water of about 1.6 mg/L at 20°C and 1 bar pressure requires great electrodes surface of the sensor to obtain sufficient current response level, shown in Fig. 1. The developed voltammetric sensor was analytically characterized and applied for the hydrogen production efficiency evaluation of the wild variety B10 and genetically modified one IR3 of the strain *Rhodobacter capsulatus*.

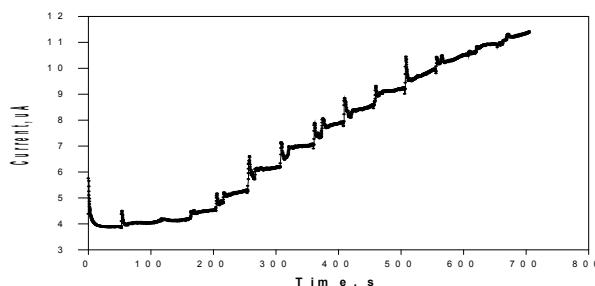


Fig. 1. Dissolved hydrogen probe response to increased H<sub>2</sub> concentration

### References

[1] Eroglu, E., Gündüz, F., Yücel, M., Türker, L. and Eroglu, I. International Journal of Hydrogen Energy, 2004, 29, 2, February 2004, 163-171.

[2] Zlatev R., Stoytcheva M., Romero P-A, Reyes A-L. Jean-Pierre Magnin J-P, ECS Transactions, 61 (24) 15-21 (2014), DOI: 10.1149/06124.0015ecst

## Detection of Heavy Metal Ions Using Chemically Modified Electrodes Based on Polyazulene

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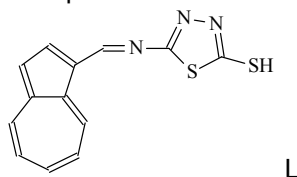
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Determination of trace levels from heavy metals in the environment is highly important, yet challenging analytical problem, because numerous health problems are associated with exposure to high levels of these metal ion due to their tendency to be accumulated in the body, toxicity and low rate of clearance. The electrochemical methods for detection of trace metals are very important since these methods offer several advantages, including remarkable sensitivity, inherent miniaturization and portability [1]. Electrochemical analysis using chemically modified electrodes represents a promising method for metals determination at trace levels [2]. Conducting polymers based on azulene are very interesting building block among the polymers for the synthesis of advanced materials.

New complexing polymer-coated electrodes were prepared by electropolymerization in acetonitrile solutions of azulene derivative L. The novel electrodes were tested for the electrochemical detection of Pb(II), Cd(II), Cu(II) and Hg(II) ions by means of the chemical preconcentration-anodic stripping technique.



### Acknowledgment

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### References

- [1] R. De Marco, G. Clarke, B. Pejic, *Electroanalysis* 2007, 19–20, 1987.
- [2] G.-O. Buica, C. Bucher, J.-C Moutet, G. Royal, E. Saint-Aman, E.-M Ungureanu *Electroanalysis* 2009, 21, 77.

## Determination of Boron in Environmental Samples with Voltammetric Method

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In this study, a simple and rapid electroanalytical method was proposed to determine boron in environmental samples with glassy carbon working electrode. After the extraction of boron in the samples, boron is complexed by addition of Alizarin Red S (ARS) to the extraction solution. An anodic peak has appeared at -0.45 V for Boron-Alizarin Red complex. Differential pulse anodic stripping voltammetry (DPASV) was used to determine the amount of the complexes. The electroanalytical parameters affecting the determination of boron have been optimized according to the experimental results. Magnitude of oxidation peak currents was used to get optimal parameters at each optimization step. The optimum stirring rate, accumulation potential, accumulation time and pH of supporting electrolyte were determined as 250 rpm, -0.6 V, 60 seconds and 7.5, respectively. Optimized method with glassy carbon working electrode showed good selectivity and sensitivity on the determination of boron. Analytical parameters such as linear working range, detection limit, etc., have been determined for boron. Then, the glassy carbon working electrode has been tested on real samples.

## Dielectric Impedance Spectroscopy – a New Technique for Rapid Screening of the Complex State of Motor Oils

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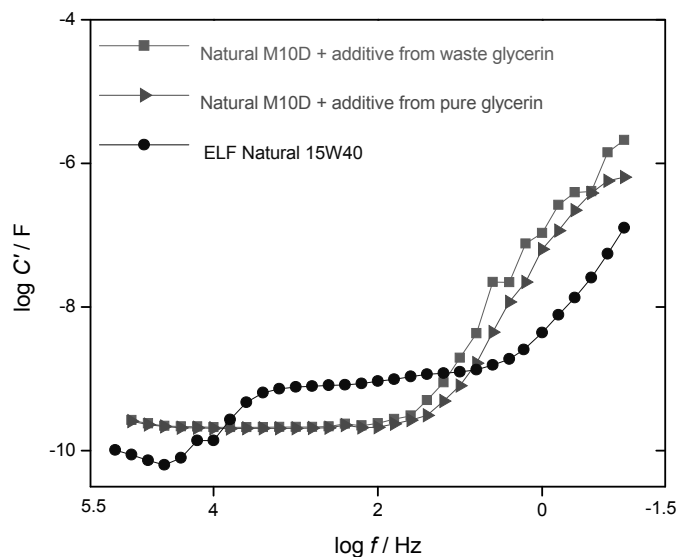
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One of the most important social, economic, and technical problems of the global world is related to the rational use of the fuel and energy resources from the nature.

The quality of the lubricants is essential both for the transport and the economy sectors since high quality oils provide reduced friction and high compression to internal combustion engines. The presence of highly active additives in motor oils can significantly increase their lubricating properties.

The classical methods used for motor oil quality characterization are slow and time consuming. Therefore, the development of modern methods for their rapid screening is of great interest.

The present investigation aims to use Dielectric Impedance Spectroscopy (DIS) to perform rapid characterization of the complex properties of motor oils. DIS can be also used as a basis for non-destructive oil quality analysis.



**Fig.1. Effective capacity frequency dependence of 3 motor oil samples**

The conducted experiments led to the development of a new methodology. It is based on the frequency analysis of the real part  $C'$  of the impedance in a wide frequency range. At low frequencies a "gigantic enhancement" of the effective capacitance  $C'$  is observed. The value of this enhancement is used as a measure of the oiliness. In high quality oils, the enhancement of  $C'$  is larger and faster, and occurs at higher frequencies.

The phenomenon can be explained with the formation of a highly polarizable dipole structure called "dipole micelle". The results obtained by the DIS study are fully consistent with the results obtained by classical testing in an accredited laboratory.

### Acknowledgement

The authors acknowledge Operational Programme "Development of the Competitiveness of the Bulgarian Economy" 2007-2013 Grant Agreement № BG161PO003-1.1.06-0102-C0001 and the National Innovation Fund Grant Agreement BG 6IF-02-28 for the financial support that made possible the publication of this paper.

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## The Influence of Donor Density on Electrochemical Processes Taking Place across the Ti|TiO<sub>2</sub> Interface

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Although the mechanism for oxide breakdown and local metal dissolution are not completely understood for Ti, it is widely accepted that electric-field assisted electron and/or ion transfer processes on the passive oxide film are involved [1]. The chemical and electronic properties of the native and/or anodically formed oxide film on Ti that control interfacial charge transfer are, therefore, of both fundamental and technological importance. Microscopic models that may account for both chemical/ionic and electronic properties of the oxide are based on the point defect model (PDM), suggested by Macdonald [2] to describe either the oxide growth and breakdown for many metals, as well as the electrochemical oxygen reduction/evolution reactions on passive Ti [3,4]. Moreover, modified PDMs were utilized to gain understanding of the metastable pitting induced by chlorides [5,6] and the spatially-localized electrochemical activity of Ti interacting with bromides [7]. TiO<sub>2</sub> is an n-type semiconductor with oxygen vacancies (donors,  $N_D$ ) as the main charge carrier.

The role of oxygen vacancies on interfacial electrochemical reactions occurring across the Ti|TiO<sub>2</sub>|electrolyte system is investigated in this study. Tuning of the oxygen vacancy concentration controls the rate and extent of surface processes. In contrast to the destabilizing effect of the bromide oxidation leading to localized corrosion, the electrochemical oxidation of aniline (AN) results in the polyaniline (PAN) film formation and oxide stabilization. The Ti|TiO<sub>2</sub>-PAN electrodes were stable in air, while exhibit a characteristic electrochemical response in acidic solutions, that differs from that obtained for PAN deposited on conventional electrodes.

The Ti|TiO<sub>2</sub> electrodes were prepared galvanostatically by applying different current densities,  $j_{app}$ , on a Ti substrate immersed in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. Different  $j_{app}$  led to TiO<sub>2</sub> films of same thickness but with varied concentrations of oxygen vacancies ( $V_O^{\bullet\bullet}$ ). The concentration of  $V_O^{\bullet\bullet}$  in TiO<sub>2</sub> was estimated via Mott-Schottky analysis. To ensure that the oxide thickness remained constant for different  $j_{app}$ , a constant upper potential limit was used during the galvanostatic formation. The pretreatment procedure, namely electrochemical reduction of the native TiO<sub>2</sub> (of a thickness,  $L \sim 20\text{\AA}$ ) or chemical etching, affects the reaction rates. The former procedure facilitates electron transfer processes as the galvanostatically grown oxide film found to contain a higher concentration of oxygen vacancies, in comparison with the chemical etching procedure. The rate of oxidation reactions and polymerization increases upon increasing the donor density,  $N_D$ . Cyclic voltammetry and electrochemical impedance spectroscopy were used to characterize the Ti|TiO<sub>2</sub> and Ti|TiO<sub>2</sub>-PAN electrodes in sulfuric acid solutions. The morphology of the unmodified and modified Ti|TiO<sub>2</sub> electrodes was examined by scanning electron microscopy. The different redox behavior of the Ti|TiO<sub>2</sub>-PAN electrodes seems to be related with the electronic properties of the interfacial system that lead to a multistep PAN reduction. Its origin is discussed on the basis of the different electrochemical response obtained for PAN films, upon limiting the upper switching potential for a cyclic potential sweep deposition, and when galvanostatic and potentiostatic techniques were used for the PAN formation.

### References

- [1] N. Casillas, S.R. Snyder, W.H. Smyrl, H.S. White, *J. Phys. Chem.* 95 (1991) 7002.
- [2] D.D. Macdonald, *Pure Appl. Chem.* 71 (1999) 951.
- [3] B. Roh, D.D. Macdonald, *Russ. J. Electrochem.* 43 (2007) 125.
- [4] S. Ahn, D.Y. Kim, H.S. Kwon, *J. Electrochem. Soc.* 153 (2006) B370.
- [5] Z. Jiang, T. Norby, H. Middleton, *Corrosion Science* 52 (2010) 3158.
- [6] Z. Jiang, X. Dai, T. Norby, H. Middleton, *Corrosion Science* 53 (2011) 815.
- [7] D. Sazou, K. Saltidou, M. Pagitsas, *Electrochim. Acta* 76 (2012) 48.

## Structural Changes During the Overoxidation of Electrochemically Deposited Poly(3,4-Ethylenedioxythiophene) Films

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Among the organic conducting polymers poly(3,4-ethylenedioxythiophene), often abbreviated as PEDOT, and its derivatives appear to be among the most stable organic conducting polymers currently available. Previous studies with metal|PEDOT|electrolyte solution systems have shown that at sufficiently positive electrode potentials degradation of the polymer film takes place. In some cases structural changes of the polymer layer (the change in the film stress) caused by overoxidation could be detected by using the electrochemical bending beam method [1,2]. The morphological changes of the films during the degradation process in aqueous sulfate solutions were analyzed by scanning electron microscopy (SEM). Changes of the effective mass of the Au|PEDOT film were studied by EQCM. Impedance spectra recorded before and after overoxidation were analyzed. The results support the mechanistic picture, according to which the originally compact and strongly adherent polymer films undergo structural changes during electrochemical degradation [2,3], and agree with earlier observations that the porosity of the film increases progressively during the degradation process.

This topic may be an interesting subject for further studies, since according to literature reports conducting polymers in different overoxidation states show unique features useful for analytical, sensing and biomedical applications, e.g. it has been reported in [4] that overoxidized poly(3,4-ethylenedioxythiophene) film-modified screen-printed carbon electrodes exhibited superior sensitivity and selectivity for the recognition of electrochemical probes. The basis for the observed selectivity of overoxidized films is not entirely clear, although in some cases it has been attributed to the increase in porosity of the polymer layer [5].

In order to highlight some of the features mentioned above, PEDOT (Poly(3,4-ethylenedioxythiophene)) films deposited on gold (and immersed in sulfate or perchlorate solutions) have been selected as illustrative examples. It can be seen from the SEM images of overoxidized Au|PEDOT that the degradation process induces a partial delamination of the polymer film from the underlying metal. Delamination may occur due to stress induced crack growth between the film and substrate. According to SEM images the overoxidation/degradation of PEDOT films can result in random-like, but quite well-ordered arrays of islands and trench-like structures. X-ray diffraction results showed that besides degradation, the crystallinity of the PEDOT film was also gradually improved with increasing number of overoxidation cycles [6]. These changes may result in the generation of sites with novel catalytic and binding properties that may be advantageous for specific applications.

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### References

- [1] G.G. Láng C. Barbero, Laser techniques for the study of electrode processes, in: Scholz F (ed) Monographs in electrochemistry, Springer, Berlin, Heidelberg, 2012.
- [2] M. Ujvári, M. Takács, S. Vesztergom, F. Bazsó, F. Ujhelyi, G.G. Láng, J Solid State Electrochem 15 (2011) 2341-2349.
- [3] G.G. Láng, M. Ujvári, F. Bazsó, S. Vesztergom, F. Ujhelyi, Electrochim Acta 73 (2012) 59-69.
- [4] J.M. Lin, Y.L. Su, W.T. Chang, W.Y. Su, S.H. Cheng, Electrochim. Acta 149 (2014) 65–75.
- [5] A. Boateng, F. Iraque, A. Brajter-Toth, Electroanalysis 25 (2013) 345–355.
- [6] M. Ujvári, J. Gubicza, V. Kondratiev, K. J. Szekeres, G.G. Láng, J. Solid State Electrochem. 19 (2015) 1247–1252.

## Galvanic Replacement as a Route for the Preparation of Multi-Metallic $M_{\text{noble}}(M)$ Electrocatalysts

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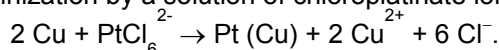
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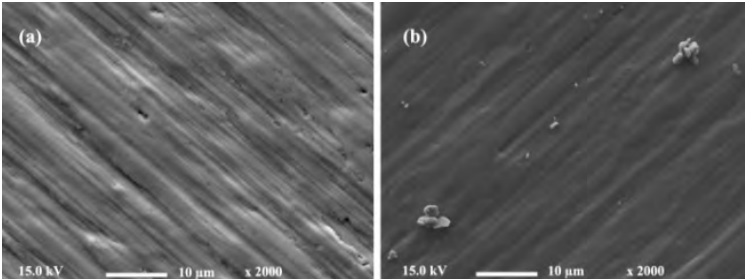
Multi-metallic catalysts with a noble metal shell,  $M_{\text{noble}}$  ( $M_{\text{noble}}$ : Pt, Au, Ru, or their combinations), and a core consisting of their alloy with a less noble metal, M (M: Pb, Cu, Co or Ni), have been prepared by the galvanic replacement method [1, 2] and are denoted as  $M_{\text{noble}}(M)$  hereafter. The method is based on the spontaneous replacement of layers of M (which have been chemically, electrochemically or photochemically deposited on an electrode substrate) by  $M_{\text{noble}}$ , during the immersion of M into solutions of  $M_{\text{noble}}$  ions. For example, Cu platinization by a solution of chloroplatinate ions, Pt(IV), occurs according to the reaction:



The initial deposits of M are formed either by electrodeposition on a glassy carbon substrate (for basic research studies) or by chemical or electroless deposition on high surface area carbons of the fuel cell technology (Vulcan XC72R; for the preparation of practical catalysts) or semiconductor photocatalyst powders ( $\text{TiO}_2$  or  $\text{WO}_3$ ). In the case of  $\text{TiO}_2$ , Cu can be photodeposited from its ionic solutions during illumination by UV light. SEM and TEM micrographs reveal the formation of micro- or nano-  $M_{\text{noble}}(M)$  particles (depending on the substrate and the method of M deposition), whereas EDS and Auger spectroscopy points to  $M_{\text{noble}}$  penetration into the core of the particles. XPS spectroscopy has confirmed the metallic nature of both metals, while XRD measurements indicate their alloying. Finally, the surface electrochemistry of the  $M_{\text{noble}}(M)$  catalysts in deaerated acid solutions, following electrochemical and/or acid treatment, points to the formation of a pure  $M_{\text{noble}}$  shell. The modification of the electronic properties of the  $M_{\text{noble}}$  shell by strain or/and ligand effects due to the underlying M alters the catalytic properties of the former for a number of fuel cell related reactions (namely ORR, BOR, MOR and CO oxidation). In this communication, emphasis is given in: a) methanol and CO oxidation on PtRu(Ni) trimetallic catalyst layers, b) methanol and CO oxidation on Pt(Cu) and Pt(Ni) supported either on C or  $\text{TiO}_2$  or  $\text{WO}_3$  and c) the operation of a  $\text{H}_2/\text{O}_2$  PEM fuel cell based on the developed catalysts in CO-contaminated streams of  $\text{H}_2$ .

### References

- [1] Papadimitriou, S., Armyanov, S., Valova, E., Hubin, A., Steenhaut, O., Pavlidou, E., Kokkinidis, G., Sotiropoulos, S.\*, J.Phys.Chem. C, 114 (11) (2010) 5217-5223.
- [2] Mintsouli, I., Georgieva, J., Armyanov, S., Valova, E., Avdeev, G., Hubin, A., Steenhaut, O., Dille, J., Tsiplakides, D., Balomenou, S., Sotiropoulos\*, S. Applied Catalysis B: Environmental Volume 136-137, 5 June 2013, 160-167.



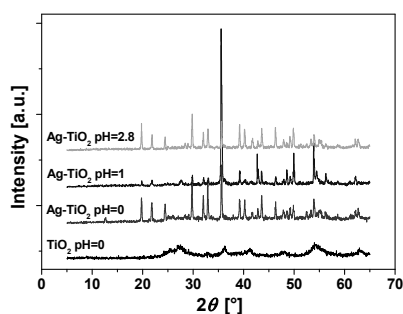


Fig. 2. XRD spectra for Ti-coated for TiO<sub>2</sub> sol (pH = 0) and Ag-TiO<sub>2</sub> sol at different pHs (0, 1, 2.8).

Electrochemical measurements performed in a simulated body fluid (pH 7.4) demonstrate good protection of the TiO<sub>2</sub> and Ag-TiO<sub>2</sub> coatings for the titanium substrate (Fig. 3). The presence of silver can be detected electrochemically as the peak at ~0.1 V related to the dissolution of silver. Topographic image of the surface of Ag-TiO<sub>2</sub> coatings identifies the presence of silver nanoclusters and surface roughening (Fig. 3).

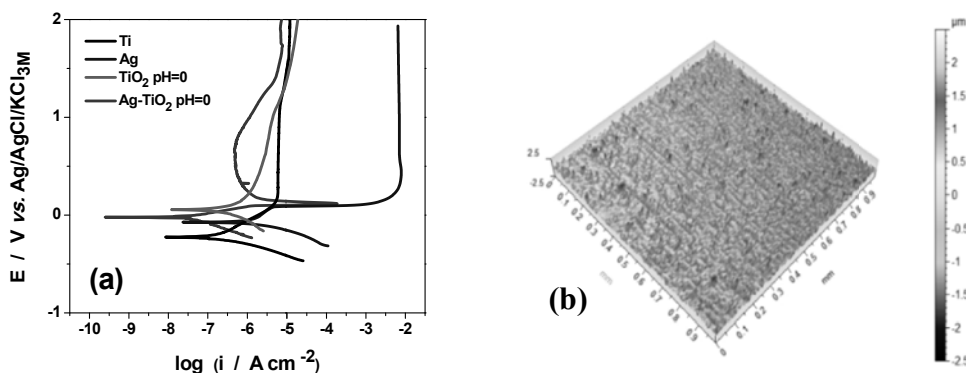


Fig.3. (a) Potentiodynamic polarization curves recorded in simulated body fluid (SBF) at 37 °C for Ti and Ag substrates, and Ti substrates coated with TiO<sub>2</sub> and Ag-TiO<sub>2</sub> coatings obtained from sol of pH=0.

(b) Side view of profiles of Ag-TiO<sub>2</sub> coated titanium substrates recorded after measurement in SBF. The colouring is according to the scale on the right which spans the  $\pm 2.5 \mu\text{m}$  range.

It was concluded that the coatings prepared from sols at very low pH values (pH=0) confer best anticorrosion protection to Ti substrates. These coatings will be the basis for the further study of antibacterial properties.

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## References

- [1] K. Niespodziana, K. Jurczyk, M. Jurczyk, *Rev. Adv. Mater. Sci* 18 (2008) 236.
- [2] Y. Liu, X. Wang, F. Yang, X. Yang, *Microporous Mesoporous Mater.* 114 (2008) 431.
- [3] I. C. Lavos-Valereto, B. König, C. Rossa, E. Marcantonio, A. C. Zavaglia, *J. Mater. Sci. Mater. Med.* 12 (2001) 273.
- [4] I. C. Lavos-Valereto, S. Wolynec, I. Ramires, A. C. Guastaldi, *J. Mater. Sci. Mater. Med.* 15 (2004) 55.
- [5] G. Fu, P. S. Vary, C.-T. Lin, *J. Phys. Chem. B* 109 (2005) 8889.
- [6] S. A. Amin, M. Pazouki, A. Hosseinnia, *Powder Technol.* 196 (2009) 241.
- [7] A. Amarjargal, L. D. Tijing, H. R. Pant, C. H. Park, C. S. Kim, *Curr. Appl. Phys.* 12 (2012) 1106.
- [8] B. Zhao, Y-W. Chen, *J. Phys. Chem. Solids* 72 (2011) 1312.

## Simultaneous Determination of Cd(II) and Pb(II) by Square Wave Voltammetry Based on Carbon Paste Electrode Modified with Bisdoped Carbon Xerogel

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The toxic heavy metal ions Cd(II) and Pb(II) may simultaneously exist in real samples, their detection being necessary in these conditions [1]. The paper presents a new carbon paste electrode (CPE), containing Bi doped carbon xerogel (BiCXe). The proposed electrode was used for the Pb(II) and Cd(II) ions determination at trace levels by using square wave anodic stripping voltammetry (SWASV) [2,3]. The *ex situ* preparation of BiCXe involved the sol-gel technique. The electrochemical properties and applications of the modified CPE were studied by SWASV. Operational parameters such as a graphite powder:xerogel mass ratio, deposition potential, deposition time, pH, preconcentration time were optimized for the purpose of trace metal ions determination in 0.1M acetate buffer solution (pH 4.5) under the optimal conditions determined for the individual detection of ions [4]. The SWASV voltammograms obtained in a solution containing Cd(II) and Pb(II) ions are shown in fig 1. The anodic peak currents of both metal ions were well-defined and placed at -0.8 V vs. Ag/AgCl, KCl<sub>sat</sub> and -0.54 V vs. Ag/AgCl, KCl<sub>sat</sub>, for Cd/Cd(II) and Pb/Pb(II) oxidation, respectively. From the calibration curves for the Cd(II) and Pb(II) ions mixture the calculated sensitivities are:  $9.36 \pm 1.13$  A/M for Cd(II) ( $R = 0.980$ ,  $n = 5$ ) and  $17.31 \pm 1.68$  A/M for Pb(II) ( $R = 0.986$ ,  $n = 5$ ). BiCXe-CPE has been found sufficiently selective, so it can be applied not only to individual determination of Cd(II) or Pb(II), but also to the simultaneous determination of Cd(II) and Pb(II).

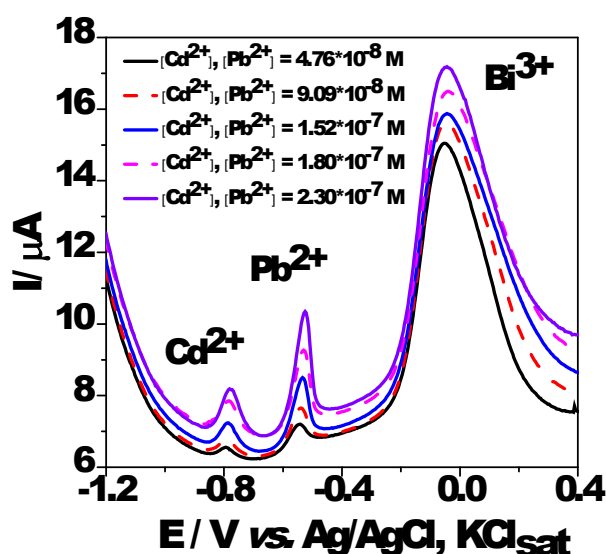


Fig.1. SWASVs responses for increasing concentrations of Cd(II) and Pb(II) at BiCXe-CPE. Experimental conditions: electrolyte, 0,1 acetate buffer pH=4.5, starting potential, -1.3 V vs. Ag/AgCl, KCl<sub>sat</sub>; deposition time 120 s under continuous stirring; frequency 25 Hz; amplitude 0,05 V; step potential, 0.004V, electrode conditioning, +0.3 V vs. Ag/AgCl, KCl<sub>sat</sub>; duration, 20 s under continuous stirring at 500 rpm, equilibration time, 10 s.

### References

- [1] W. Wonsawat, S. Chuanwatanakul, W. Dungchai, E. Punrat, S. Motomizu and O. Chailapakul, *Talanta*, **2012**, *100*, 282–289
- [2] J.H Luo, X.X Jiao, N.B Li and H.Q Luo, *J. Electroanal. Chem.*, 2013, 689, 130–134
- [3] K.C. Armstrong, C.E. Tatum, R.N. Dansby-Sparks, J.Q. Chambers and Z.L Xue, *Talanta*, 2010, 82, 675–680.
- [4] D. Li, J. Jia and J. Wang, *Talanta*, **2010**, *83*, 332-336

## Fabrication of Superhydrophobic Stearic and Myristic Salt Layers by Anodic Growth and Cathodic Deposition

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Superhydrophobic surfaces are characterized by a static water contact angle greater than 150 degrees. These surfaces have certain interesting properties, such as self-cleaning ability, corrosion protection etc.

In the present work, superhydrophobic surfaces on metallic substrates are fabricated by electrochemical methods and studied by electrochemical, optical and spectroscopic techniques. The superhydrophobic surfaces consist of salts of saturated fatty acids, specifically myristic and stearic acid. The growth of these layers is achieved either by anodic or cathodic polarization in a two electrode electrochemical cell. The electrolytic solutions are methanolic or ethanolic solutions of the corresponding acid, with or without supporting electrolyte.

An example of a deposited myristic salt layer on a copper substrate for different anodic growth times and applied potential of 100 V, is shown in Figure 1(a) and (b). The hydrophobic layers have a characteristic blue color, having the best performance when the growth time is between 150 and 195 minutes.

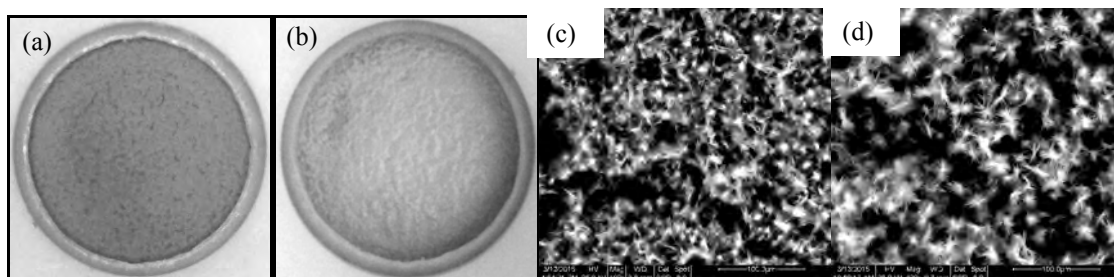


Fig. 1. Images of the myristic salt layer after (a) 150 and (b) 195 min. SEM images after (c) 150 and (d) 240 min. Applied voltage 100 V.

As can be seen in the SEM images (400x magnification), Figure 1(c) and (d), the layer has a characteristic morphology, consisting of flower-like structures, having a diameter of about 10  $\mu\text{m}$ . It is believed that the superhydrophobic properties are a result of this special morphology, as air is trapped in the cavities and prevents the water from further wetting the surface. FTIR, XRD and EDS measurements confirmed that the layer consists of a copper (II) salt of the corresponding fatty acid.

The ability of the above layers to protect the metallic substrate against corrosion was tested by immersing in 3.5% NaCl and 0.1 M  $\text{H}_2\text{SO}_4$  solutions. For 1 week of immersion, the layer was acting as a perfect barrier and the system was exhibiting only capacitive properties, with no sign of corrosion. Corrosion tests performed with Electrochemical Impedance Spectroscopy for thin/incompletely formed layers at low applied voltages (approx. 1 V) revealed that even these layers exhibit high impedance values, corresponding to low corrosion rates.

### References

- [1] T. Darmanin, E.T. De Givenchy, S. Amigony, F. Guittard, *Adv. Mater.* 25 (2013) 10.
- [2] Y. Huang, D.K. Sarkar, X.-G. Chen, *Mater. Lett.* 64 (2010) 24.
- [3] Y. Huang Y., D.K. Sarkar, D. Gallant, X.-G. Chen, *Appl. Surf. Sci.* 282 (2013) 689.
- [4] Z. Chen, L. Hao, C. Chen, *ECS Electrochem. Lett.* 1 (2012) D21.

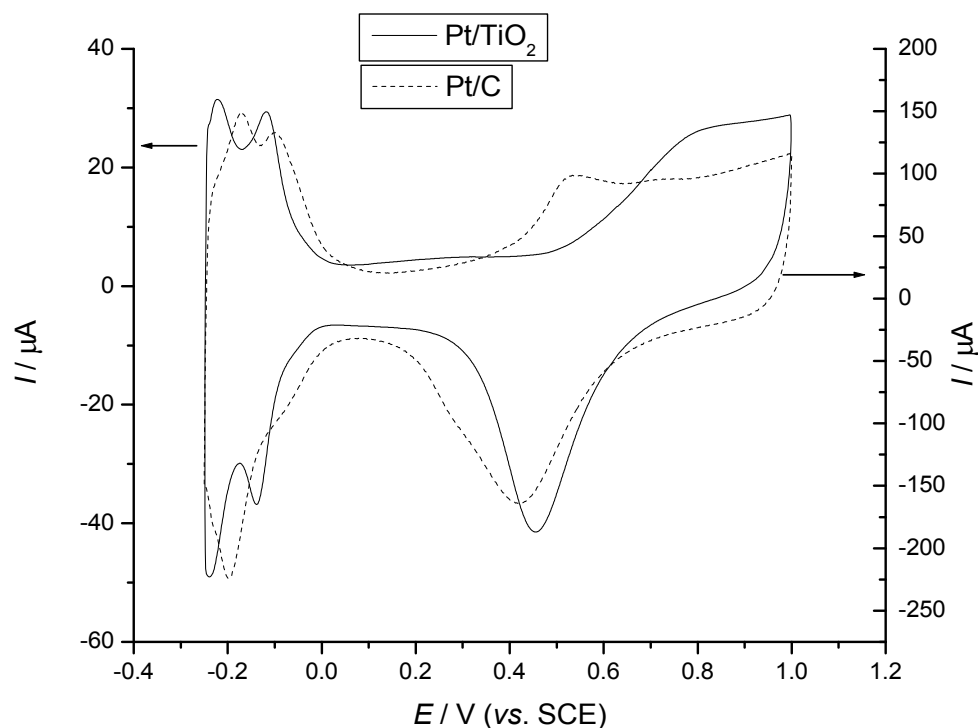
## Controlled Colloidal Synthesis and Basic Electrochemical Properties of TiO<sub>2</sub>-Supported Pt

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TiO<sub>2</sub> was synthesized by forced hydrolysis process in order to be used as the support for Pt electrocatalyst (Pt/TiO<sub>2</sub>). Pt was deposited from Pt colloid solution synthesized by microwave-assisted polyol process. TiO<sub>2</sub> powder (or C) was dispersed into H<sub>2</sub>O and 2 M H<sub>2</sub>SO<sub>4</sub>. The obtained suspension was stirred and Pt colloid was added afterwards. Upon filtration and rinsing with water, the obtained Pt/TiO<sub>2</sub> (or Pt/C) catalyst was thermally treated at 160 °C in N<sub>2</sub> atmosphere. The catalyst water suspension for the preparation of 0.31 mg/cm<sup>2</sup> thin layer electrode was loaded onto glassy carbon disk. Physical and chemical properties of the TiO<sub>2</sub> and supported Pt catalyst were characterized by EDS, SEM, dynamic light scattering and XRD techniques. The influence of TiO<sub>2</sub> thermal treatment on the electrochemical properties of Pt/TiO<sub>2</sub> was also checked. Nominal Pt loading was 20 wt. %. EDS method revealed 18 wt. % loading of Pt on TiO<sub>2</sub>. The electrochemical properties of the Pt/TiO<sub>2</sub> were examined by cyclic voltammetry in 0.1 M HClO<sub>4</sub>. The obtained results were compared with those obtained for carbon-supported Pt under the same conditions (Figure 1). The charge corresponding to the hydrogen desorption on Pt/TiO<sub>2</sub> is lower than expected for 20 wt. % Pt. Although the voltammetric response is typical for Pt-based electrode material, the charge corresponds only to ~3 wt. % Pt. SEM images showed that TiO<sub>2</sub> particles tend to form 3µm-sized agglomerates of ellipsoidal shape. The results indicate the possibility for platinum particles to be trapped inside TiO<sub>2</sub> agglomerates. Even though calcination of TiO<sub>2</sub> improved the Pt uptake from colloidal dispersion, it is still not as effective as commercial carbon support.



**Figure 1.** Cyclic voltammograms of Pt supported on thermally treated TiO<sub>2</sub> and Pt/C in deaerated 0.1 M HClO<sub>4</sub>, sweep rate 50 mV s<sup>-1</sup>.

## Structure and Giant Magnetoresistance of Electrodeposited Co/Cu Multilayers Prepared by Two-Pulse (G/P) and Three-Pulse (G/P/G) Plating

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Co/Cu multilayers produced by two different deposition strategies were compared. One series of Co(2 nm)/Cu( $t_{Cu}$ ) multilayers with  $t_{Cu}$  ranging from 0.5 nm to 6 nm was prepared with the conventional two-pulse plating by using a galvanostatic/potentiostatic (G/P) pulse combination for the magnetic/non-magnetic layer deposition [1], respectively, whereby the Cu layer deposition was carried out at the electrochemically optimized potential [2]. Another Co(2 nm)/Cu( $t_{Cu}$ ) multilayer series with the same  $t_{Cu}$  range was prepared with the help of a G/P/G pulse combination. In this latter case, first a bilayer of Co(2 nm)/Cu(6 nm) was deposited in each cycle as in the G/P mode after which a third G pulse was applied with a small anodic current to dissolve part of the 6 nm thick Cu layer in order to ensure the targeted  $t_{Cu}$  value.

The comparison of the two series revealed that the G/P/G pulse combination yields multilayers for which giant magnetoresistance (GMR) can be obtained even at such low nominal Cu layer thicknesses where G/P multilayers already exhibit bulk-like anisotropic magnetoresistance only. Surface roughness measurements by AFM revealed that the two kinds of pulse combination yield different surface roughnesses the value of which correlates with the structural quality of the multilayers as indicated by the absence or presence of multilayer satellite reflections in the XRD patterns. A separation of the superparamagnetic (SPM) contribution from the total observed GMR [3] provided useful hints at the understanding of differences in layer formation between samples prepared with the two kinds of pulse combination. The results of multilayer chemical analysis revealed that mainly an increased Cu content of the magnetic layer is responsible for the onset of SPM regions in the form of Co segregations in the G/P/G multilayers with small Cu layer thicknesses.

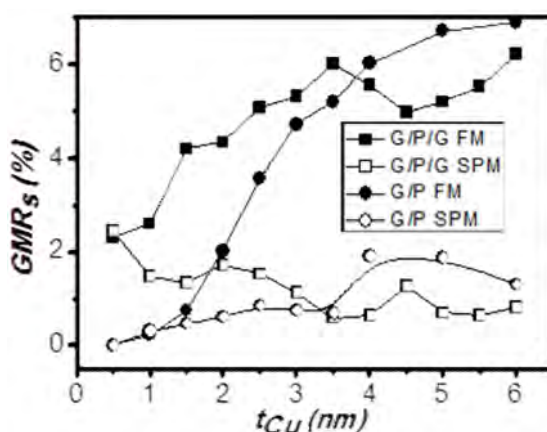


Fig. 1. Ferromagnetic (FM) and superparamagnetic (SPM) components of the magnetoresistance of the multilayers produced with two-pulse and three-pulse plating

### References

- [1] V. Weihnacht, L. Péter, J. Tóth, J. Pádár, Zs. Kerner, C. M. Schneider, I. Bakonyi, J. Electrochem.Soc. 150 (2003) C507.
- [2] L. Péter, Q. X. Liu, Zs. Kerner, I. Bakonyi, Electrochim. Acta 49 (2004) 1513.
- [3] I. Bakonyi, L. Péter, Z. Rolik, K. Kis-Szabó, Z. Kupay, J. Tóth, L. F. Kiss, J. Pádár, Phys. Rev. B 70,(2004) 054427.

## Electrodeposition of Cd-Ni alloys: comparison of the modified Watts bath and the chloride bath

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Both nickel and cadmium are a prominent components of anticorrosive coatings. They form two equilibrium alloys, Cd<sub>5</sub>Ni and CdNi with a few atomic percent homogeneity range [1]. The establishment of the phase diagram of the Cd-Ni system was based on structural studies of metallurgically processed samples [2-4]. Although some studies have revealed the possibility of the formation of these alloys by electroplating [5,6] and their dissolution behaviour [6], no parallel electrochemical and structural study is available on the Cd-Ni system. The goal of the present research is to correlate electrochemical, composition and structural properties of Cd-Ni deposits obtained from two bath types, a modified Watts bath and a full-chloride bath.

The solutions were first investigated with cyclic voltammetry. An unusually large difference was found between the voltammograms recorded for macroscopic electrodes and microelectrodes. While at macroelectrodes the Cd deposition and dissolution could hide the signs of alloy formation, the stripping peaks characteristic of the Cd-Ni alloys were always present if microelectrodes were used. This clearly indicates the role of spatial confinement on the codeposition phenomenon. The formation of Cd-Ni alloys could be verified with voltammograms of multiple stages in combination with a quartz crystal microbalance observation.

The ratio of the stripping peaks related to the dissolution of Cd-Ni alloys was different in the two baths. The chloride bath was much more favourable for the alloy formation than the modified Watts bath. If saccharine was also present in the Watts-type bath, the sulphur incorporation to the Cd-Ni alloys was significant, which was identified as a possible reason for the lack of lines corresponding to the alloys in the X-ray diffractograms. However, a few lines of the CdNi phase could be observed on samples produced from the sulphur-free chloride bath. The Ni content of the samples deposited from the chloride bath was much larger compared to the modified Watts bath. The scanning electron micrographs could help to identify the crystals of pure Ni in the deposit.

### References

- [1] T.B. Massalski (Ed.), Binary Alloy Phase Diagrams Plus Updates on CD-ROM. ASM International, Materials Park, Ohio, USA, 1996.
- [2] F.A. Shunk, P. Nash, J. Phase Equilibra 8 (1987) 122.
- [3] H.J. Goldschmidt, M.J. Walker, J. Appl. Cryst. 2 (1969) 273.
- [4] P. P. Jana, S. Lidin, Cryst. Eng. Comm. 15 (2013) 745.
- [5] U.S. Mohanty, B. C. Tripathy, P. Singh, S.C. Das, J. Electroanal. Chem. 526 (2002) 63.
- [6] V.D. Jović, N. Tošić, J. Electroanal. Chem. 441 (1998) 69.

## TEM and XRD Investigation of Grain and Defect Structure in Electrodeposited Nanocrystalline Nickel

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Electrodeposited thin films usually have a grain size in the nanocrystalline range [1], especially if some kind of organic additive is used in the electrolyte [2] since additives have an effect on the defect structure. Microstructural features are responsible for many macroscopic properties of materials (eg. corrosion, conductivity, abrasion resistance, plasticity threshold etc.). In the present work, the effect of two kinds of organic additive (saccharin and formic acid) on the microstructure (texture, grain size, twin boundaries and dislocations) of electrodeposited Ni films was investigated by transmission electron microscopy (TEM) and X-ray diffraction (XRD) line profile analysis.

A detailed analysis of the defect structure was carried out: not just the average parameters of the microstructure but the detailed distribution of grain sizes, twin boundary spacings and twin texture were determined. In comparison with former papers of this area, new results of our work are the homogeneity investigations in both planar and cross-sectional directions and the detailed TEM measurements about the twin spacing and grain size distributions. A particular virtue of the present study is the comparison of TEM and XRD results on the very same samples, both without and with additives.

In films deposited with no additive, a columnar structure with (200) texture was observed after a structure stabilization period of a few micrometer thickness, showing similarities to the T-zone of structure zone models [3] proposed for atom-by-atom deposition methods used for growing thin films.

The addition of both formic acid and saccharin resulted in nanocrystalline films with decreased grain size (20-50 nm) and increased defect density (both the density of dislocations and twin boundaries). Both effects were stronger in deposits obtained with saccharin additive (in this case, the Ni film contained about 0.3 at.% S as revealed by energy dispersive X-ray spectroscopy). In addition, in the presence of these additives in the bath, the structure became homogeneous and free of texture throughout the total deposit thickness. Detailed grain size and twin boundary spacing distributions were determined from TEM which confirmed the presumptions of X-ray line profile analysis (viz. spherical grains, lognormal and geometric distributions of grain size and twin spacing, respectively). According to the cross-sectional TEM images taken on the sample deposited with saccharin, the average grain size remained constant throughout the total deposit thickness. Both films deposited with an organic additive contained numerous nano-twins [4]. Their density can be hardly measured by TEM but can be well evaluated from XRD profiles. TEM shows that twin boundaries typically span over the whole grain, have no texture and the average size of grains containing twin boundaries is two or three times larger than the average grain size.

In conclusion, both XRD and TEM methods evidenced that the application of organic additives induces smaller grain size and higher number of lattice defects and also eliminates the strong texture. Saccharin as additive was more successful in this regard, presumably due to the codeposited sulphur.

### References

- [1] A.M. El-Sherik et al., *Surf. Coat. Technol.* 88, (1996) 70
- [2] A. M. El-Sherik and U. Erb, *J. Mater. Sci.*, 30 (1995) 5743
- [3] I. Petrov, P.B. Barna, L. Hultman and J.E. Greene, *J. Vac. Sci. Technol. A* 21 (2003) S117
- [4] G.Z. Meng, Y.W. Shao, T. Zhang and F.H. Wang, *Electrochimica Acta* 53 (2008) 5923

## Electrochemical Studies of $\text{YBaCo}_2\text{Fe}_2\text{O}_{7.5}$ in Aqueous Solutions

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$\text{YBaCo}_4\text{O}_{7+\delta}$  cobalt perovskite, called Y-114, originally discovered by Valldor and Andersson in its stoichiometric oxygen  $\delta = 0$  [1], shows remarkable ability for the intake/release oxygen [2-4]. Layered crystal structure of this compound allows local changes in arrangement of atoms, which leads to a variable oxygen content. Thermogravimetric studies have revealed that the perovskite Y-114 captures an excess of oxygen corresponding to  $\delta \geq 1$  during heating it in air or oxygen flow, and then release it the further increase in temperature, the whole process of intake/ release of oxygen being achieved in a narrow range of temperature between 200 and 400°C [1]. From the point of practical use, a critical problem is the thermal instability of Y-114 at high temperature. As soon as the optimum temperature of the reversible process of intake/release oxygen, by continuing the heating to 700-800°C, Y-114 phase begins to decompose in a mixture of  $\text{BaCoO}_{3-\delta}$  and CoO and other compounds containing Y and Co [1].

In order to increase the stability of the Y-114 phase, the control of the chemical composition is one of the most promising methods. It is known that perovskite Y-114 supports different types of cation substitutions, of which the most important are: Ca and smaller atoms such as rare earth elements (Dy, Ho, Er, Tm, Yb and Lu) to substitute Y and Fe, Zn, Al and Ga for substitution of Co [5]. It was proposed the substitution of half number of cobalt ions with iron ions; the new compound has the formula  $\text{YBaCo}_2\text{Fe}_2\text{O}_{7+\delta}$ , and using the method of preparation chosen  $\delta=0.5$ . The paper presents how the substitution affects the electrochemical behavior of the new compound and the ability to intake/release of oxygen by electrochemical methods.

In the present study it was followed the electrochemical characterization of  $\text{YBaCo}_2\text{Fe}_2\text{O}_{7.5}$  compound correlated with the study of oxygen intake/release process in neutral and alkaline aqueous solutions. Electrochemical behavior has been studied by cyclic voltammetry, chrono electrochemical methods and electrochemical impedance spectroscopy. In correlation with these techniques the compound morphology was determined by scanning electron microscopy. Compound porosity was determined using BET technique.

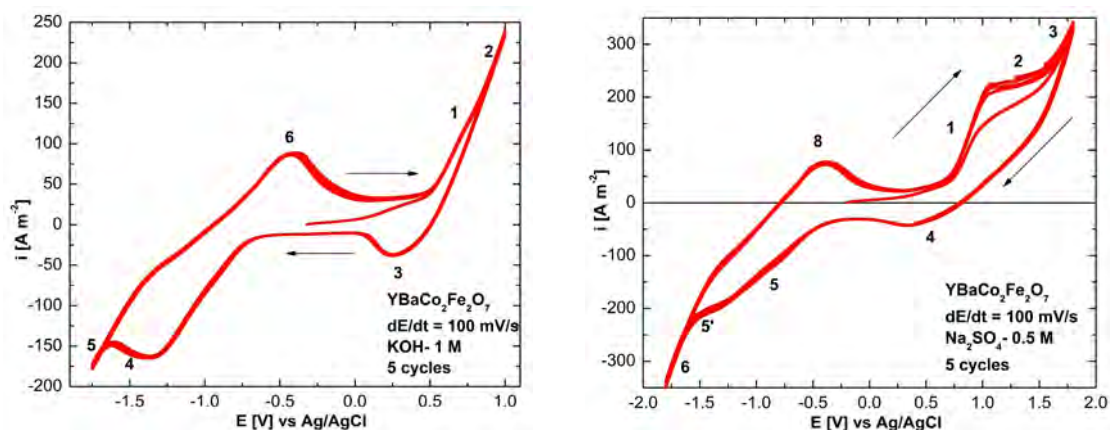


Fig.1. Cyclic voltammograms plotted on  $\text{YBaCo}_2\text{Fe}_2\text{O}_{7.5}$  in alkaline (a) and neutral (b) aqueous solutions

### References

- [1] M. Valldor and M. Andersson, *Solid State Sci.* 4 (2002) 923-931;
- [2] O. Chmaissem, H. Zheng, et al., *J. Solid State Chem.*, 181, (2008), 664-672;
- [3] M. Dan, N.Vaszilcsin, A. Kellenberger, N. Duteanu, *Studia Universitatis Babes-Bolyai, Chemia*, 56(1), (2011), 119-126;
- [4] M. Dan, N.Vaszilcsin, A. Kellenberger, N. Duteanu, *J. Solid State Electrochem.*, 15(6), (2011), 1227-1233;
- [5] O. Parkkima, H. Yamauchi, M. Karppinen, *Chem. Mater.*, 25(4), (2013), 599-6

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## Electrocoagulation: an Electrochemical Process for Water Cleaning

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Electrocoagulation is a collective term for a couple of procedures that are generally used for removing various – mostly suspended material type - contaminants from water.

The basics of all of these procedures are as follows: Assume an electrolysis cell with a metal (Me = Al or Fe) anode, and some neutral aqueous solution with *dc* flowing through it. On the cathode hydrogen evolution, on the anode metal dissolution proceeds, the metal dissolution yields  $\text{Me}^{z+}$  ( $\text{Al}^{3+}$  or  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ) ions. These cations induce the decontamination by two different ways:

(1) The ions of high positive charge, in accord with the Schulze-Hardy rule, cause the coagulation of the contaminant colloids of negative surface charge. Decontamination in this case means that the coagulated colloids finally are separated from the liquid phase.

(2) In neutral aqueous solutions the hydrolysis of the  $\text{Me}^{z+}$  proceeds immediately yielding  $\text{Me}(\text{OH})_z$ . The growth of  $\text{Me}(\text{OH})_z$  particles starts as polynuclear complexes, continues as growth of colloids, which finally merge yielding flocs. During the growth, certain components of the solutions, like the contaminating particles, substances can be incorporated in the flocs, thereby finally the flocs comprise of the metal-hydroxide and the contamination. Decontamination effect is a consequence of incorporation, which is much more pronounced at the initial stage of the hydroxide formation. In other words, the "nascent"  $\text{Me}(\text{OH})_z$  colloids are the active particles rather than the big flocs.

Depending on their specific density, the merged particles are separated from the liquid in two ways: either precipitate, or form a float or a scum (note that even the relatively heavy flocs may float if are attached to hydrogen bubbles evolved on the cathode). The difference between the two basic separation techniques of the electrocoagulation: electroflocculation and electroflotation, is ultimately based on the specific density of the merged particles (sink or swim).

Here we note that  $\text{Me}^{z+}$  ions just as the  $\text{Me}(\text{OH})_3$  colloids can be generated by simply dissolving Me-salts in water, the main advantage of the electrochemical generation of the coagulant ion (over that of dissolving the salts) is that electrochemically the "nascent" colloid is formed and introduced in the bulk of the solution in a much more controlled way – this is why electrocoagulation is regarded to be more efficient [hiv].

Various sorts of electrocoagulation - as water cleaning, or wastewater processing industrial procedures - have been introduced since the begin of the past century. However, due to big energy costs and to various technical problems (mostly: inhibition of electrodes' dissolution) the procedure could not penetrate in industrial water- and waste-water processing up till recently. In the recent years a number of enterprises appear and sell electrocoagulation process units, typically with 1-10 m<sup>3</sup>/h capacity. Also the number of the technical papers have been increasing in the past twenty years. Most of these are on experiments on removal of some, usually organic contaminants from some wastewater. The list of the substances which can be - or at least were attempted to be - removed is fairly long; most of them are oily emulsions or other colloid-forming organics. Nevertheless, removal of inorganic compounds (e.g. heavy metals from groundwater or from effluents of various metal industries) has also been implemented.

Despite the boom of the technical papers, the number of studies published in scientific – in particular, electrochemistry-related – journals is small. The lack of interest of the researchers of the academia is probably due to the complicated nature of phenomena associated with electrocoagulation; in which many and diverse physico-chemical processes are scrambled. There is a big need for results of well-defined, "single issue" experiments characterizing the main processes of electrocoagulation. Our aim is to highlight single electrochemical steps (issues) within this complex phenomenon/procedure.

## Zn-Cr Electroplating of Steel

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The alloying with Cr significantly improves the corrosion resistance and the protective potential of Zn coatings at a reduced layer thickness. This main benefit determines the interest of the automotive industry and leading steel manufacturing companies to the production of Zn-Cr alloy coatings for corrosion protection of steel substrates. The electrodeposition of Zn-Cr alloy coatings has been optimized for high speed deposition on steel strips for car body application in the automotive industry [1]. Best results in corrosion protection, respectively lifetime have been obtained with Zn-Cr coatings in combination with a corrosion resistant layer, making the final product costly. Further achievement in the Zn-Cr alloy production would be the optimization of the deposition process for batch galvanizing, focused on coatings with higher Cr content, good exposed quality and sufficient corrosion protection without additional layers. Following this concept, a part of a comprehensive study of the effect of the electrolyte composition and hydrodynamics upon appearance, morphology and composition of the alloy will be presented. Cyclic voltammetry, galvanostatic and potentiostatic methods were used for investigating the deposition process. Experiments were carried out on rot, flat samples and rotating cylinder electrodes. Coatings were characterized by using RFA, SEM, EDX and XRD.

### References

- [1] T. Steck, J. Gerdenitsch, A. Tomandl, W. Achleitner, J. Faderl, T. Lavric, T. Boiadjieva-Scherzer, H. Kronberger, "Zinc-chromium coated steel sheet: properties and production", *8th International Conference on Zinc and Zinc Alloy Coated Steel Sheet, IAM* (2011), 1133

## Electrodeposition of Nickel and Nickel Alloys from Alcoholic Solutions

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Although the overwhelming majority of technologically relevant electroplating procedures are based on various aqueous solvents, there are cases where the application of non-aqueous solutions offers advantages over the traditional baths or even in some cases represents the only way to electrodeposit some metals. While the appearance of non-aqueous molecular solvents is rather scattered in the literature of electroplating, the application of ionic liquids soon became a hot topic. In the present study, the comparison of aqueous bath, non-aqueous solutions and ionic liquids will be compared from many view-points.

A comparative study of the electrodeposition of Ni from various alcoholic solutions will be presented. The list of solvents used include the following alcohols: methanol, ethanol, ethylene glycol, glycerol, 1,2 propanediol and 1,3 propanediol. The dry nickel(II) salt was in all cases nickel chloride which is commercially available in non-hydrated form and it is soluble in all alcohols used in the present study. The solubility of NaCl was also sufficient to use it in 0.1 mol/liter concentration as a supporting electrolyte.

The conductivity of various solutions has been measured. The detailed cyclic voltammetric study of the solutions applied will be shown to establish the background of the sample preparation. The cyclic voltammetric experiments were completed with a quartz crystal microbalance study of the deposition and dissolution of Ni in the methanolic bath. The surface morphology, crystal structure and texture as well magnetic properties of the deposits have also been investigated. The best results were obtained with methanol as solvent. The nickel samples deposited were comparable to those obtained with aqueous solutions in terms of both structural and magnetic properties. The lattice distance of nickel obtained from methanol corresponds to metallurgical standards, while its magnetization behaviour was identical to nickel electroplated from aqueous baths. However, some other alcohols led to non-metallic deposits, which was due to the formation of a precipitate of the nickel salt and the decomposition product of the solution.

Deposition of Fe-Ni alloys also proved to be possible from methanol. The composition of these samples showed that the electrodeposition of Fe besides Ni can be classified as anomalous codeposition, similarly to the aqueous baths.

Since the electrodeposition of manganese alloys is a particularly difficult task in the case of aqueous solutions, Mn-Ni deposits were produced from methanol. The preliminary assessment of the deposit quality was performed with the help of optical micrographs. The trends related to the deposit composition as a function of the sample preparation parameters have been established. Although the codeposition of manganese took place, the diffraction patterns were all characteristic of nickel rather than a Mn-Ni alloy. The ratio of metallic Mn in a Ni-rich deposit was determined with X-ray photoelectron spectroscopy. These experiments showed that the majority of Mn incorporated is not metallic, similarly to deposits obtained from aqueous solutions.

### References

- [1] K. Neuróhr, L. Pogány, B. G. Tóth, Á. Révész, I. Bakonyi, and L. Péter, *J. Electrochem. Soc.* 162 (2015) D256

## Optimization of Electrochemical Copper Recovery Process: Effect of the Steering Speed in Chloride Medium of pH=3

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The wastewater pollution by heavy metals remains today one of the important problems to solve in the industrialized countries. Various conventional methods are used to remove these metals. In the present work, the effect of the steering speed on copper recovery by electrodeposition from synthetic medium of pH=3 has been studied. In order to optimize electrodeposition and facilitate recovery, we have used a chloride electrolyte [1].

Copper was deposited potentiostatically on a graphite electrode with graphite auxiliary electrode and saturated calomel electrode as a reference.

Cyclic voltammetry, electrochemical impedance spectroscopy and chronoamperometry were used to characterize the kinetics of nucleation and electroplating of copper deposits. The study of the effect of the scanning rate on cyclic voltammograms in the presence and absence of agitation shows that the copper was deposited under diffusion control in quasi reversible process with partial oxidation of bulk deposited copper.

Characterization of the deposits formed at different stirring speeds was done by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The quality of the deposits obtained depended strongly on agitation. Our goal was to obtain copper deposit which was easily removable from the cathode due to a dendritic growth mechanism in the presence of chlorides ions.

Excellent copper removal percentage and the current efficiency of the deposition, equal to 94% and 99% respectively, have been obtained at a steering speed of 1500rpm [2].

### References

- [1] C. Gabrielli, P. Moçotéguy, H. Perrot, R. Wiart, J. Electroanal. Chem. 572 (2004) 367.
- [2] A.S. Pilla, M.M.E. Duarte, C.E. Mayer, J. Appl. Electrochem, 30 (2000) 831.

## Ni-(Ebonex-Supported-Ir) Composite Coatings as Cathodes for Hydrogen Evolution Reaction in Alkaline Solution

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The hydrogen evolution reaction (HER) was studied at electrodeposited Ni and Ni-(Ebonex-30wt.%-Ir) coatings in 1 mol dm<sup>-3</sup> NaOH solution at 25°C. The Ni-(Ebonex-30wt.%-Ir) coatings were electrodeposited from a nickel Watt's type bath containing corresponding suspended particles (0 to 2 g dm<sup>-3</sup>) onto Ni 40 mesh substrate. The electrodes were investigated by cyclic voltammetry (CV), scanning electron microscopy (SEM-EDS), electrochemical impedance spectroscopy (EIS) and polarization measurements. It was shown that the roughness factor of coatings increases with increasing the content of the Ebonex-30wt.%-Ir particles to a maximum value of 26.9, while that of pure Ni coating was found to be 3.15. In the whole potential range of the HER only one Tafel slope of about -120 mV dec<sup>-1</sup> was present at all polarization curves. The increase of catalytic activity for the HER at Ni-(Ebonex-30wt.%-Ir) coatings was attributed only to the increase of the electrochemically active surface area, while the high intrinsic catalytic activity has already been achieved with addition of the lowest amount of incorporated Ebonex-30wt.%-Ir particles (0.1 g dm<sup>-3</sup>).

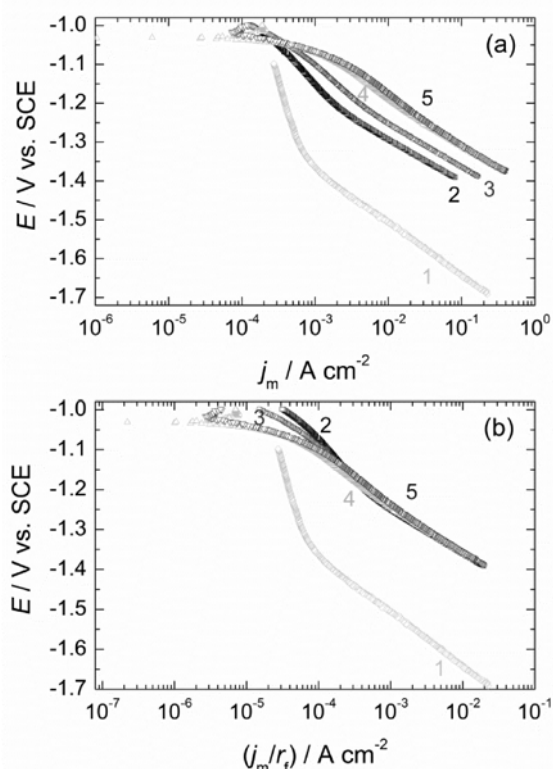


Fig. 1. (a) Measured polarization curves for all investigated samples: 1 – Ni; 2 – Ni + 0.1 g dm<sup>-3</sup> Ebonex-30wt.%-Ir; 3 – Ni + 0.5 g dm<sup>-3</sup> Ebonex-30wt.%-Ir; 4 – Ni + 1.0 g dm<sup>-3</sup> Ebonex-30wt.%-Ir; 5 – Ni + 2.0 g dm<sup>-3</sup> Ebonex-30wt.%-Ir (b) The same polarization curves corrected for the  $r_f$

## Removal of Heavy Metals from Wastewaters by Electrodialysis in the Presence of Ion Exchange Membranes

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The treatment of plating rinse waters containing dissolved metals represents a major environmental concern in the metal plating industry. This paper aims the cadmium ions removal from wastewater by electrodialysis in the presence of ion exchange membranes.

The use of electrodialysis to remove cadmium from water has been shown to be feasible in a wide range of conditions. As much as three orders of magnitude reduction in the concentration of cadmium was observed for the feed with the concentrate stream from the process containing cadmium concentrations greater than 100 mg/L. The effect of cadmium concentration and water pH was also discussed.

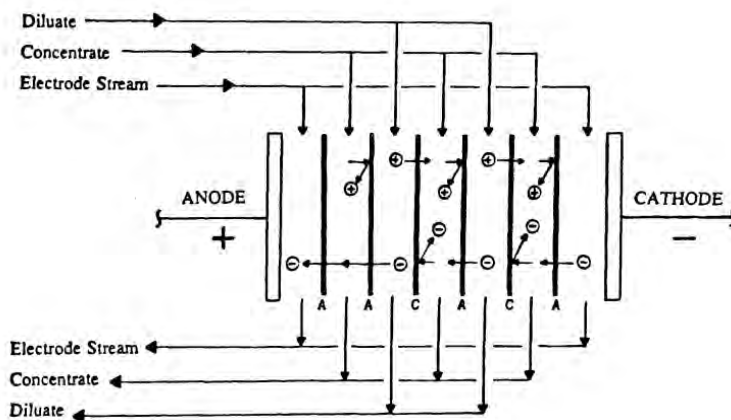


Fig. 1 Schematic representation of of experimental set-up (A – anion exchange, C – cation exchange) [1]

The results of this study allowed identifying and relating significant parameters that influence the cadmium ion transport through different polymer membranes which contained various resins (Purolite A500 and Hypersol-Macronet MN500). The results showed that the cadmium ions removal ratio by electrodialysis was increased with the augmentation in the metal ion concentration. The removal ratio of the ionic species was higher (>85%) when concentrated solution were treated (0.1 g/L). This fact demonstrated the excellent separation features of the studied membranes.

### Acknowledgements

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### References

- [1] R. Delimi, N. Boutemine and Z. Benredjem, E3S Web of Conferences published by EDP Sciences, 2013, p. 25011
- [2] A. Smara, R. Delimi, E. Chainet, J. Sandeaux, Separation and Purification Technology, Volume 57, Issue 1, 1 October 2007, Pages 103–110
- [3] M. G. Minciuna, P. Vizureanu, D. C., Achitei, Brandusa Ghiban, A. V. Sandu, D. Mareci, Adriana Balan Rev chim, 65 (10), 2014, p. 1138-1141.

## Mathematical and Kinetic Modeling of Aluminium Anodes Behavior during Electrocoagulation Process

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The drastically increase of legislative regulations regarding the wastewater discharged lead to an urgent need to develop innovative and more effective methods. In this context, electrocoagulation seems to be one of the most effective alternatives [1,3]. Electrocoagulation is an electrochemical technique used for potable water and various wastewaters containing: dyes, fluoride, surfactants, oil-in-water treatment [2].

In this paper, aluminium sacrificial anodes behavior was monitored. Different operational parameters, namely: electrolysis time, temperature and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) concentration influence on aluminium anodes dissolution was investigated in a systematic manner. The optimum temperature and sulphuric acid concentration were found to be 333 K and 6%, respectively. The reaction rate strongly depends on the temperature reason for which activation energy was calculated. The activation energy values obtained for different H<sub>2</sub>SO<sub>4</sub> concentrations and correlation coefficient are similar to those obtained in other studies presented in the literature ( $E_a = 23.2 \text{ J/mol}$ ,  $R^2 = 0.9777$ ). The results of this study were optimized by means of an experimental mathematical model created using Mathcad 14 programme. The use of this mathematical programme allows the identification of optimal operating conditions, important for further experimental studies. Partial order of reaction and reaction rate constant were determined by means of the graphical integral method.

**Keywords:** mathematical, kinetic, modeling, aluminium, anodes, electrocoagulation

### References

- [1] G.Mouedhen, M.Feki, M.DePetris Wery, H.F.Ayedi, J.Haz.Mat., 150, (2008), p.124
- [2] J.S.Do, M.L.Chen, J.Appl.Electrochem., 24, (1994), p.785
- [3] A. R. Miron, C. Modrojan, O. D. Orbuleț, Rev. Chim., 61, (2010), p.646-650

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## Iron and Manganese Removal from Drinking Water

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The purpose of the study is to find a suitable method for removal of iron and manganese from ground water, considering local economic and environmental aspects. Ground water is highly important source of drinking water in Romania. Ground water is naturally pure from bacteria at a depth of 25 m or more, however solved metals may occur and if the levels are too high the water is unsuitable to drink. Different processes, such as electrochemical and combined electrochemical-adsorption methods were used to obtain both metals content to the level in accordance to reports of National Water Agency from Romania (ANAR). Every water source contains dissolved or particulate compounds. The concentrations of these compounds can affect health, productivity, compliance requirements, or serviceability and may not be economically removed by conventional filtration means.

In this study we made a comparison between the electrochemical and adsorption (using membranes) methods. Both methods have been used to evaluate the efficiency to remove iron and manganese at different times and temperatures. We used two membranes: composite and respectively cellulose. Different approaches including lowering the initial current density and increasing the initial pH were applied. Kinetics of the reaction was achieved using mathematical models: Jura and Temkin isotherms.

*Keywords:* Ground water, manganese, iron, mathematical models

### Acknowledgements

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### References

- [1] W.-L. Chou, C.-T. Wang, K.-Y. Huang, T.-C., Desalination 271 (2011) 55.
- [2] M. Malakootian, N. Yousefi, Iran. J. Environ. Health. Sci. 6 (2009) 131.
- [3] M. Zaw, B. Chiswell, Water Res. 33 (1999) 1900.
- [4] H.D. Doan, M. Saidi, Journal of Hazardous Materials, 151 (2008) 306.

## The Effect of Organic Compounds on the Oxidative Dissolution of Chalcopyrite (CuFeS<sub>2</sub>)

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In the presence of dissolved oxygen CuFeS<sub>2</sub> undergoes an oxidative dissolution reaction which contributes to the phenomenon of acid mine drainage (AMD). AMD is characterized by low pH and high concentrations of toxic elements, such as Cu, Cd, Hg, As, etc. [1,2]. As the rate of the oxidative dissolution of mineral sulfides can be influenced by the organic molecules, the purpose of this study is to investigate by electrochemical techniques the effect of three organic compounds (Pr02: 4-Phenyl-2-N-morpholinyl-thiazole; Pr04: N, N-diethyldithiocarbamate 1-(3,5-dibromo-2-hydroxyphenyl) -1-oxoetan-2-yl; and Pr06: a-ethylxantogenat of 1-(5-bromo-2-hydroxy-3-methylphenyl) -1-oxoetan-2-yl) on the chalcopyrite oxidation.

Potentiodynamic polarization measurements were performed at pH 2.50 and 25°C. The working electrode was a carbon paste electrode (CPE) containing pretreated CuFeS<sub>2</sub>. The pretreatments were carried out with ethanol or 1 mM ethanolic solutions of Pr02, Pr04 and Pr06, respectively.

The experimental results show that the three organic compounds accelerate the oxidative dissolution of CuFeS<sub>2</sub>. The current densities corresponding to the oxidative dissolution of CuFeS<sub>2</sub> ( $i_{ox}$ ) increase from 84  $\mu\text{A cm}^{-2}$  (ethanol) to 124  $\mu\text{A cm}^{-2}$  (Pr02), 351  $\mu\text{A cm}^{-2}$  (Pr04) and 173  $\mu\text{A cm}^{-2}$  (Pr06), respectively.

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### References

- [1] P. Chirita, M.I. Duinea, C.E. Badica, M.L. Schlegel, *Procedia Earth and Planetary Science*, 10 (2014) 149.
- [2] P Chirita., C.E. Badica, C.A. Constantin, M.L. Birsa, E. Matei, M. Baibarac, *Surface and Interface Analysis*, 46 (2014) 842.

## The Oxidative Dissolution of Galena (PbS) in the Presence of Hydrogen Peroxide

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The oxidative dissolution of PbS produces divalent lead ( $\text{Pb}^{2+}$ ), which is a toxic species. Because the hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is among the most powerful natural oxidants of PbS [1], the main objective of this study is to investigate the oxidative dissolution of galena in the presence of hydrogen peroxide using electrochemical methods.

Electrochemical measurements were performed with a carbon paste electrode (CPE) covered with PbS powder. The concentration of  $\text{H}_2\text{O}_2$  was varied in the range of 1-10 mM, the temperature was  $30^\circ\text{C}$  and pH 2.00. The results of the potentiodynamic polarization experiments (Fig. 1) show that the current density associated to the oxidative dissolution of galena ( $i_{\text{ox}}$ ) increases when the concentration of the oxidant increases from 1 mM ( $0.13 \mu\text{A cm}^{-2}$ ) to 10 mM ( $4.61 \mu\text{A cm}^{-2}$ ).

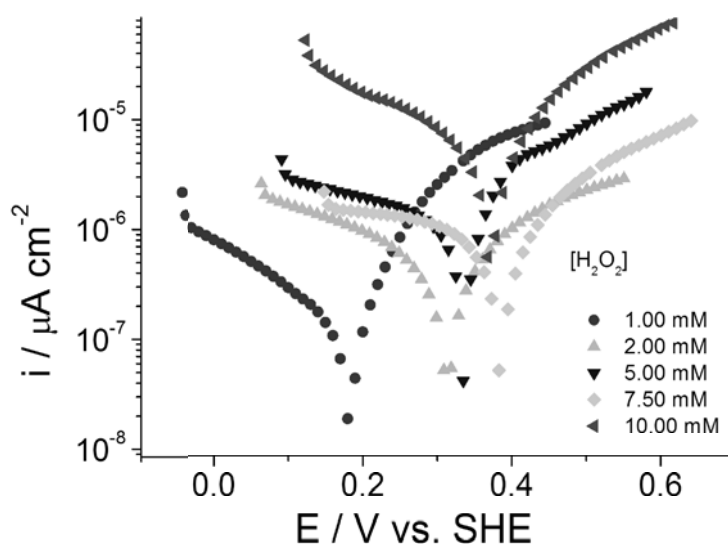


Fig. 1. Potentiodynamic polarization curves for PbS in  $\text{H}_2\text{O}_2$  solutions at pH 2.00 and  $30^\circ\text{C}$

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### References

- [1] A.J. Nooshabadi, K.H. Rao, *Adv. Powder Tech.*, 25 (2014) 832.

## Corrosion Resistance of Electrodeposited Zn-Cr Alloy Coatings

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Number of studies demonstrate better corrosion protective properties of electrodeposited Zn-Cr alloy coatings on steel in comparison to Zn coatings. The electrodeposition of the Zn-Cr alloy coatings has been optimized for high speed deposition on steel strips for car body application in the automotive industry [1, 2]. In order to achieve the final product, the electrogalvanized steel sheet undergoes intermediate treatments, including application of additional layers in alkaline and acidic solutions. In this respect, the question about the corrosion resistance of the alloys rises. The present work is focused on the corrosion behavior of Zn-Cr alloy coatings with different Cr content in a model corrosion media, in the range of pH 1-13. The investigations were performed by means of electrochemical methods, atomic-absorption analysis (AAA), X-ray fluorescent analysis (XRFA), X-ray microanalysis (EDX) and scanning electron microscopy (SEM). It is shown that the Zn-Cr alloys are corrosion resistant in a wide range of pH. The dissolution rate significantly increases at  $\text{pH} \leq 3$ .

### Acknowledgement

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### References

- [1] T. Steck, J. Gerdenitsch, A. Tomandl, W. Achtleiner, J. Faderl, T. Lavric, T. Boiadjeva-Scherzer, H. Kronberger, Zinc-chromium coated steel sheet – properties and production, 8<sup>th</sup> International Conference on Zinc and Zinc Alloy Coated Steel Sheet Galvatech 2011, Genova (Italy), 21-24 June, 2011, Proceedings.
- [2] G. Luckeneder, M. Fleischanderl, T. Steck, K.-H. Stellnberger, J. Faderl, S. Schuerz, G. Mori, Corrosion mechanisms and cosmetic corrosion aspects of zinc-aluminium-magnesium and zinc-chromium alloy coated steel strip, 8<sup>th</sup> International Conference on Zinc and Zinc Alloy Coated Steel Sheet Galvatech 2011, Genova (Italy), 21-24 June, 2011, Proceedings.

## Co-Electrodeposition of Nickel and Hybrid Multi-Walled Carbon Nanotubes/ $\text{Al}_2\text{O}_3$ Particles

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In principle, nano-composite materials present superior properties than their simple counterparts. Such nano-composites can be fabricated by electrochemical cathodic co-deposition. In the present work, the effect of hybrid multi-walled carbon nanotubes/ $\text{Al}_2\text{O}_3$  particles (MWCNT/ $\text{Al}_2\text{O}_3$ ) on the deposition of Ni from Watts solution is studied by Linear Sweep Voltammetry (LSV), Electrochemical Impedance Spectroscopy (EIS) and Scanning Electron Microscopy (SEM). Moreover, the fabrication of a MWCNT electrode is attempted by selective electrodeposition of the nanotubes.

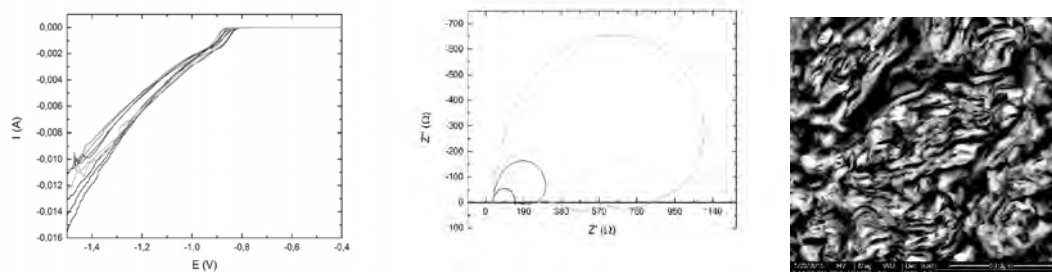


Fig. 1. (a) LSV for pure Watts (red), Watts-MWCNT/ $\text{Al}_2\text{O}_3$  (black) and Watts-MWCNT/ $\text{Al}_2\text{O}_3$ -SDS (green), (b) Nyquist plot at -0.8 V and (c) SEM image of MWCNT modified electrode.

In Figure 1(a), the LSVs for the electrodeposition of Ni from different baths are shown. The presence of nanotubes enhances the current in comparison to the case of the pure Watts solution. The presence of SDS does not further increase the cathodic current. The increase of the cathodic current may be due to increase of the Ni electrodeposition rate or the increase of the proton reduction rate. As can be seen in Figure 1(b), the Nyquist plots of the three different baths present the same qualitative features but they are quantitatively different. The charged transfer resistance in the case of the Watts-MWCNT/ $\text{Al}_2\text{O}_3$  bath is very small, indicating that Ni electrodeposition is catalyzed by the hybrid nanotubes. Similar conclusions are derived by comparing the LSVs with impedance spectra at various cathodic potentials.

In order to achieve selective deposition of MWCNT on a graphite electrode, potentiostatic pulse electrodeposition/electrodissolution was performed. During the cathodic portion of the pulse, co-deposition of Ni and nanotubes was occurring whereas during the anodic portion of the pulse, Ni was dissolved from the composite matrix. The resulting surface is shown in Figure 1(c). This surface morphology is completely different than the morphology of a graphite electrode, indicating that MWCNT actually remained on the electrode surface. This modified electrode has very good capacitive properties, estimated around  $9 \times 10^{-4}$  F, for apparent area of  $0.07 \text{ cm}^2$ . The capacitive properties of the electrode were evident during Cyclic Voltammetry in  $\text{K}_4\text{Fe}(\text{CN})_6$ , where the redox peaks almost disappeared due to the high value of the capacitance current.

### References

- [1] A. Bai-Gang, L. Li-Xiang, L. Hong-Xi, *Mat. Chem. and Physics* 110 (2008) 481.
- [2] S.H. YeH, C.C. Wan, *J. Appl. Electrochem.* 24 (1994) 993.
- [3] S.W. Watson, *J. Electrochem Soc.* 140 (1993) 8.
- [4] F. Daneshvar-Fatah, F. Nasirpour, *Surf. Coat. Tech.* 248 (2014) 63.

## Decolorization of Reactive Violet 5 Dye in Textile Wastewater by Electrocoagulation

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The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes. Wastewater from printing and dyeing units is often rich in color, containing residues of reactive dyes and chemicals, such as complex components. This study investigates the decolorization of synthetic dye wastewater containing textile dye Reactive Violet 5 (RV5) by electrocoagulation. A laboratory batch reactor was used to investigate the effect of various operating parameters using aluminium (Al), iron (Fe) and stainless steel (SS) anode. The effect of dye concentration, current density, supporting electrolyte, supporting electrolyte concentration, electrolysis duration, and material of anode of the systems were evaluated. Color removal efficiency was 22, 91.5 and 99.8% in 15 minutes using Al, Fe and SS anode, respectively ( $j=10 \text{ mA/cm}^2$ ,  $c_{\text{NaCl}}=0.171 \text{ M}$ ).

*Keywords: electrochemical degradation, reactive dye, Reactive Violet 5, RV5, textile wastewater.*

## Computational Study of Chlorine Production in a Bipolar Electrochemical Reactor for Ballast Tank Water Treatment

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Ballast water is an important factor for the stability and proper propulsion of ships. Ships fill their tanks with water at the port of departure and eject it at the port of destination. The introduction of new microorganisms in the marine ecosystem of the port of destination constitutes a major ecological problem. One of the methods used for the disinfection of ballast water is the electrolysis of seawater for the production of chlorine by anodic oxidation of chlorides. The aim of the present study is the modeling of an electrochemical reactor for the production of chlorine, by using the COMSOL Multiphysics software. The reactor consists of two feeder electrodes (anode and cathode) and a sequence of bipolar electrodes in a parallel configuration. The feed of seawater is considered to be continuous and the problem is solved under stationary conditions. On every bipolar electrode, three reactions are taking place, the production of chlorine, the production of oxygen and the production of hydrogen. More specifically: (a) The oxidation of chloride ions to chlorine occurs at the anode, (b) chlorine is hydrolyzed to hypochlorous oxide in the aqueous solution, (c) hypochlorous oxide is dissociated to hypochlorous anions and protons, (d) the electrolysis of water to oxygen occurs at the anode, (e) the reduction of water to hydrogen occurs at the cathode.

The computational study is based on the solution of a current distribution problem with boundary conditions the electrochemical kinetics on the feeders and the bipolar electrodes. The geometric characteristics of the reactor and the operational conditions are considered as parameters. An example is presented in Fig. 1.

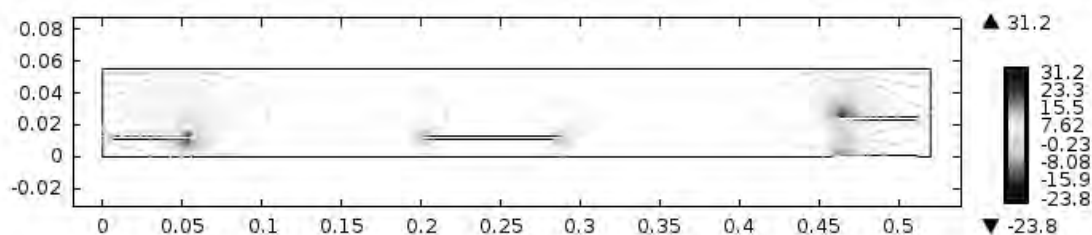


Figure 1. Contour of y-component of the current distribution in an electrolytic cell with 2 bipolar, 2 anode (left) and 3 cathode (right) electrodes while the lower axis is considered symmetric.

### References

- [1] J.O'M. Bockris, J. Chem. Phys. 24 (1956) 817.
- [2] D.M. Novak, B.V. Tilak, B.E. Conway, in: Modern Aspects of Electrochemistry, J.O'M. Bockris, B.E. Conway, R.E. White (eds), vol. 14, Plenum Press, New York, 1982, p. 195.
- [3] P. Byrne, Mathematical modelling and experimental simulation of chlorate and chlor-alkali cells, Ph.D. Thesis, Stockholm University, Sweden, 2001.
- [4] M. Deborde, U. von Gunten, Water Res., 42 (2008) 13.
- [5] J.F.L. Duval, M. Minor, J. Cecilia, H.P. van Leeuwen, J. Phys. Chem. B, 107 (2003) 4143.
- [6] J.F.L. Duval, H.P. van Leeuwen, J. Cecilia, J. Galceran, J. Phys. Chem. B, 107 (2003) 6782.
- [7] E. Mitha, Numerical Modelling of Potential and Current Distributions in a Bipolar Electrolytic Cell, Ph.D. thesis, École polytechnique fédérale de Lausanne, France, 1998.

## Electrochemical Treatment of Leather Industry Wastewater

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Leather industry wastewater is contaminated with bacteria including E.coli. The treatment of test solution of water, containing a high concentration of Cl<sup>-</sup> ion, by an electrochemical method using Mixed Metal Oxide (RuO<sub>2</sub>, IrO<sub>2</sub>) electrodes was investigated. In all experiments the same materials were used as anode and cathode except the two last where used anode was IrO<sub>2</sub> and in other RuO<sub>2</sub> and graphite cathode. Electrodes with platinum group metals or their oxides as active coatings are generally the best suited for electrochemical water disinfection. In this experiment, the efficiency of Cu and Al electrodes were tested directly and indirectly by oxidation of microorganisms present in the leather industry wastewater. After 7 min of electrolysis at only 0,018 A/dm<sup>2</sup>, Cl<sup>-</sup> was reduced and using both tested electrodes, the efficiency of microorganisms removal followed the order: Cu > Al. The electrochemical treatment of wastewater by leather industry resulted in the production of chlorine gas and hypochlorite, which is microorganisms inactivator. Also, electrocoagulation by Al anode has been in use for water production or wastewater treatment to reduce all pollutants, including chlorides and microorganisms. With this technology, metal cations are produced on the electrodes via electrolysis and these cations form various hydroxides in the water depending on the water pH. The effect of the main parameters – current density, initial pH, temperature and electrolysis cell construction on microorganism removal was investigated.

### References

- [1] J. Naumczyk, L. Szpyrkowicz, F. Zilio-Grandi, Electrochemical treatment of textile wastewater, Elsevier Science Ltd, Great Britain, 1996.
- [2] A. Kraft, M. Wünsche, M. Stadelmann, M. Blaschke, Wasserwirtschaft Wassertechnik, 2006, (9), 36.
- [3] Guohua Chen, Electrochemical technologies in wastewater treatment, Separation and Purification Technology, 2004, (38), 11–41.

## Expired Streptomycin as Additive in a Watts Nickel Electroplating Bath

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Modified Watts type baths are used in electrodeposition of nickel, nickel alloys or composite materials with special properties [1,2]. Investigation of the nickel deposition as well as its codeposition with other metals is still a challenge for electrochemists, mainly due to the availability to obtaining nanostructures and materials with magnetic properties and alloys for microelectronic applications [3]. Meanwhile, research continues in order to identify new Watts bath additives that improve its leveling capacity and corrosion resistance, adhesion, internal stress and brightness degree of deposits [4].

An important role in the achieving of the appropriate quality of nickel deposits (adherence, compactness and eventually brightness) is played by leveling agents and brighteners. Most effective additives of Watts type baths are aromatic compounds having an inhibitory effect on the cathodic nickel deposition [5]. Considering that most of the active substances of drugs are more expensive than the more common additives used in Watts baths, experiments were focused on expired drugs. Use of expired drugs active substances has two major benefits: limited environmental pollution by active pharmaceutical compounds and reduced cost of medical waste disposal.

In this paper, the studies on the inhibitory effect of streptomycin in the electrodeposition of nickel from Watts bath are presented. Streptomycin was chosen because pharmaceutical formulation of the commercial product contains only streptomycin sulphate without excipients.

Experimental studies presented in this paper demonstrate that expired streptomycin can be used as a leveling agent in nickel Watts bath. Streptomycin and its hydrolysis products inhibits the cathodic deposition of nickel.

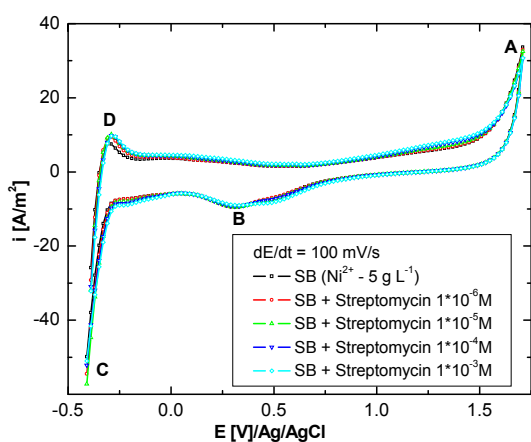


Fig. 1. Cyclic voltammograms on platinum electrode in various electrolyte solutions.

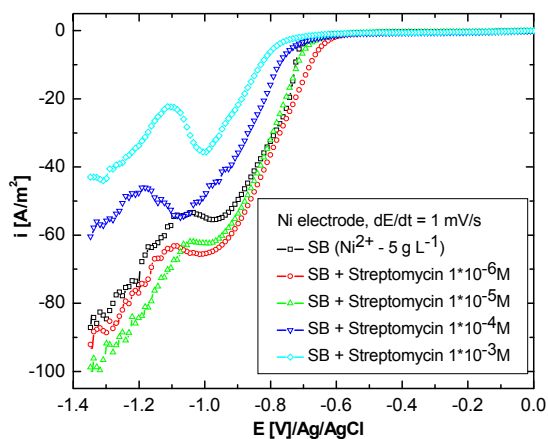


Fig. 2. Linear voltammograms on nickel electrode in various electrolyte solutions.

### References

- [1] S. Spanou, E.A. Pavlatou, N. Spyrellis, *Electrochim. Acta*, 54, (2009), 2547-2555.
- [2] N. Spyrellis, E. A. Pavlatou, S. Spanou, A. Zokis-Karathanasis, *Trans.Nonferrous Met.Soc.China*, 19, (2009), 800-804.
- [3] G.N.K.R. Bapu, S. Jayakrishnan, *Surface & Coatings Technology*, 206, (2012), 2330-2336.
- [4] A. Ciszewski, S. Posluszny, G. Milczarek, M. Baraniak, *Surface and Coatings Technology*, 183, (2004), 127-133.
- [5] E. Raub, K. Müller, *Fundamentals of Metal Deposition*, Elsevier, Amsterdam, (1967), p. 105-123.

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## Self-Deprotonation in Oxidation Mechanism of Quinoline Compounds

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The coupling of proton transfer with electron transfer was found to play an important role in the oxidation mechanism of hydroxyquinoline compounds [1]. Proton transfer often influences oxidation or reduction of organic compounds [2,3]. Auto-deprotonation takes part in their oxidation mechanism due to the nitrogen atom present in the chemical structure of studied compounds. Three starting molecules participate in oxidation of one molecule if no strong proton acceptor is present in the solution: two molecules serve as proton acceptors on account of the basicity of nitrogen heteroatom in the quinoline structure. The study is based on cyclic voltammetry and UV-Vis, IR spectroelectrochemistry. Oxidation products were identified using HPLC-MS/MS technique.

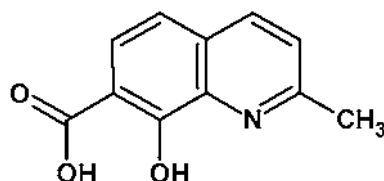


Fig. 1. Chemical structure of 2-methyl-8-hydroxyquinoline-7-carboxylic acid.

The oxidation of hydroxyquinolines proceeds quantitatively, when a strong proton acceptor for ex. pyridine, is present in the solution. Pyridine was chosen as a strong proton acceptor in this study, to mimic possible nitrogen containing heterocycles present *in vivo*. Our findings imply that in biosystems oxidation could proceed easily by the interactions with purine or pyrimidine bases and influence the efficiency of hydroxyquinoline drugs.

### Acknowledgment

This work was supported by the Academy of Sciences of the Czech Republic (M200401201).

### References

- [1] R. Sokolová, J. E. Nycz, Š. Ramešová, J. Fiedler, I. Degano, M. Szala, V. Kolivoška, M. Gál, J. Phys. Chem. B, 2015, under peer review.
- [2] C. Amatore, G. Capobianco, G. Farnia, G. Sandona, J.-M. Savéant, M.G. Severin, E.J. Vianello, J. Am. Chem. Soc. 107, 1985, 1815.
- [3] R. Sokolová, M. Hromadová, J. Ludvík, L. Pospíšil, S. Giannarelli, Electrochim. Acta 55, 2010, 8336.

## Stereoelectrochemistry of Molecules with Multiple Redox Centres. Influence of Structure on Electrochemical Reduction of Isomeric Mono- and Di-, Nitro- or Nitrosocalix[4]Arenes

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Calixarene skeleton is a favorite framework in supramolecular chemistry [1], which is, however, not electroactive. Therefore, for any direct electrochemical studies it's essential to introduce a redox probe, i.e. a functional group which undergoes reversible redox process(es) under conditions available in electrochemical measurements. Our project is focused mainly in nitro [1-5], if need by nitroso group [2]. Both of them – in the first step – are reversibly reduced in aprotic media by one electron to form a stable radical anion (1) [3]. (The next three-electron reduction process (2) yielding the corresponding hydroxylamine derivative follows at much more negative potentials.)



Calixarenes can exist in four atropoisomers: *cone*-, *paco*-, *1,2*- and *1,3-alt*. The series of studied compounds contains eight *cone*- and for comparison one *1,3-alt*-conformers, six of them bearing the nitro- and the other three nitroso group (Fig. 1-1-9). All of them contain propoxy groups on the lower rim in order to stabilize the specific conformation. The *cone*-derivatives generally don't have the ideally symmetrical bowl shape ( $C_{4v}$ ) but a "pinched" one, and are known to be involved in periodic conformational change ( $C_{2v} \rightarrow C_{4v} \rightarrow C_{2v}$ , Fig. 1-a-b) in solutions with frequency of  $10^2$ - $10^3$  Hz. This hypothesis has been confirmed experimentally by comparison of observed reduction behaviour of derivatives **1** and **2**: because both molecules are reduced by the first electron(s) in two separated steps (Table 1), consequently, there are two species which differ in energy, even in the case of the compound **1**. This effect points to the existence of two forms of mono-nitro derivative – the  $\text{NO}_2$  group is alternately at the "close" pair of the benzene rings and at the "distant" ones. According to the quantum-chemical calculations on similar systems [4] the first electron reduces the nitro group on the more "distant" pair of benzene rings. If the molecule contains more redox centres, a recent spectroelectrochemical study [5] proved formation of polyradical polyanions with unpaired spins.

On the other hand, the dinitro-*1,3-alt*-derivative **3** is rigid. This information is apart from usually used NMR techniques also readily accessible by DC-polarography and cyclic voltammetry: in contrast to the above mentioned derivative **2** there is only one single two-electron reversible process (Table 1). Such an approach when electrochemical data point to a certain actual molecular shape in the solution combining both stereochemical and electrochemical considerations, we call "stereochemistry". In the case of investigation of macrocyclic compounds it seems to be a worthy method not established yet.

The *m*- and *m/p*-nitro- and nitroso-*cone*-compounds **4-6** and **7-9** exhibit the same qualitative reduction pattern: first electron(s) reduce the molecule at one potential ( $\approx -1,25$  V in the case of nitro,  $\approx -0,96$  V for nitroso compounds). Thus, their skeleton must be rigid (the information proved independently). This finding shows that

- simple electrochemical methods can reveal the dynamics of calixarene systems in the solutions and
- the flexibility vs. rigidity of calixarene skeleton seems to be unpredictable on the basis of conformation knowledge itself.

The *m*- or *m/p*-polynitro-/nitroso-*cone*-calix[4]arenes are rigid like *p*-polynitro-*1,3-alt*-calix[4]arenes but only the *p*-substituted *cone*-calix[4]arenes are flexible. All the compounds **1-9** contain non-communicating redox centres (reduction of equivalent groups occurs within single

step). As expected, the nitroso derivatives are reduced at less negative potentials than the nitro analogues.

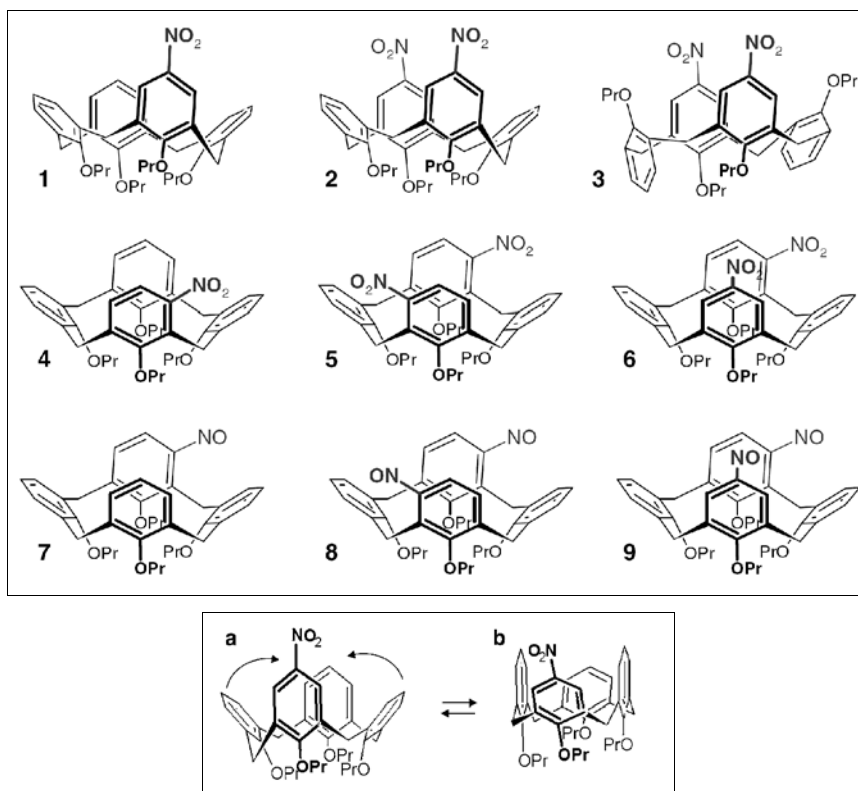


Fig. 1: Studied compounds (1-9) and schematic representation of "pinched cone-pinched cone interconversion" (a-b) [2]

Table 1: Overview of electrochemical data [2]

Compound	Potentials / V (vs. SCE)			Ratio of currents $\dot{i}_1 : \dot{i}_2 : \dot{i}_3$
	$E_{1A}$ (rev.)	$E_{1B}$	$E_2$	
1	-1,27	-1,37	-2,40 (broad wave)	0,5 : 0,5 : 3
2	-1,25	-1,43	-2,53 (broad wave)	1 : 1 : 6
3		-1,29	-2,21	2 : 0 : 6
4		-1,26	-2,26	1 : 0 : 3
5		-1,25	-2,29	2 : 0 : 6
6		-1,25	-2,32	2 : 0 : 6
7		-0,96	-1,58	1 : 0 : 0,25
8		-0,96	-1,60	2 : 0 : 0,5
9		-0,98	-1,52	2 : 0 : 0,5

### Acknowledgments

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### References

- [1] Flídrová, K., Liška, A., Ludvík, J., Eigner, V., Lhoták, P., Tetrahedron Letters (2015) DOI: 10.1016/j.tetlet.2015.02.016
- [2] A. Liška et al., Monatshefte für Chemie-Chemical Monthly, (2015) DOI: 10.1007/s00706-015-1441-8.
- [3] A. Liška, J. Ludvík, Chem Listy 104 (2010) 23.
- [4] A. Liška, P. Vojtíšek, A. J. Fry, J. Ludvík, J. Org. Chem. 78 (2013) 10651.
- [5] A. Liška, M. Rosenkranz, J. Klíma, L. Dunsch, P. Lhoták, J. Ludvík, Electrochim Acta 140 (2014) 572.

## Electrochemical Characterization of Some Obesity Regulation N-Oleoylamides

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This work is devoted to the synthesis and electrochemical characterization of some oleoylamides.

The compounds were synthesized from oleic acid and 1,1'-carbonyldiimidazole to give the oleyl-imidazol intermediate which reacted with the corresponding amines, according to the procedure described in [1]. The new oleoylamides were characterized by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR spectra.

Electrochemical investigations were performed by cyclic voltammetry, differential pulse voltammetry, and rotating disk electrode.

The results obtained are in agreement with the previous characteristics obtained for a similar compound [2].

### Acknowledgments

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/132395 and UEFISCDI projects 15/2011, and 236/2014.

### References

- [1] C. Tanase, C. Negut (Cioates), D. I. Udeanu, E.-M. Ungureanu, M. Hrubaru, C. Munteanu, S. P. Voicu, F. Cocu, A. C. Ionita, *Revista de Chimie*, 65 (7), (2014), p. 768-773.
- [2] C. Cioates (Negut), E.-M. Ungureanu, F. Cocu, C. Tanase, C. Drăghici, C. Munteanu, *Scientific Bulletin, Series B, Chemistry and Materials Science*, 76 (4), (2014), p. 173-182.

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## Concept of New Azulene Modified Electrodes for Heavy Metal Ions Analysis

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Electrochemical behaviour of several azulene-derivatives (L) has been investigated. Complexing polymer-coated electrodes have been synthesized by oxidative electropolymerization of L in acetonitrile solutions containing 0.1M tetrabutylammonium perchlorate. The films were characterized by cyclic voltammetry, differential pulse-voltammetry and scanning electron microscopy [1]. The complexing properties of L and these new polymer-coated electrode materials were investigated towards heavy metals leading to complexation of lead and cadmium metal cations inside the polymer film. The novel chelating chemically modified electrodes were used for the electrochemical detection of Pb(II) and Cd(II) ions by means of the chemical preconcentration–anodic stripping technique. The electrode material showed a particular selectivity towards lead ions, even in the presence of a large excess of other metal cations. Detection limits for lead(II) and cadmium(II) ions were in the range of nanomolar concentrations [2]. These modified electrodes have been used for the determination of lead in water samples.

### Acknowledgment

This work was supported by: UEFISCDI projects 15/2011 and 236/2014, Sectorial Operational Programme Human Resources Development (SOP HRD), financed from the European Social Fund and the Romanian Government under the contract number POSDRU/159/1.5/S/137390 (L.-R. MANDOC (POPESCU))

### References

- [1] G.-O. Buica, E.-M. Ungureanu, A. Razus, L. Birzan, M.-R. Bujduveanu, *Elchim. Acta*, 56 (2011) 5028-5036.
- [2] G.-O. Buica, E.-M. Ungureanu, L. Birzan, A.C. Razus, L.-R. Mandoc, *J. Electroanal. Chem.*, 693 (2013) 67 – 72.

## Investigation of Li Mass Transfer in Metal

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During the course of studying the Li insertion/deinsertion process of Li in the negative electrode material of Li-ion battery we happened to find the Li insertion in solid metal at room temperature. This induced us to measure the rate of diffusion of Li particle in solid phase. For the purpose of the determination of the Li diffusion rate in solid we found that the use of bipolar cell was quite convenient. We constructed a bipolar cell where a sample metal plate is sandwiched between the two facing cylindrical cell compartments, the plate being used as a working electrode. Propylene carbonate (PC) dissolved with 1 Molar LiClO<sub>4</sub> was filled in one of the cell compartment (Cell A) and 1 Molar NaClO<sub>4</sub> containing PC was filled in the other cell compartment (Cell B). The schematic figure of the cell system is shown in Fig. 1

In case of the measurement process, the working electrode in Cell B was polarized positively against the counter Pt electrode in Cell B and the working electrode in Cell A side was polarized negatively against the counter electrode in Cell A. The Li ion concentration (activity) in Cell B was measured with a Li ion sensing electrode (W/WO<sub>3</sub>) set near the working electrode in Cell B.

Time dependence curve of the output signal of the Li ion sensing electrode in Cell B is shown in Fig. 2. Fig. 2 indicates that the increase of Li concentration in Cell B starts after a time delay (breakthrough time,  $t_b$ ). The breakthrough time  $t_b$  is the time for Li particle to travel via the centering metal plate. Boes and Züchner showed that  $t_b$  is denoted by  $t_b = 0.5l^2/\pi^2D$ , where  $l$ , thickness of the foil,  $D$ , the diffusion coefficient of Li in metal [1], by which we can obtain the numerical value of the diffusion coefficient of  $1.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  at room temperature. This value is about 1/100 of that of ions in solution, but larger than that expected in solid phase.

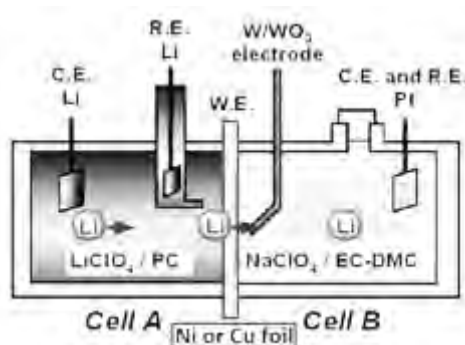


Fig. 1 Schematic figure of bipolar cell where the sample metal is sandwiched between two facing cylindrical cells. The Li ion sensing electrode (W/WO<sub>3</sub>) was prepared by coating with WO<sub>3</sub> on the tungsten wire electrode

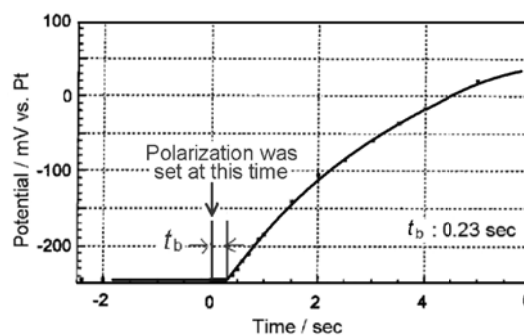


Fig. 2. Time dependence curve of the output signal of the Li ion sensing electrode in Cell B during the negatively polarization of the centering working electrode in Cell A side.

### Reference

[1] N. Boes and H. Züchner, J. Less-common Metals, **49**, 223 (1976).

## Quinone-Mediated Electrochemical Detection for the Determination of Total Acid in Food

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Total acid contents in food and beverage are usually determined for the food quality control, since the acid contents exhibit significant effects on both taste and aroma of foods. A commonly used method for determining acid content is neutralization titration using an appropriate indicator and/or potentiometry. However, the titration method requires large amount of sample and much time to conduct. We had developed a voltammetric method using a quinone reagent as a mediator for measuring the total acid concentration, and it was shown to be quite sensitive and selective for the acid determination [1].

In the present study, the method was assessed for determining the total acid content in food and beverage, such as vinegars etc. Moreover, flow injection analysis with electrochemical detection (FIA-ECD) system was fabricated to provide a simpler, more sensitive and rapid method for determining acid content in various food and beverage.

The FIA-ECD system was comprised of a pump, a sample injector, an electrochemical flow cell, a potentiostat, and a recorder. The electrochemical flow cell was constructed from a glassy carbon working electrode ( $\phi$  6 mm), an Ag/AgCl reference electrode, and a stainless steel counter electrode. An ethanol-water (1:1, v/v) mixture solution containing 3 mM 3,5-di-*tert*-butyl-1,2-benzoquinone (DBBQ) and 50 mM NaCl served as a carrier solution, and flow rate of the carrier solution was set at 0.1 mL/min. The detection potential for monitoring acids were set at -0.15 V vs. Ag/AgCl. Each food and beverage sample was diluted with the ethanol-water (1:1, v/v) mixture solution containing 3 mM DBBQ and 50 mM NaCl to prepare a test solution, and a 5  $\mu$ L aliquot of test solution was injected into the FIA-ECD system to observe a flow signal.

A linearity of the flow signal obtained by the present FIA-ECD against the acid content in vinegar was examined. A 5  $\mu$ L standard solution of acetic acid was injected into the FIA-ECD to observe a flow signal caused by acetic acid. The height of the flow signal was found to be proportional to the acetic acid concentration ranging from 2.0  $\mu$ M to 0.1 mM ( $r = 0.999$ ).

The determination of acid content in vinegar was performed by the present FIA-ECD method. The values of the acid contents are shown as the concentration of acetic acid, since acetic acid is the major acid component in vinegars. The acid content value in cider vinegar obtained by the present FIA-ECD was 5.22 g/dL, while that by the potentiometric titration using 0.1 M NaOH was 5.06 g/dL. The acid contents in rice, cereal, and wine vinegars determined by the present FIA-ECD also agreed with those by the conventional titration ( $r = 0.973$ ). The FIA operating conditions made possible the processing of 45 samples/h. The present FIA-ECD method is superior in sensitivity, and accordingly it requires small sample volume (1  $\mu$ L), unlike the titration which requires relatively large sample volumes (ca. 10 mL). Although the precision of the present FIA-ECD method is less than the titration, the RSD values of the data in the former are less than 3% ( $n=5$ ). The present FIA-ECD method was thus proved to be suitable as an alternative to the conventional potentiometric titration method.

In addition to vinegars, the present FIA-ECD method should be widely applicable to determine the acid contents in other foods and beverages including fruit juice and seasoning. Thus, the present method for determining the total acid content is expected to have a potential for checking the quality in food analysis as criteria.

### Reference

- [1] K. Takamura, F. Fuse, K. Arai, F. Kusu, *J. Electroanal. Chem.*, 468 (1999) 53.

## Thermodynamic Approach for Calculating Potential - Ph Diagrams in the System Cr – Natural Waters

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Chromium (Cr) is one of the most strategically important materials in the world, having a wide range of applications in metallurgy and chemical industry. Alloys containing chromium metal enhance such properties as the resistance, stability to corrosion and oxidation. Furthermore, chromium is used as an additive in the production of stainless steel, in the treatment of leather, metal plating, in the production of catalysts and in other industries.

The increased knowledge regarding the behavior of chromium in natural waters and soils is essential for the complete and accurate determination of its possible toxicity to the particular ecosystem, as well as for the development of methods which minimize the risk of pollution areas. Due to the complex, heterogeneous nature of the soil and surface waters, the determination of the chromium behavior may be a very difficult task. Only by understanding the specific mechanism of the reactions, in which chrome may participate, one can expect a truthful forecast of its behavior.

In this paper an original approach for calculating the potential - pH (Pourbaix) diagrams, based on rigorous thermodynamic analysis of chemical equilibria in the system Cr – natural waters, has been applied. This approach implies the implementation and application of a wide range of new graphical representations of complex chemical, geochemical and electrochemical equilibria, namely heterogeneous chemical equilibrium diagrams, revised Frost diagrams (displaying processes of disproportionation, complex metal formation, hydrolysis) etc. In natural waters, chromium exists in only two stable states, Cr(III) and Cr(VI). The presence and the ratio between these two forms dependent on the various processes that include chemical, photochemical, and redox processes, reactions of precipitation/dissolution and adsorption/desorption.

On the basis of currently revised thermodynamic data for Cr(III) and Cr(VI) hydrolysis and photolytic equilibria in addition to original thermodynamic and graphical approach, used in this paper, the repartition of their soluble and insoluble chemical species has been investigated. By means of the diagrams “ $\Delta G - pH$ ”, the areas of thermodynamic stability of chromium (III) hydroxide have been established for a number of the analytical concentration of Cr(III) in heterogeneous mixtures. The degree of polynuclearity for Cr(III) and Cr(VI) has been calculated for different initial composition of aqueous solutions. The diagrams of heterogeneous and homogeneous chemical equilibria have been used for graphical representation of complex equilibria in aqueous solutions containing Cr(III) and Cr(VI). It is worthy to note that our results, based on the thermodynamic analysis and graphic design of the calculated data in the form of the diagrams of heterogeneous chemical equilibria, are in good agreement with the available experimental data.

Based on thermodynamic analysis, the exact value of the beginning of disproportionation (or comproportionation) is found. After that, the diagrams of heterogeneous chemical equilibria, developed by us earlier, as a function of pH and the total concentration of metal ion in solution, are built. Then, it is derived a system of electrochemical equations of electrode reactions between chemical species in different degrees of oxidation, the predominance areas of which are overlapped. Finally, the dependence of E on pH is calculated for different redox pairs.

The calculated potential—pH diagrams within our approach agree well with the previously reported experimental data.

The developed approach has been applied for calculating redox environments in natural heterogeneous aqueous systems with participation of other toxic heavy metals and other important inorganic and organic ionic and molecular components.

## Clark Oxygen Probe Application for *On-Line* H<sub>2</sub>O<sub>2</sub> Quantification in GaAs Etching Solution in Semiconductor Industry

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The etching process (wet etching) GaAs wafers is applied in the semiconductor industry for the removal of nucleus of roughness and cracks at the edges of the dice, thereby preventing subsequent emergence of the hidden cracks in semiconductor dice. The more effective in this process is the solution known as SC-1 [1] consisting of H<sub>2</sub>O<sub>2</sub>, NH<sub>4</sub>OH, and H<sub>2</sub>O (1:1:10). Unfortunately, the SC-1 solution is very unstable: H<sub>2</sub>O<sub>2</sub> (the most important component) is continuously decomposed both because of its reaction with the semiconductor material, as well as by its instability in alkaline medium (NH<sub>4</sub>OH).

To be effective the SC-1 solution, the H<sub>2</sub>O<sub>2</sub> concentration should be kept constant by adding of fresh H<sub>2</sub>O<sub>2</sub>. This correction requires measurement of the actual H<sub>2</sub>O<sub>2</sub> concentration automatically - in real time and online. Analytical techniques such as UV-VIS spectroscopy, Raman spectrometry [2, 3] and some electrochemical methods able to be used cannot be applied automatically online requiring highly trained personnel and equipped laboratories. The objective of this work is the development and characterization of an analytical method for automatic online quantification of H<sub>2</sub>O<sub>2</sub> based on its decomposition and measurement of the produced oxygen concentration by the application of a Clark type oxygen probe.

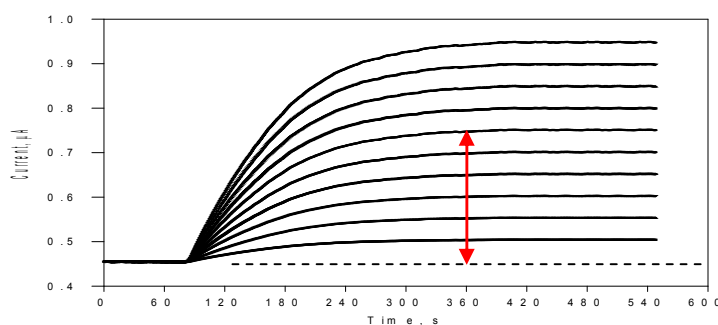


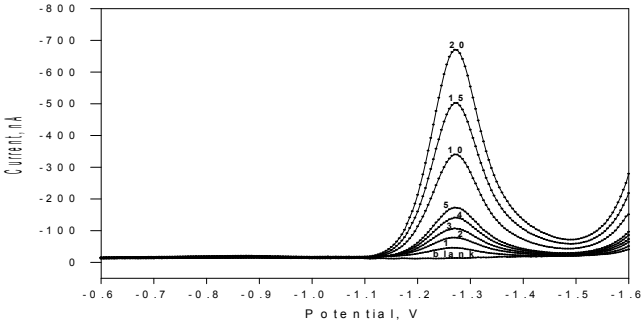
Fig. 1. Clark oxygen probe responses to H<sub>2</sub>O<sub>2</sub> concentrations from 0.3 to 3% (step 0.3%)

H<sub>2</sub>O<sub>2</sub> undergoes decomposition by KI in accordance with equation:  $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2(\text{g})$  which is the total of the following reaction:  $\text{H}_2\text{O}_2(\text{aq}) + \text{I}(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{IO}(\text{aq})$  and  $\text{IO}(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) + \text{I}(\text{aq})$ . The optimum KI concentration to obtain maximum reaction rate and minimum analysis time respectively was experimentally determined to be 0.75 mol L<sup>-1</sup>. The following steps were applied: the measuring cell was equipped with a Clark oxygen probe and magnetic agitator was completely filled by KI solution. Then micro-liter volume of the H<sub>2</sub>O<sub>2</sub> containing solution was added to the cell registering the current through the Clark oxygen probe. Clark oxygen probe responses to various H<sub>2</sub>O<sub>2</sub> concentrations are shown in Fig. 1.

The maximum analysis duration was found to be 360s at the highest H<sub>2</sub>O<sub>2</sub> concentration of 2.5% (vol) used in the etching process. The H<sub>2</sub>O<sub>2</sub> concentration in % (vol) was calculated employing the following previously constructed calibration curve:  $C_{\text{H}_2\text{O}_2} = 0.198 I$ . The limit of detection (LOD) was determined to be 0.02% (vol) that meets the requirements of the semiconductor industry. The relative error of the analysis was found to be from 6.2% at LOD concentration down to 2.8% for the top of the measured concentration range.

### References

- [1] W. Kern, J. Electrochem. Soc. 137/6 (1990) 1887
- [2] C. Bryce, D. Berk, Ind. Eng. Chem. Res. 35 (1996) 4464
- [3] P. Tanner, A. Wong, Analytica Chimica Acta 370 (1998) 279



## Electrochemical Biosensor with Pulsed Amperometric Detection for Organophosphorus Pesticides Determination

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The organophosphorus pesticides (OPs) are widely used in the agricultural and veterinary practices because of their high toxicity, fast biodegradation, low bioaccumulation, and broad target spectrum [1]. Nevertheless, the extensive and indiscriminate application of OPs causes public and environmental concerns and creates a demand for the development of reliable, sensitive, simple and low-costing methods for their determination. Such are the electrochemical biosensors based techniques, which meet all these analytical requirements [2]. The direct and specific quantification of a large group of organophosphorus pesticides, namely the phenyl-substituted OPs, relies on their organophosphorus hydrolase (OPH) catalyzed hydrolysis followed by the amperometric detection of the released p-nitro phenol (PNP). However, PNP oxidation produces phenoxy radicals which couple to form an insulating polymeric film. The resulting passivation of the electrode surface alters the precision of the analysis.

The objective of this work is to develop an OPH based sensor with pulsed amperometric detection for the precise determination of OPs pesticides. It was expected that the in situ cleaning and reactivation of the electrode surface, achieved by applying an appropriate pulse waveform would allow the efficient elimination of the electrode fouling and would result in amperometric biosensor precision improvement.

The phenyl-substituted OPs selected were paraoxon-ethyl, parathion-ethyl, and parathion-methyl. Their quantification using an OPH-modified graphite electrode was performed applying a detection potential of +1.1 V/Ag, AgCl, and a cleaning potential of +1.4 V/Ag, AgCl. The detection and the cleaning time periods were respectively 66.64 ms and 166.6 ms. The obtained at these conditions calibration plots are shown in Fig. 1.

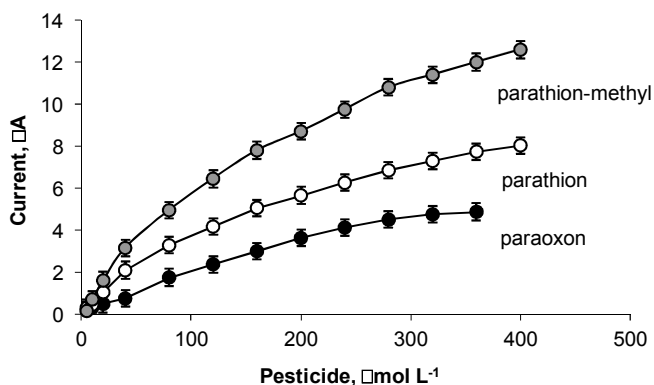


Fig. 1. Calibration plots for OPs determination

The pulsed amperometric detection allowed achieving a RSD of 0.41% at 40 mmol L<sup>-1</sup> p-nitrophenol after 10 determinations, instead of 43.93% without the pulsed cleaning application. The RSD for paraoxon-ethyl, parathion-ethyl, and parathion-methyl was correspondingly 1.45%, 2.96%, and 2.08% at 0.2 mmol L<sup>-1</sup>, which demonstrates the feasibility of the suggested approach.

### References

- [1] R. Krieger (Ed.), Handbook of pesticides toxicology. Principles and agents, 2nd ed., Academic Press., London, 2001.
- [2] M. Stoytcheva, R. Zlatev, in: Pesticides in the Modern World-Trends in Pesticides Analysis, M. Stoytcheva (ed.), InTech, Croatia, 2011, p. 143.

## A Novel Highly Sensitive Graphene Oxide Based Carbon Electrode: Preparation, Characterization and Heavy Metal Analysis in Food Samples

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Heavy metal concentration in food samples is very important for human health [1-3]. This is the cause of various health problems, such as cardiovascular diseases, *kidney failure*, cancer, etc. [4]. It is important to accurately determine levels by using various analytical techniques. Techniques such as spectroscopic and electrochemical methods are used for metal analysis [5-7]. Electrochemical techniques on modified electrodes are especially very sensitive for metal solutions with very low concentrations [8-10].

Graphene oxide (GO) was covalently attached to glassy carbon (GC) electrode (GC-O-GO) for fabricating nanosensors to determine trace Pb<sup>2+</sup> and Cd<sup>2+</sup> using differential pulse anodic stripping voltammetry (DPASV). Surface characterization of the nanofilm covered electrode was performed via electrochemical cyclic voltammetry (CV), transmission electron microscopy (TEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) techniques. Surface pK<sub>a</sub> of the GO covalent attached GC (GC-O-GO) was calculated via CV. Under optimal conditions, a linear response was found for Pb<sup>2+</sup> and Cd<sup>2+</sup> in the range from 1×10<sup>-8</sup> M to 1×10<sup>-12</sup> M. The limit of detections (LODs) of Pb<sup>2+</sup> and Cd<sup>2+</sup> were 0.25 pM and 0.28 pM, respectively. The method shows good reproducibility and stability was successfully applied to measure Pb<sup>2+</sup> and Cd<sup>2+</sup> levels in rice, soya, milk, and tap water samples, with good agreement with those obtained by the standard ICP-OES method. The method was evaluated by application with the simultaneous determination of the ions in food samples (n=6) using the standard addition method. The recoveries of the Pb<sup>2+</sup> and Cd<sup>2+</sup> were up to 98%.

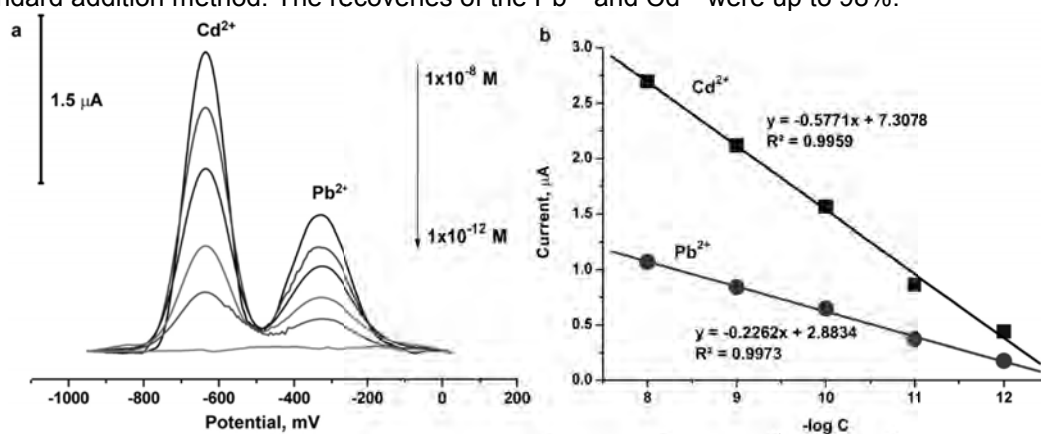


Fig. 1 DPASV calibration voltammograms (a) of 1×10<sup>-8</sup> M, 1×10<sup>-9</sup> M, 1×10<sup>-10</sup> M, 1×10<sup>-11</sup> M and 1×10<sup>-12</sup> M Cd<sup>2+</sup> and Pb<sup>2+</sup> on the GC-O-GO (b) calibration curves of Cd<sup>2+</sup> and Pb<sup>2+</sup> on the GC-O-GO

### References

- [1] A. Afkhami, M. S.-Tehrani, H. Bagheri, T. Madrakian, *Microchim. Acta* 172 (2011) 125.
- [2] A. Cayir, M. Coskun, The heavy metal content of wild edible mushroom samples collected in Canakkale Province Turkey *Biological Trace Element Research* 134 (2010) 212.
- [3] C.V.S. Ieggli, D. Bohrer, P.C. Nascimento, L.M. de Carvalho, S.C. Garcia, *Talanta* 80 (2010) 1282.
- [4] Y.K. Kadioğlu, Z. Üstündağ, A.O. Solak, G. Karabiyikoğlu, *Spectrosc. Lett.* 43 (2010) 247.
- [5] A. S.-Madeja, M. Welna, *Food Chem.* 141 (2013) 3466.
- [6] Z. Üstündağ, İ. Üstündağ, Y.K. Kadioğlu, *Appl. Radiat. Isotopes* 65 (2007) 809.
- [7] L. Tormen, D.P. Torres, I.M. Dittert, R.G.O. Araújo, V.L.A. Frescura, A.J. Curtius, *J. Food Comp. Analysis* 24 (2011) 95.
- [8] Y. Wei, R. Yang, X.-Y. Yu, L. Wang, J.-H. Liu, X.-J. Huang, *Analyst* 137 (2012) 2183.
- [9] Z. Wang, H. Wang, Z. Zhang, G. Liu, *Sensor Actuat. B-Chem.* 199 (2014) 7.
- [10] A.A. Ensafi, *J. Electroanal. Chem.* 640 (2010) 75.E. Franco, E. López-Torres, M. Mendiola and M. Sevilla, *Polyhedron* 19 (2000) 441.

## A Novel MPTHP Modified Glassy Carbon Sensor Electrode: Determination of Cu (II) Ions by DPV technique

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In nature many metals are present. They have a very high atomic weight and so they are called heavy metals which have density much greater (at least 5 times) than water<sup>1</sup>. Heavy metals are found almost every creature body in nature. Especially they are settled down in the centre of enzymes and hormones hence they play crucial role in the live metabolism. One of the heavy metal elements is copper. It is obedient to as a cofactor in leastways 30 essential enzymes<sup>2</sup>. At the beginning of the nineteenth century Hugo Schiff has claimed condensation between an amine compound and an aldehyde compound causing a new compound that was bind or coordinated with metals<sup>3</sup>. After that Schiff bases have been worked by many researchers and these works show that Schiff base can be used for many purposes<sup>4</sup> such as biosensors<sup>5</sup>, optic sensors<sup>6</sup>, electrocatalytic<sup>7</sup>, antimicrobial<sup>8</sup> inhibitors of corrosion<sup>9</sup>. This type of compound can be easily characterized and determined with using electrochemical methods especially voltammetric techniques which in used cyclic voltammetry because of having metal atoms in their structure<sup>10,11</sup>.

In the present work reports; a compound, which has been newly synthesized and characterized, 2-methyl-6-((2-(4-(3-methyl-3-phenylcyclobutyl)thiazol-2-yl)hydrazono)methyl) phenol (MPTHP). The new molecule has been used to modify the glassy carbon (GC) electrode surface with alcohol oxidation method due to –OH group on its structure. MPTHP modified GC (MPTHP/GC) electrode has been used a chemical sensor electrode for the quantitative determination of Cu (II) ions. After the modification process done by cyclic voltammetry (CV) technique, the surface characterization process of modified electrode has been carried out using CV, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). In this work, Cu (II) ions have been detected quantitatively by using differential pulse voltammetry (DPV) technique. The limit of detection (LOD) was found to be  $1 \times 10^{-9}$  M. For the calibration curve, solutions of Cu (II) ions changing from  $1 \times 10^{-9}$  M to  $1 \times 10^{-3}$  M have been prepared using Britton-Robinson (BR) buffer solution at pH 5. The developed sensor electrode has been applied to natural water sample for the quantitation of Cu (II) ions.

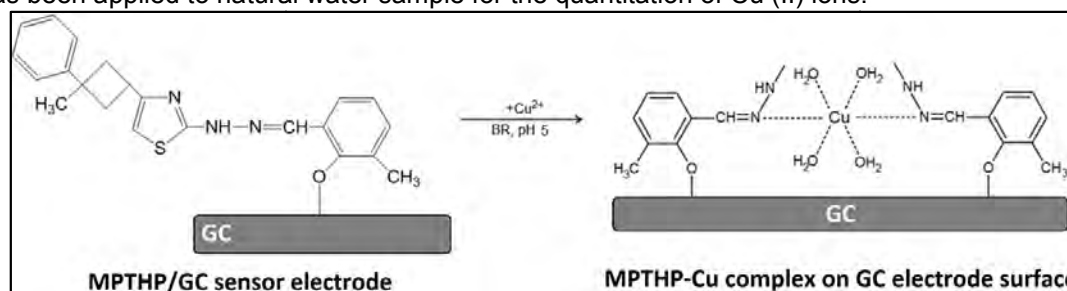


Fig. 1 The proposed electrochemical grafting mechanisms of MPTHP onto the GC electrode surface and MPTHP-Cu complexes on the modified GC electrode surface.

### References

- [1] J. Raj, A. Raina and T.D. Dogra, E3S Web of Conferences 1 (2013) 09009.
- [2] M.B. Gholivand, A. Sohrabi and S. Abbasi, Electroanalysis 19 (2007) 1609.
- [3] P.G. Cozzi, Chem. Soc. Rev. 33 (2004) 410.
- [4] S. Kumar, D.N. Dhar and P.N. Saxena, J. Sci. Ind. Res. 68 (2009) 181.
- [5] R. Rasool, S. Hasnain and N. Nishat, Des. Monomers Polym. 17 (2014) 217.
- [6] N. Aksuner, E. Henden, I. Yilmaz and A. Cukurovali, Dyes Pigments 83 (2009) 211.
- [7] C. Fengying, L. Kezhi and L. Hejun, Synth. React. Inorg. Me. 44 (2014) 1029.
- [8] A.D. Kulkarni, S.A. Patil and P.S. Badami, J. Sulfur Chem. 30 (2009) 145.
- [9] M. Rizzi, M. Trueba and S.P. Trasatti, Synthetic met. 161 (2011) 23.
- [10] J.M. Fernández-G, F.A. López-Durán, S. Hernández-Ortega, V. Gómez-Vidales, N. Macías-Ruvalcaba and M. Aguilar-Martínez, J. mol. Struct. 612 (2002) 69.
- [11] E. Franco, E. López-Torres, M. Mendiola and M. Sevilla, Polyhedron 19 (2000) 441.

## Computational and Experimental Study of Coupled Pairs of Electrochemical Oscillators: Spatio-Temporal Distributions and Effect of External Perturbations

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Electrochemical oscillators can form networks by communicating through the electrolytic solution. The resulting dynamical response can be synchronized in-phase or out-of-phase, depending on the electric and geometric characteristics of the network.

In the present work, networks of electrochemical oscillators are studied both experimentally and computationally. The aim of this work is to elucidate the physical meaning of the coupling between the electrodes and to investigate the influence of external perturbations on the dynamics of such networks.

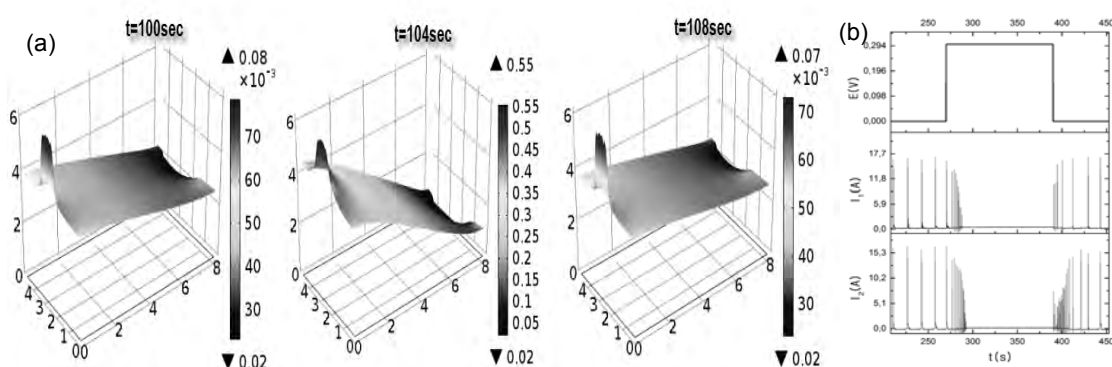


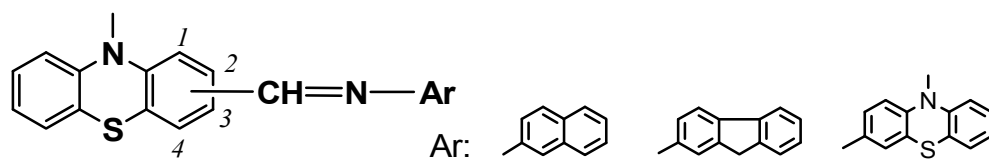
Fig. 1. (a) Spatio-temporal variation of the electric potential in the solution between the anode and the cathode during oscillations and (b) experimental observation of the effect of an external perturbation (top) to a network consisting of two coupled electrochemical oscillations.

For the computational study, a tertiary current distribution is assumed, taking into account the Nernst-Planck equation and electroneutrality for all diluted species. A two electrode configuration is considered for three different kinds of geometries (one-dimensional, two-dimensional for plate electrodes and two-dimensional for disc electrodes). The computational study revealed the spatio-temporal distributions of the concentrations and the electric potential, as shown in the example of Figure 1(a).

The effect of external perturbations was studied experimentally by constructing a simple network consisting of two coupled electrochemical oscillators and a third couple, playing the role of a perturbation source. As can be seen in Figure 1(b), the oscillators are synchronized in phase in the absence of perturbation. When the perturbation is influencing one of the oscillators, the oscillators move to a silent state. Once the perturbation is removed, both oscillators wake up and revert to the in-phase synchronized oscillatory state. It is evident that external perturbations can modify the dynamics of the network reversibly between an oscillatory and a silent state. A similar result is observed when the perturbation amplitude is smaller; in this case the reversible transition is between two in-phase synchronized responses, the one having a greater frequency than the other. Hence, the amplitude of the perturbation can control the frequency of the synchronized dynamics.

### References

- [1] A. Karantonis, S. Koutalidi, J. Appl. Electrochem. 42 (2012) 689.
- [2] A. Karantonis, Y. Miyakita, S. Nakabayashi, Phys. Rev. E 65 (2002) 046213.
- [3] Ph. Russel, J. Newman, J. Electrochem. Soc. 134 (1987) 1051.
- [4] M. Koper, J.H. Sluyters, J. Electroanal. Chem. 347 (1993) 31.





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**HISTORY OF BULGARIA**  
SAINTS CYRIL AND METHODIUS

24 May - Bulgarian Education and Culture,  
and Slavonic Literature Day

wiki: saints cyril and methodius  
wiki: early cyrillic alphabet

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NIKOLA FICHEV alias KOLYU FICHETO

wiki: kolyu ficheto

LIKE.



Oil Painting: Vasil Stoilov

**HISTORY OF BULGARIA**  
VLADIMIR DIMITROV - MAYSTORA  
1882 - 1960

wiki: vladimir dimitrov

LIKE.



Oil Painting: Maiden

**Presentation of the Book “Rise Of Electrochemistry in the Eastern Europe Countries” to be published by Springer In 2015**

Alexander Milchev<sup>1,2</sup>

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The book contains valuable information on scientists from the former Eastern bloc countries, who contributed essentially to different fields of electrochemical science. The idea for this book belongs to Professor Fritz Scholz from the University of Greifswald, Germany, who is also the Editor of the Journal of Solid State Electrochemistry and the ChemTextJournal.

Professor Scholz asked colleagues from Czechoslovakia, East Germany, Poland, Romania and Soviet Union to select scientists from their own countries and he suggested to me to select also Bulgarian scientists and to provide information on their most important scientific achievements. Here is my choice: Prof. Zakhary Karaoglanov, Prof. Ivan Stranski, foreign member of the Bulgarian Academy of Sciences and the academicians Rostislav Kaishev, Stephan Christov, Alexey Scheludko, Evgeni Budevski and Jordan Malinovski.

I would like to believe that readers of this book will find it interesting and worth reading.

## Structure-Conductivity Correlation of $(\text{TiO}_2)_x(\text{V}_2\text{O}_5)_y(\text{P}_2\text{O}_5)_{100-x-y}$ System for SOFCs Application

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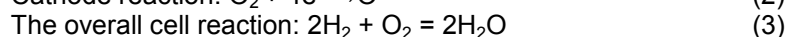
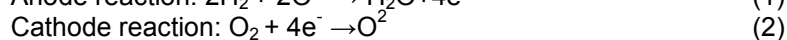
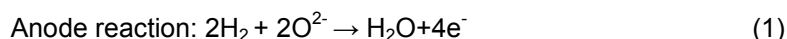
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The ever increasing energy needs of the modern society lead to gradual exhaustion of fossil fuels while, at the same time, their use is accompanied by release of a big amount of noxious gases. All these facts require ceaseless development of novel materials with improved structure and properties. This drift is valid for all major energy fields and to a great extent for both energy sources and storage. In this respect, the solid oxide fuel cells (SOFCs) are a forward-looking approach for highly efficient, environmentally friendly power generation.

The SOFC is a high-temperature (800-900 °C) device that converts the chemical energy of fuels (such as hydrogen, natural gas or other hydrocarbons) directly into electricity through electrochemical oxidation of the fuel with an oxidant, typically oxygen from air. The conversion of chemical into electrical energy is achieved by separating the chemical reaction into two electrochemical reactions ((1) and (2)) taking place inside the porous electrodes and the overall reaction (3). At the negative electrode (anode) the hydrogen and carbon monoxide are oxidized with oxygen ions from the electrolyte to form water and carbon dioxide, respectively. The resulting electrons are transported through an external circuit to the positive electrode (cathode) where they are used to reduce oxygen to oxygen ions which are subsequently transported through the electrolyte to the negative electrode [1].



The SOFC with its solid state components may in principle be constructed in any configuration (tubular, flat plate, etc.). The material selected for use in the SOFC are constrained by the chemical stability in oxidizing and/or reducing conditions, the conductivity and the thermo mechanical compatibility in high temperatures. Another restriction placed on the cell components is that they must be capable of withstanding thermal cycling.

Economically competitive SOFC systems appear suited for commercialization but widespread market penetration requires continuous innovation of materials and fabrication processes to enhance system lifetime and reduce costs. An effective approach to cost reduction is the lowering of the operating temperature without inferring performance losses [2]. This can be achieved either by using of thin electrolytes and/or electrolytes with high ionic conduction [3-5]. It was found that decreasing the electrolytic membrane width leads to a decrease in electrolytic resistivity. This had been attained in SOFCs with planar geometry by using an additional porous anode, on which firstly a uniform thin film (10 μm) from the electrolyte material and thereafter a porous cathode material with a thickness around 50 μm are deposited. For such a type of configuration a very high energy density at temperatures from 700 to 800 °C was achieved [6].

Modification in a property of a material is directly related to both controlled microstructure and the way it is produced. In other words, revealing the microstructure of a material opens the door for improving its macroscopic properties and consequently its practical use. Therefore, this work is dedicated to searching of a direct relationship between structure of a material and some characteristic properties such as a. c. conductivity of oxide  $(\text{TiO}_2)_x(\text{V}_2\text{O}_5)_y(\text{P}_2\text{O}_5)_{100-x-y}$  system in view of its potential use as a electrolyte in SOFCs. It is widely accepted that proton transport depends on the interface region in the composite materials. The presence of hydrogen bonds and grain boundaries in the oxides is advantageous for the proton conduction process. Based on both these arguments and the results from this study, we may propose that the materials under study can act as an electrolyte in a fuel cell that works in the intermediate-temperature region. The glass-crystalline samples are more beneficial compare to amorphous samples showing better conductivity values. The small  $\text{TiO}_2$  content introduces additionally

interface and supplies high conductive paths. The presence of titanium facilitates the depolymerization of the phosphate network and the outcome is appearance of isolated orthophosphate structural units.

Among the best strategies for achieving high proton conductivity is to obtain cation-offstoichiometric materials. The charge imbalance caused by the cation non-stoichiometry is compensated by protons. Phosphates are among the materials that receive much attention due to their high-temperature proton conduction. Depolymerization of the phosphate network and incorporation of vanadium ions produces new pathways by modification and deformation of the crystal structure. Furthermore, transition metals, when combined with other elements, can form variety of compounds which range in chemical bonding from ionic (oxides), through covalent (sulfides, arsenides) to metallic (carbides, nitrides). This range in valence character promises a great variety of energy band structures and transport processes and offer rich field for theoretical and experimental investigations [7]. Taking all these into account we have selected for study the oxide  $(\text{TiO}_2)_x(\text{V}_2\text{O}_5)_y(\text{P}_2\text{O}_5)_{100-x-y}$  system, where  $x = 5, 10, 15, 20$  and  $y = 30, 40, 50, 60, 70$ . Bulk materials were synthesized by means of melt quenching method from initial compounds of  $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$  powders. We used orthophosphoric acid  $\text{H}_3\text{PO}_4$  for the  $(\text{TiO}_2)_5(\text{V}_2\text{O}_5)_{70}(\text{P}_2\text{O}_5)_{25}$  and  $(\text{TiO}_2)_{10}(\text{V}_2\text{O}_5)_{50}(\text{P}_2\text{O}_5)_{40}$  compositions and meta-phosphoric acid  $\text{HPO}_3$  for  $(\text{TiO}_2)_{10}(\text{V}_2\text{O}_5)_{60}(\text{P}_2\text{O}_5)_{30}$  and  $(\text{TiO}_2)_{20}(\text{V}_2\text{O}_5)_{50}(\text{P}_2\text{O}_5)_{30}$  samples as third component. The structure of obtained materials was investigated by both Infrared spectroscopy and X-ray diffraction. Their electrochemical behavior was studied with the aid of Electron Impedance Spectroscopy (EIS).

The results from the XRD analysis revealed two of the samples, i. e.  $(\text{TiO}_2)_5(\text{V}_2\text{O}_5)_{70}(\text{P}_2\text{O}_5)_{25}$  and  $(\text{TiO}_2)_{10}(\text{V}_2\text{O}_5)_{50}(\text{P}_2\text{O}_5)_{40}$  are amorphous, while the other two, i.e.,  $(\text{TiO}_2)_{10}(\text{V}_2\text{O}_5)_{60}(\text{P}_2\text{O}_5)_{30}$  and  $(\text{TiO}_2)_{20}(\text{V}_2\text{O}_5)_{50}(\text{P}_2\text{O}_5)_{30}$  are glass-crystalline (amorphous with nanocrystalline inclusions) defined by peaks. The peaks correspond to NASICON and Rutile ( $\text{TiO}_2$ )-type structure. NASICON is acronym of Na superionic conductor. This is a mixed metal-phosphate type structure with a formula  $\text{A}_x\text{B}_2(\text{PO}_4)_3$ , where A is an one-valence ion and B is one or more ions in a three-, four- or five-valence state. The IR technique was used to elucidate the microstructure and vibrational behavior of the molecules. For all studied samples, we found presence of  $\text{VO}_5$  groups and isolated  $\text{PO}_4^{3-}$  structural units, as well as  $\text{TiO}_6$ -octahedra. With increasing of both  $\text{TiO}_2$  and  $\text{P}_2\text{O}_5$  contents, we found appearance of new  $\text{VO}_4$  structure units. The EIS analysis showed a jump in the conductivity above  $300^\circ\text{C}$ . This behavior is discussed in view of the structure and adequate conclusions are made.

#### **Acknowledgement**

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*Participation of O. Koleva in RSE-SSE 5 has been made possible with the financial support of Bulgarina Ministry of Education and Science.*

#### **References**

- [1] H. A. Taroco, J. A. F. Santos, R. Z. Domingues and T. Matencio (2011). Ceramic Materials for Solid Oxid Fuel Cells, Advances in Ceramics - Synthesis and Characterization, Processing and Specific Applications, Prof. Costas Sikalidis (Ed.), ISBN: 978-953-307-505-1, InTech, Available from: <http://www.intechopen.com/books/advances-in-ceramics-synthesis-and-characterization-processing-and-specific-applications/ceramic-materials-for-solid-oxide-fuel-cells>
- [2] A. Barbucci, P. Piccardo, M. P. Carpanese, M. Viviani, Portable and Emergency Energy Sources, Ed. by Z. Stoyanov and D. Vladikova, Prof. Marin Drinov Publishing House, Sofia 329 (2006)
- [3] B. C. H. Steele, Solid State Ionics, 134 3 (2000)
- [4] J. Will, A. Mitterdorfer, C. Kleinogel, D. Perednis, L. J. Gauckler, Solid State Ionics 131 79 (2000)
- [5] M. Mogensen, N. M. Sammes, G. A. Tompsett, Solid State Ionics 129 63 (2000)
- [6] Fuel Cell Today: 2007 Technology Article Solid Oxide Fuel Cells: <http://www.fuelcelltoday.com/media/pdf/surveys/2007-SOFC-Survey.pdf>
- [7] F. J. Morin, Chapter "Oxides of the 3d Transition metals", Semiconductors, edited by N. B. Hannay, Reinhold Publishing Corp. New York, American Chemical Society Monograph Series 1958

## Electrochemistry of Immobilized Multicopper Ascorbic Oxidase (*Cucurbita* Sp.): a Third Generation Amperometric Biosensor for Ascorbate

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The electrochemical activity of the oxidative enzyme ascorbate oxidase (AOx) has been examined on smooth gold electrodes and on electrodes modified with gold nanostructures. The electrode modification was performed through electrodeposition, i.e. the gold nanoparticles (GNPs) have been grown on the electrode's surface by electrochemical reduction of tetrachloroaurate in acidic medium. Both on smooth and GNPs-modified electrodes, the biocatalyst has been attached to the surface using gold-thiol chemistry (also known as self-assembly process) which warrants the monolayer formation. It has been found that the self-assembled on GNPs modified electrodes enzyme manifests high electrochemical activity and acts as an efficient electrocatalyst at the electrochemical reduction of oxygen, or oxidation of L-/D- ascorbic acid and sodium ascorbate.

Alternatively, when self-assembled onto a smooth gold electrode, the protein shows a negligible electrochemical activity and shows poor electrocatalytic activity in the above processes which takes place at a considerably higher applied potential – very close to the one at which electrooxidation process takes place in absence of the enzyme. Above findings support to a great extent the hypothesis that the electrochemical and electrocatalytic activity of the redox-active biocatalyst is promoted by the gold nanostructures.

Enzyme inhibition with phenol and with NaF performed in both absence and presence of the enzyme substrates (oxygen and ascorbate) has proved that the electrocatalytic oxidation of ascorbate is due to the enzyme presence. Moreover, the electrooxidation of ascorbate has been found to be much more efficient under anaerobic than under aerobic conditions.

The established electrocatalytic activity of the redox enzyme immobilized onto GNPs-modified electrodes has been successfully applied in the development of electrochemical biosensor for the assay of Vitamin C using the self-assembled on GNPs ascorbate oxidase enzyme as bio-recognition element.

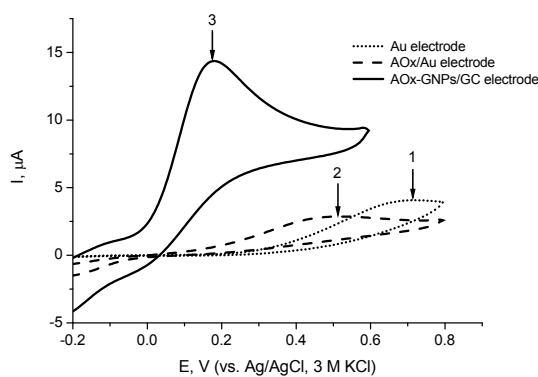


Fig.1. Cyclic voltammograms (CVs) in 0.1 M phosphate buffer pH = 7.0, 1 mM L-ascorbic acid present of: 1) smooth gold electrode; 2) gold electrode with chemisorbed AOx enzyme; and 3) GNPs-modified glassy carbon electrode with chemisorbed AOx.

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## Investigation and Application of Pyrolyzed Cotmpp Catalysts

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In the present paper the experience of the “Electrochemistry of Biocatalytic and Metal-air Systems” Department team in the field of investigation and application of pyrolyzed CoTMPP (Co-tetramethoxyphenylporphyrine) catalysts in air gas-diffusion electrodes for metal-air batteries and in enzyme electrodes (for glucose and lactate) is summarized.

These types of catalysts possess high activity for the electrochemical reduction of oxygen and are widely used in air gas-diffusion electrodes for Zn-air, Mg-air and Li-air primary cells. Because of their high activity for electrochemical oxidation of hydrogen peroxide ( $H_2O_2$ ), these catalysts are also successfully applied in enzyme electrodes and biosensors with enzymes-oxidases in which the electrochemical oxidation of  $H_2O_2$  is used as indicator reaction.

Many attempts have been made to clarify the structure of the pyrolyzed catalysts by using various physical methods.

Methods for diagnostics of the activity and transport hindrances of air gas-diffusion electrodes with pyrolyzed CoTMPP catalysts are proposed. It is shown that these electrodes can be successfully utilized in metal-air cells with different types (alkaline, saline or non-aqueous) of electrolyte.

## **Applications and Trends of Ultrasound Treatment for Activation and Preparation of Perspective Nanosized Materials for Energy Conversion and Storage**

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The current presentation is intended to show some useful ultrasound techniques and methods for treatment, activation and modification of properties of materials by using simple and cheap physical treatment and processing methods.

Ultrasound treatment is based on the well-known phenomena in liquids called cavitation. Powerful cavitation caused by high power irradiation – ultrasonication by intensive waves causing both micro thermobaric acting bubbles and micro cumulative acting hydro-jets.

Several applications of ultrasound treatment techniques are described.

Some examples for utilization of ultrasound treatment:

**In Sodium-Sulfur battery for Beta"-Alumina solid electrolyte preparation route**, as well as for ceramic composite solid electrolyte – for activation purposes. By intensive ultrasonication 50% increase of ceramic powder surface area is achieved leading to higher reactivity. This leads even to a necessity for ceramic sintering procedure parameters reduction.

**Treatment of Ebonex as catalytic support used in PEM water electrolysis.** The ultrasonication affects the material mainly by reducing particle size observed by SEM, as well as, crystallite size and accumulation of additional micro stresses which leads to widening of diffraction peaks. Moreover it is observed a change in the intensity of corresponding peaks which means that there is a change in the ratio between the separate Magneli phases caused by the ultrasound cavitation.

**Presynthesis and synthesis of ceramic materials.** Preliminary ultrasound activation of powdered materials and nanomaterials for pre-synthesis synthesis of various materials. In our case bismuthate-titanate ceramic powders are tested by this method and in some cases sonochemical solid-state reaction produces phases that usually without treatment is achieved by heating 500-700°C higher. Investigations are made in the example in system  $\text{Bi}_2\text{O}_3\text{-Ti}_2\text{O}_3\text{-SiO}_2\text{-Nd}_2\text{O}_3$ . Different available equipment for ultrasonication is used for comparison. The investigation is under way to elucidate the parameters of treatment.

Our long-term experience show that this useful method - ultrasonication exhibits wide applicability in electrochemical applications, in future hydrogen energy conversion systems, for optical, electro-optical and ferroelectric ceramic materials production. We suggest using it for production of other glass ceramics, materials for battery applications, metal ceramics and composite materials, and also as an alternative or addition to the mechanochemical methods for both synthesis and activation of materials.

## Influence of metal loading on morphology and performance of Co-based Magnelli-phase titania supported electrocatalyst

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Alkaline water electrolysis is the most mature technology for electrochemical hydrogen production due to its less corrosive environment and cheaper materials of construction. In the recent years the substitution of the commonly used aqueous KOH solution by OH-conductive polymer electrolyte membranes has become increasingly attractive since the membrane electrode assembly exhibits lower overpotentials and higher current densities. The catalysts and alkaline anion exchange membranes are the key components for development of efficient hydrogen production technology free of noble metals.

In this study composite nanosized Co-based materials are deposited by sol-gel method from acetylacetonate precursors  $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$  on Magnelli phases titania (commercial product of Ti-dynamics Co. Ltd, denoted N82)) and are investigated as anode catalysts for alkaline water electrolysis. The metal loading is varied in the range 20-40 wt.% (Co20/N82; Co30/N82; Co40/N82, respectively). The composition, surface structure and morphology of the synthesized composite catalysts are characterized by XRD, EDX, and SEM analysis. The activity toward the partial oxygen evolution reaction is assessed in aqueous alkaline media (25% KOH) at room temperature applying common electrochemical techniques. Cyclic voltammetry and polarization curves are used to obtain information about the proceeding changes in the surface oxidation state as well as to determine the potentials of oxygen offset and the corresponding current densities. A standard three electrode electrochemical cell is used with Ag/AgCl and Pt wire as reference and counter electrodes, respectively. The working electrode contains  $0.5 \text{ mg}\cdot\text{cm}^{-2}$  of the synthesized catalysts, spread as catalytic ink on a commercial gas diffusion electrode (carbon Toray paper, ETEK).

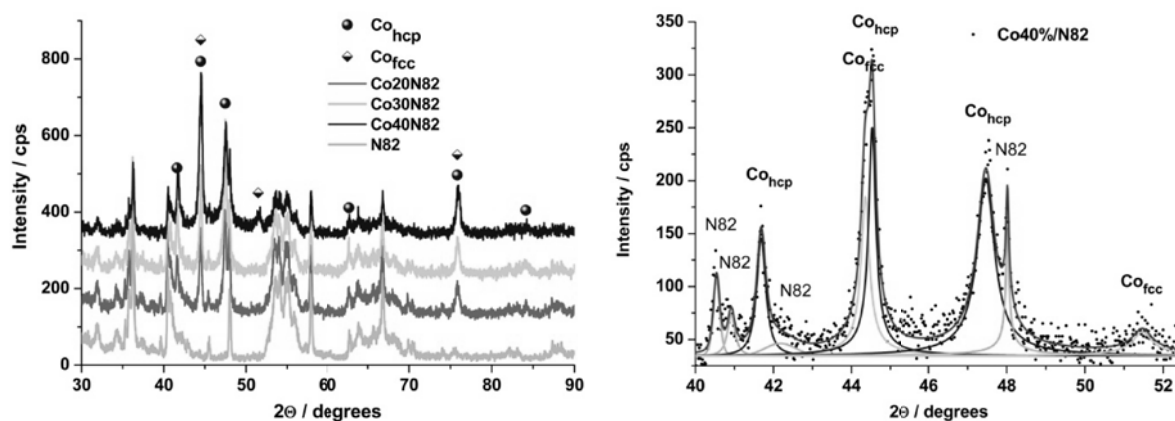


Fig.1: X-ray diffraction patterns of: a) all samples taken in the range  $2\Theta = 30\text{--}90^\circ$  and b) zoomed patterns of Co40/N82

In figure 1a are shown the XRD patterns for all catalysts under study, recorded in the angular range  $2\Theta = 30\text{--}90^\circ$ . The spectrum of the support is shown for comparison. The peaks of cobalt are well recognized. The analysis shows that in the Co20/N82 and Co30/N82 catalysts cobalt is crystallized in hexagonal syngony, while in Co40/N82 both cubic and hexagonal phases are present (Co-fcc and Co-hcp).

Fig. 1b illustrates the profile line analysis performed to separate the overlapping XRD peaks and to determine the size of the crystallites. It is found that all samples are with relatively large crystallites. In the hexagonal phase the  $D_{\text{hcp}}$  size is varies in the range 30-50 nm depending on the diffraction reflection. In fcc phase, registered only in Co40/N82 catalyst the crystallite size is smaller ( $D_{\text{fcc}} \leq 30 \text{ nm}$ ).

The performed scanning electron microscopy (fig.2) proved that the metal particles are homogeneously distributed on the substrate forming a well defined spherical clusters.

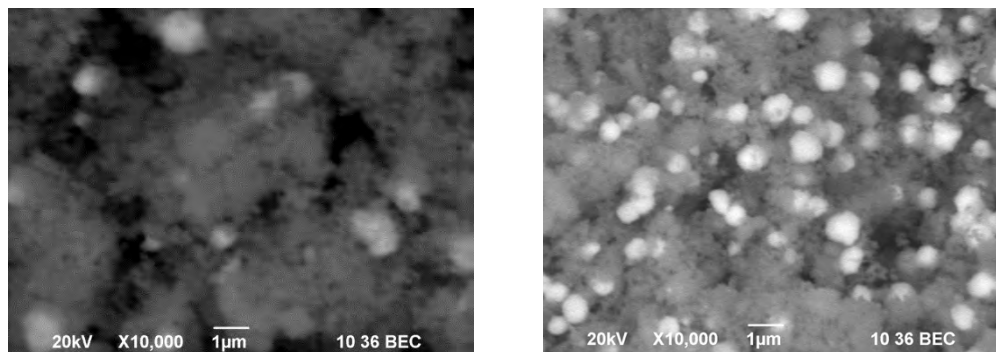


Fig.2: SEM of catalysts with different metal loading a) 20 wt%Co and b). 40 wt.% Co

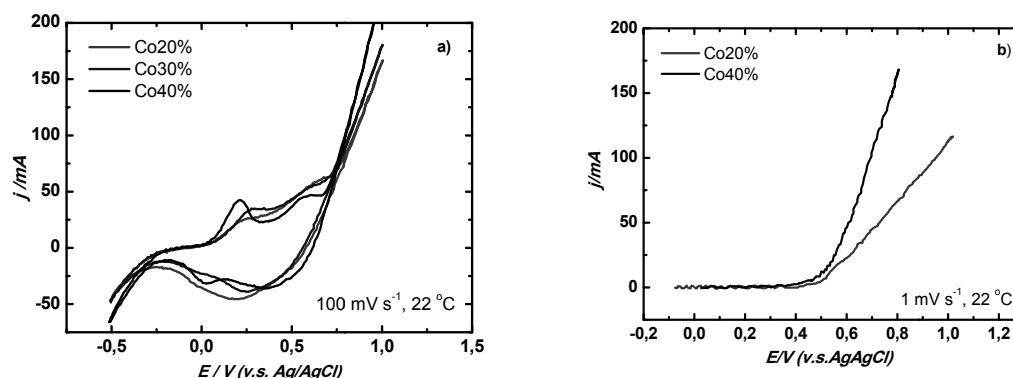
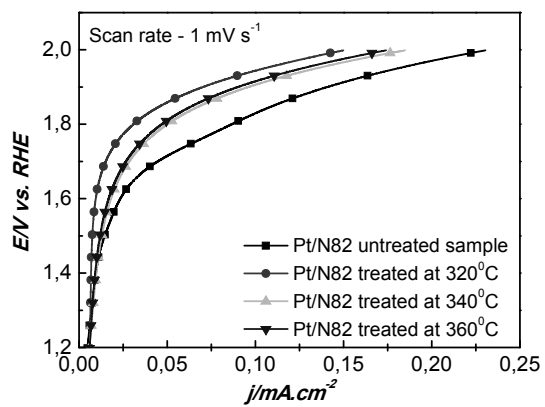
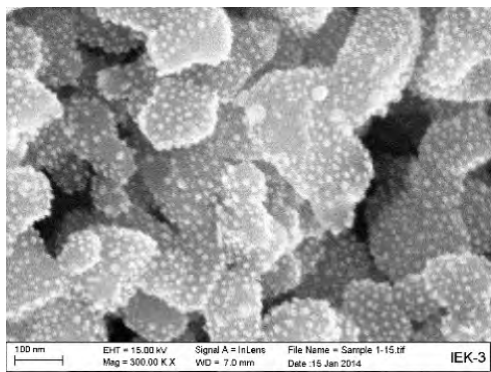


Fig.3: Cyclic voltammetry (a) and steady state polarisation curves (b) recorded in 25% KOH

The results from the electrochemical investigation of the synthesized catalysts are presented in fig.3. The cyclic voltammograms of the samples with lower metal loading are rather shapeless, while the CV of Co40/N82 has two well defined anodic peaks related to changes in the oxidation state of Co (Co to  $\text{Co}^{2+}$  and  $\text{Co}^{2+}$  to  $\text{Co}^{3+}$ ) and two corresponding reduction peaks during the reverse cathodic potential scan. The oxygen evolution for reaction starts at anodic potentials in the range 0,62-0,70 V and at 0,75 V the process is already very intensive reaching current densities above  $150 \text{ mA cm}^{-2}$ . The superior behavior of Co40/N82 is clearly seen in Fig.3b, where the anodic steady state polarisation curves of this sample are compared with that of Co20/N82. The results obtained are explained with the smaller crystallite size, ensuring more active surface sites for the proceeding of the electrochemical reaction and the registered presence of two crystallographic phases in this sample. The chosen catalytic support plays a key role for the established corrosion stability of the catalysts. At the same time due to its hypo-d-electron character it interacts with Co having hyper-d-electron character thus, leading to changes in the mechanism of the oxygen evolution and increase of the reaction rate.



## Silver Cementation by Iron from Used Photographic Solutions by Magnetically Assisted Beds: Batch and Recirculation Modes

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Experimental work on silver cementation from spent photographic fixer thiosulphate solutions by iron in magnetically assisted beds has been performed in axial magnetic fields. Batch modes allow to establish the optimal structures of the magnetized beds a by adjustment of both the field intensity and flow rate in various operating modes [1]. The recirculation mode is the main operating approach following the batch mode step thus allowing deep recovery of the metal for runs lasting about 1.5 hours. With flow rates slightly exceeding the minimum fluidization point in absence of a field the preferable operating regimes are: a fixed bed (FB) and moderately expanded magnetically stabilized beds (MSB) regimes, both of them with the Magnetization FIRST mode. However, when high flow throughputs are required, the frozen beds with the Magnetization LAST exhibit higher separation efficiencies and higher mass transfer coefficients than those with FB and MSB.

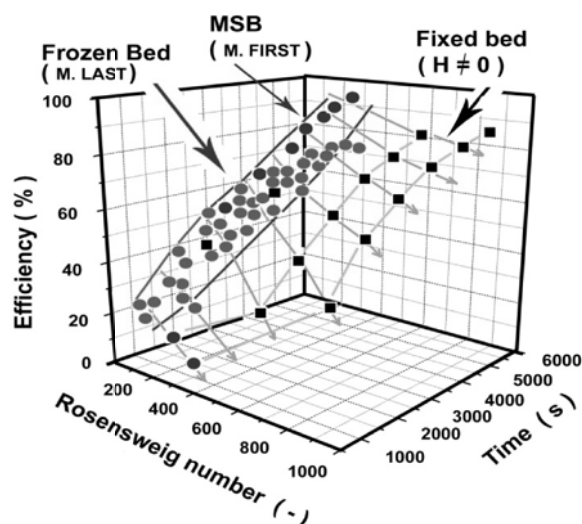


Fig.1. Three-dimensional representation of the efficiency of the silver recovery by cementation in magnetic beds as a function of the time and the Rosensweig number

The main results can be outlined as:

The preferable operating modes are slightly expanded MSBs (Magnetization FIRST mode) and frozen beds (Magnetization LAST mode). However, the frozen beds exhibit about 5 time higher mass transfer coefficients than those of MSBs.

The increase in the experimental runs up to 1.5 h allows about 90 % recovery of the silver from the solution in the form of cemented deposits.

### References

[1] Petrova T. M., Tzaneva, B., Fachikov L., Hristov J., Chem. Eng. Process-PI, vol. 71, 2013, pp. 83-96, DOI: [10.1016/j.cep.2013.03.014](https://doi.org/10.1016/j.cep.2013.03.014)

## **An Impedance Study of the Influence of Anti-Cancer Agent Erufosine on Breast Cancer Cells**

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The impedance spectroscopy is a fast and non-invasive electrochemical method which usage in cancer cell investigations in the last years has rapidly increased. In this paper we present the possibility to use the impedance spectroscopy as a technique for breast cancer cells studies and the effect of the anti-cancer agent Erufosine on such cells.

Obtained results show in real-time the adhesion of L929 and MDA-MB-231 cells. An evaluation of the development of the cytotoxic effect of Erufosine on cancer cells has been performed.

## **Sulfite Driven Fuel Cell: Choice of Membrane**

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Sulfites are wastes produced from different industries and mainly from the flue gas desulfurization processes. For their stabilization or transformation into commercial product they have to be oxidized to sulfates that are more stable. The efforts of our team are to oxidize the sulfites in a newly constructed fuel cell thus gaining electrical energy while solving this environmental problem at the same time. In this paper the choice of membrane is investigated. Five different membranes were tested: Cel Gard 3501, Fumapem FAA-3-PK-75, Neosepta, porous sintered PVC and Nafion. The influence of the initial concentration, the concentration of the product and the pH is studied on the obtained electrical power of the cell. The electrodes used are graphite rods covered with activated carbon. The latter is proved to be a catalyst of the process. Although the Cel Gard 3501 membrane has shown very good exploitation characteristics for a sulfide driven fuel cell it is not appropriate for our purposes. Best overall results were obtained with Fumapem FFA-3-PK-75.

*Key words:* sulfites, oxidation, fuel cells, membranes

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## Corrosion Behaviour of Nitrogencontaining Stainless Steel in Ringer's Solution

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The orthopedic materials used in medicine are made from different materials and the principle requirement to each material used is its biocompatibility [1]. The materials have to be corrosion resistant to body fluids since the release of metallic ions could provoke degradation of implants as well as undesired reactions in the human body. Therefore, the electrochemical tests of any new material suggested as implants should be performed in controlled media simulating human body fluids.

This work reports preliminary results regarding assessment of high nitrogen stainless steel (HNS) as an implant material replacing of the common Ni containing stainless steels which are toxic [2].

Two austenitic stainless steels (the conventional Cr18Ni9 and the new HNS Cr18Mn12N) were investigated in Ringer's solution [3] with pH 7.25. All tests were carried out in a conventional three electrodes cell in open air conditions at 37°C. Three electrochemical methods were used: Cyclic potentiodynamic polarization method, Open circuit potential (OCP) - time measurement and Potentiostatic method. In addition, after the electrochemical experiments the specimen surfaces were observed by an optical microscope.

Two types of OCP - time measurements were done: *short-time* (for 1 h) and *long-time* (for more than 200 h). During the short-time measurements the OCP - time dependencies revealed that both steels are in the passive state and the potentials shift in the positive direction. After 1 h stay in the experimental solution the potentials do not reach constant values. That was the reason to extend the measurements for the HNS up to 230 h. During the long-time experiments two types of dependencies were observed. The first dependence revealed that the potential was slightly shifted in negative direction after the initial ennoblement and attained almost stable value of about -0.05 V(SCE). The second type dependencies was characterized by sharp decreasing in the potential due to crevice corrosion development (between the steel sample and the insulation).

The potentiodynamic studies revealed that both the scan rates of 0.16, 1 and 5 mV.s<sup>-1</sup>, and the preliminary treatment of the samples affect significantly the obtained electrochemical parameters such as: corrosion potential ( $E_{\text{corr}}$ ), pitting potential ( $E_{\text{pit}}$ ), repassivation potential ( $E_{\text{rp}}$ ), passive current density ( $j_{\text{pass}}$ ), etc. The increase in the scan rate, for instance, is manifested by increase in  $j_{\text{pass}}$  for both steels tested but does not affect  $E_{\text{corr}}$  and  $E_{\text{pit}}$ . The preliminary treatment affects mainly the  $E_{\text{corr}}$ ,  $E_{\text{pit}}$  and  $E_{\text{rp}}$ , but does not change  $j_{\text{pass}}$ .

The tests by potentiostatic method reveal that the  $E_{\text{pit}}$  and the incubation time for pits initiation ( $t_i$ ) can be determined. The results show that the HNS is more susceptible to metastable pits nucleation and needs long times to form stable pits. However, the Ni-base steel samples demonstrated stable pits developed faster for short times

The optical microscopy after the potentiostatic experiments indicated numerous pits on Cr18Ni9 steel surfaces which are larger in contrast to surface of the Cr18Mn12N samples

In conclusion, it could be outlined the HNS steel exhibits better corrosion resistance in Ringer's solution, but additional studies in various media stimulating human body fluids should be carried out.

### References

- [1] Anna C. Fraker, Corrosion of Metallic Implants and Prosthetic Devices in ASM Handbook, vol.13, ASM International, USA, p. 3313
- [2] M. Sumita, T. Hanawa, S.H. Teoh, Materials Science and Engineering C 24, 2004, p. 753
- [3] M.V. Popa, I. Demetrescu, E. Vasilescu, P. Drob, D. Ionita, C. Vasilescu, M.F. Popa, 16th International Corrosion Congress, September 19-24, 2005, Beijing, China

## Porous Carbon for Electrochemical Application

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A novel nanoporous furfural-resin-derived carbon, with improved pore size distribution, was synthesized by carbonization of a mixture of furfural and pyrolysed tar, and subsequent steam activation. The synthesized carbon is characterized by high BET surface area of 1140 m<sup>2</sup>·g<sup>-1</sup> (Fig. 1).

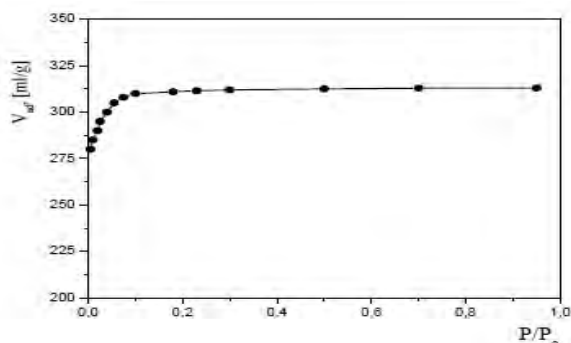


Fig.1 N<sub>2</sub> (77 K) adsorption isotherm of nanoporous carbon

Laboratory capacitor is built using 100 mg activated carbon. Electrochemical characteristics of the novel carbon material in two electrolytes, 1 M LiBF<sub>4</sub> and Et<sub>4</sub>NBF<sub>4</sub> in PC solution, were studied using cycling charge-discharge test at constant electrical current (Fig. 2).

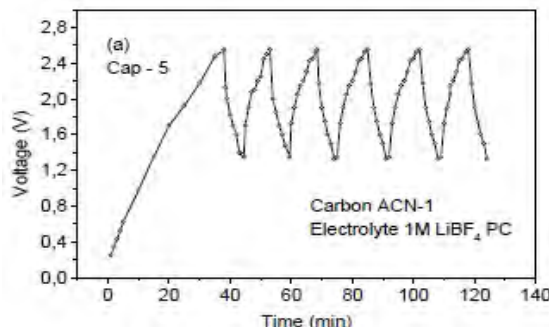


Fig.2. Cycling performance of symmetric cell with nanoporous carbon electrodes in the voltage range of 1.25–2.5 V at electrical current loading 25 mA·g<sup>-1</sup> in cell with carbon ACN-1 and electrolyte 1 M LiBF<sub>4</sub>– PC

It is shown that furfural-resin-derived carbon electrode material demonstrates very good capacitive characteristics. Although the specific gravimetric capacitance of the novel carbon in Et<sub>4</sub>NBF<sub>4</sub> in PC solution (24 F·g<sup>-1</sup>) does not surpass that of other advanced activated carbon materials, the volumetric capacitance of this sample (over 18 F·cm<sup>-3</sup>) is excellent for non-aqueous supercapacitors, using working voltage up to 2.5 V. The internal resistance of the laboratory supercapacitor is 1.2 mΩ, and the stored capacitance was calculated to be 25 mA·g<sup>-1</sup> at cell voltage of 2.5 V. The carbon material properties, as well as the resulting energy system properties, are taken into account, when integrating the energy units into a power source. The power flows are actively controlled in order to assure the energy system effectiveness.

### Acknowledgement:

Financial support by Project DFNI-E02/18 is gratefully acknowledged.

## Investigation of Pitting Corrosion by Potentiostatic Polarisation

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The investigation of pitting corrosion is really important for evaluation of corrosion behaviour of stainless steels. The most used method of pitting corrosion studies is the Cyclic potentiodynamic polarisation method (CPPM). However, some of the corrosion parameters determined by it strongly depend from scan rate. Therefore, the use of additional electrochemical method for proving and clarification of pits nucleation kinetic is recommendable.

One of these rarely used electrochemical methods is the potentiostatic polarisation method (PPM). The latter could surmount the problems of CPPM and obtain more real evaluation of pitting potential ( $E_{\text{pitt}}$ ). The method consists in continuous polarisation of the examined samples at potentials before and after the pitting and repassivation ( $E_{\text{rp}}$ ) potentials previously defined by CPPM. Some of the authors [1] accepted that pits start to appear when the resulting current exceeds  $10 \mu\text{A}/\text{cm}^2$ . The time in which the current suddenly rise is called incubation time ( $t_i$ ). This is other important information which might be obtained only by PPM.

In the present study, two austenitic stainless steels (conventional Cr18Ni9 and high nitrogen Cr18Mn12N) are examined with the purpose of demonstrate applicability and sensibility of PPM to pitting corrosion investigation. The experiments were conducted in  $0.1 \text{ M Na}_2\text{HPO}_4 + 0.5 \text{ M NaCl}$  at room temperature and open air conditions.

The typical potentiostatic dependencies obtained at the applied potentials around the  $E_{\text{pitt}}$  are given in Fig. 1-a. In addition the rate of pits nucleation (expressed by  $1/t_i$ ,  $\text{s}^{-1}$  [2]) vs. applied potential is shown in Fig. 1-b.

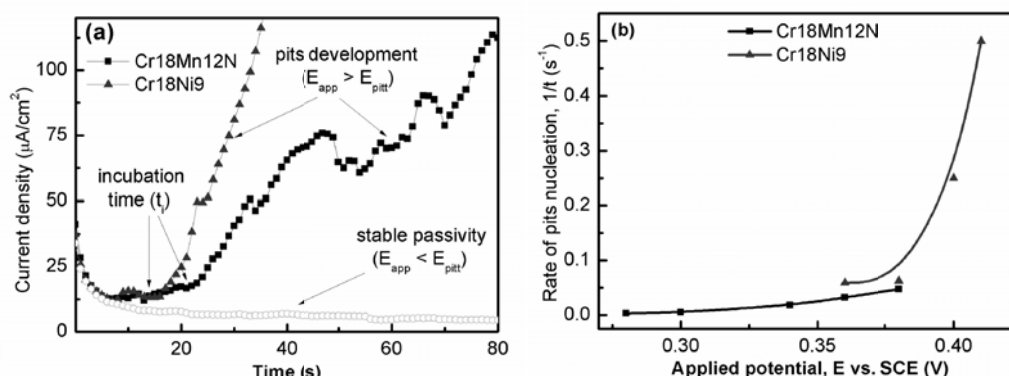


Fig.1. (a) Current density vs. time dependencies, (b) Rate of pits nucleation vs. applied potentials

Regarding the curve of Cr18Ni9 steel (Fig. 1-a) the pits appear in about 15 s and grow up very fast. The pits on Cr18Mn12N arise in around 25 s and try to repassivate which is obvious from the fluctuations in current density. The minimum current values are bigger than mentioned above for pits initiation, but after the experiments pits were not found on the samples surface. That is why this current value could be connected to the thickness and structure of the passive layers. The rate of pits initiation also gives valuable information (Fig. 1-b). It is clear that the pits onto Cr18Ni9 steel surface appear at more positive potential but develop faster than pits on Cr18Mn12N steel surface.

Taking into consideration all written above it can be concluded that during electrochemical studies of pitting corrosion the using of potentiostatic experiments after the CPPM will provide really important and useful information for the susceptibility of materials to pitting corrosion and the type of the appeared pits. What is more the evaluation of properties of the passive layers could be made.

### References

- [1] D. E. Williams, J. Stewart, P. H. Balkwill, Corros. Sci., 46 (1994) 1213
- [2] M. A. Amin, S. S. Abd El Rehim, E. F. El Sherbini, Electrochim. Acta, 51 (2006) 4754

## **Comparative Study on Electrodeposition of Co-Cu Alloys from Ammonia-Sulphate and Citrate Electrolyte**

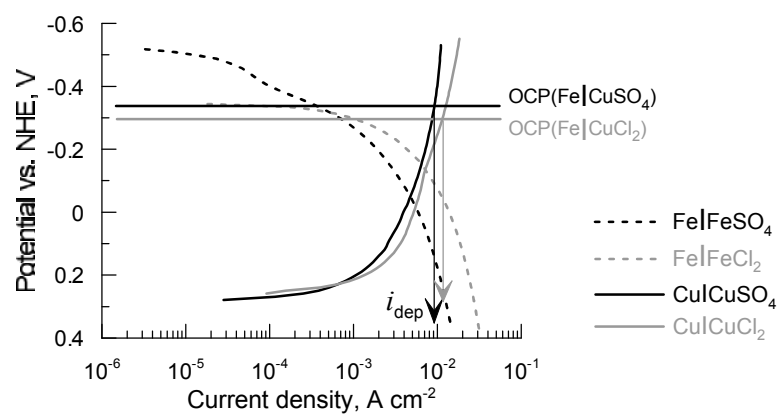
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Compared are the kinetics of deposition of Cu and Co, and the possibility for their co-deposition in Co-Cu alloy from ammonia-sulphate electrolyte (AMSE), weakly acidic citrate electrolyte (CE) and from CE with addition of saccharin (CE+SHR) in constant potential mode. Data are obtained about the chemical content (from Atomic Absorption Analysis, AAA and Energy Dispersive Spectral Analysis, EDSA), the cathodic current efficiency (upon Faraday law), and the morphology (from SEM-images) of Co-Cu coating deposited from the above working electrolytes. The kinetics investigation of the processes indicate that the deposition of Co-Cu alloys from AMSE occurs without initial polarization, while the individual deposition of both Co and Cu is a two-step processes of reduction of complex ions. The deposition from CE occurs with long initial polarization and the overall polarization is higher compared to that in AMSE because of the greater difficulties associated with the formation of more stable citrate complexes of the metals. It is found that Co-Cu alloys with cobalt content up to 50-60wt% deposited from AMSE have coarse-grained crystalline structure with comparable amount of elongated and spheroid crystals with average size in the range from 2 to 10  $\mu\text{m}$ , as compared to those deposited from CE with average size of about and less than 1  $\mu\text{m}$ . The increase of Co content in the alloys up to 80wt% results in decrease of the average size of crystallites in AMSE to less than 5 $\mu\text{m}$ , and to about 500 nm in CE. The addition of saccharin in the citrate electrolyte yields a glossy, smooth coating with close to nano-sized structure with average size of crystallites in the range from 100 to 300 nm.

*Key words:* electrodeposition kinetics, cobalt alloys, nanostructured coatings, morphology, chemical composition, constant potential mode.



## Electrochemically Obtained Bi-Component Catalysts with Enhanced Photoelectrocatalytic Activity under Visible Light

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Photocatalysts for organic pollutants degradation and hydrogen generation from water using solar light energy has attracted increasing interest in the past years due to the growing environment concerns and the energy demand [1]. An ideal photocatalyst should have both a wide photoabsorption range and a low recombination rate of the photogenerated charge carriers. WO<sub>3</sub>, a semiconductor of a smaller bandgap which is active under visible (Vis) light is a well-known multi-functional material with interesting photoconducting behaviour. In addition, the use of bi-layer TiO<sub>2</sub>/WO<sub>3</sub> anodes can significantly improve the photooxidation efficiency and the usage of the visible part of the solar light too [2, 3]. Modifying the semiconductor oxides by precious metals (especially Pt) is a well-established practice to improve their photocatalytic activity by reducing photogenerated electron-hole recombination rates [4].

Pt doped WO<sub>3</sub> and bi-layer TiO<sub>2</sub>/WO<sub>3</sub> coatings were prepared by electrodeposition / electrosynthesis of the semiconductors on graphite (Gr) substrates from acidic aqueous solutions, photodeposition of Cu on WO<sub>3</sub> or TiO<sub>2</sub>/WO<sub>3</sub>, followed by a galvanic replacement process in a chloroplatinate solution. The resulting Pt/WO<sub>3</sub>/Gr and Pt/TiO<sub>2</sub>/WO<sub>3</sub>/Gr electrodes were characterized by SEM microscopy/EDS and XPS spectroscopy. The feasibility of improving the photocatalytic activity of the semiconductor oxides towards the oxidation of water and organic pollutant under Vis light by combining the presence of Pt nanoparticles with the application of anodic bias was investigated. The electrochemical and photoelectrochemical behavior of Pt/WO<sub>3</sub>/Gr and Pt/TiO<sub>2</sub>/WO<sub>3</sub>/Gr anodes was assessed by voltammetry and chronoamperometry in 0.1M Na<sub>2</sub>SO<sub>4</sub> and 0.1M HClO<sub>4</sub> in the absence and presence of methanol in the dark and under Vis light irradiation. The experimental results showed that the deposited Pt has an apparent enhancement effect with respect to suppressing the recombination between the photogenerated charge carriers and enhancing the oxidation of water or methanol. The photoelectrocatalytic activity of platinized WO<sub>3</sub> and bi-layer TiO<sub>2</sub>/WO<sub>3</sub> coatings was considerably dependent on the amount of deposited Pt.

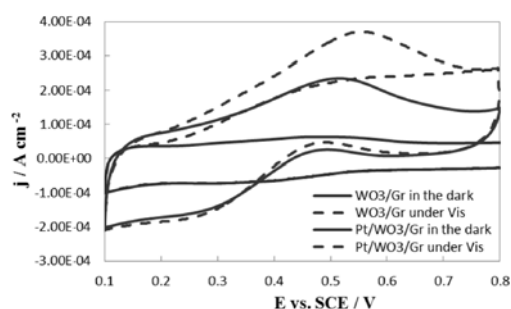
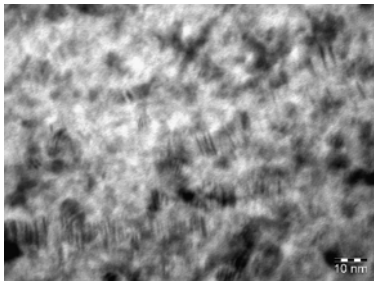


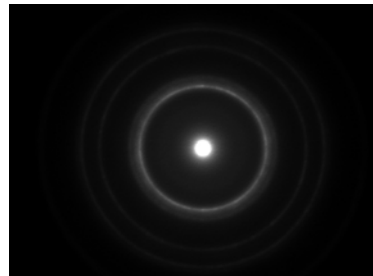
Fig.1. Cyclic voltammograms (at 10 mV s<sup>-1</sup> potential scan rate) of WO<sub>3</sub>/Gr and Pt/WO<sub>3</sub>/Gr electrodes in deaerated 0.1 M HClO<sub>4</sub> + 0.5 MeOH solutions.

### References

- [1] A. Hagfeldt, M. Gratzel, Chem. Rev. 95 (1995) 49.
- [2] J. Georgieva, S. Armyanov, E. Valova, I. Poullos, S. Sotiropoulos, Electrochem. Commun. 9 (2007) 365.
- [3] S. Somasundaram, C.R. Chenthamarakshan, K. Rajeshwar, N.R. Tacconi, J. Electroanal. Chem. 577 (2005) 167.
- [4] V. Subramanian, E. Wolf, P.V. Kamat, J. Phys. Chem. B 105 (2001) 11439.



a)



b)

## XPS Study of Nanosecond-Laser Processing of Polydimethylsiloxane (PDMS) as a Pretreatment for Electroless Metallization

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Due to its properties and biocompatibility polydimethylsiloxane (PDMS) is an important material for the development of microelectromechanical systems or long-term, biocompatible implants. Selective electroless metallization is applied for building electrical micro-circuits on PDMS. Laser pre-treatment is an advanced method for designing circuits geometry.

Data about the chemical status of PDMS after near infrared, visible and ultraviolet radiation of the nanosecond-laser treatment are presented. As result of laser treatment  $\mu$ -Raman spectroscopy analyses reveal a sharp peak of crystalline silicon (c-Si) adjacent to the peaks of native PDMS. In addition, broad bands also appear assigned to the D band of amorphous carbon and to the G band of microcrystalline and polycrystalline graphite. The  $\mu$ -Raman spectra are variable in different inspected points in the laser-formed tracks. This can be explained by the inhomogeneity of the laser spot. In fact the laser spot has multimode structures.

XPS and  $\mu$ -Raman spectroscopy analyses are conducted about a month after the laser treatment. The surface survey spectra indicate that the deposits contain the constituent elements of PDMS: C, O and Si. The spectra of detailed XPS scans illustrate the influence of the laser treatment. The position of Si 2p peaks of all treated samples are close to the value of non-treated except the one exposed to near infrared 1064 nm radiation with 66 pulses, which is shifted at 0.9 eV. On the O 1s peaks a shift at 0.4 eV is noticed, which reflects again a stronger oxidation of Si. The curve fitting of Si 2p and O 1s peaks after this particular laser treatment shows the oxidation degree attained during the irradiation - Fig.1. A possible recovering of the surface after the laser ablation similar to the development after plasma treatment should not be overruled. This can explain why after one month following uniquely exposure to near infrared radiation a noticeable oxidation is revealed. The aim of the laser treatment is to enable selective electroless deposition with high resolution on threated areas. In addition the processes of sensibilization and activation, usual before plating on insulators, are eliminated.

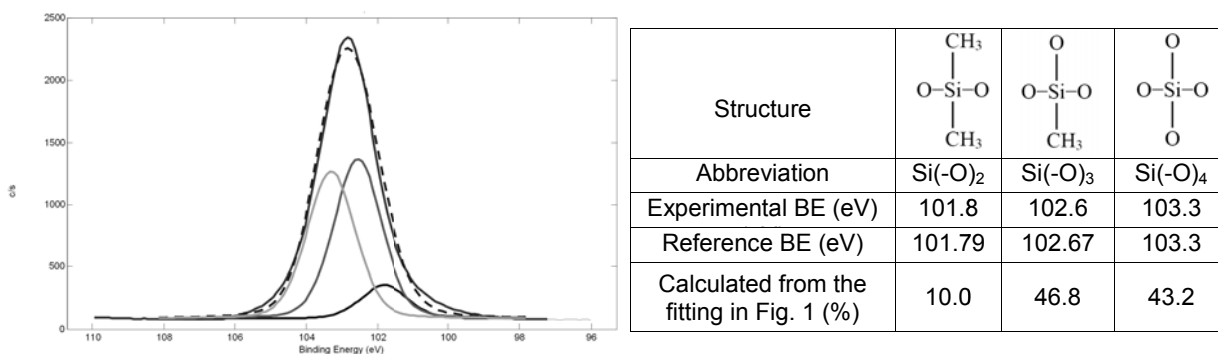


Fig. 1. Curve fitting of XPS Si 2p for 1064 nm 66 pulses 6.5 J/cm<sup>2</sup>. The dashed line is the fitting curve. Blue line - Si(-O)<sub>2</sub> 101.79 eV; green line - Si(-O)<sub>3</sub> 102.55 eV; orange line - Si(-O)<sub>4</sub> 103.3 eV. The scheme of silicon chemical environments and the corresponding Si 2p are also shown.

## Electrolytic Membrane Preparation of Boron Hydrofluoric Tin Concentrates

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Using three-cell membrane electrolyser in which the anolyte and the catholyte are separated with cationite and anionite membranes MK-4 and MA-4, the transport numbers ( $t_{\pm}$ ) in highly concentrated boron hydrofluoric acid with  $C_{\text{HBF}_4}=400$  g/l are determined. It is found that  $t_{\pm}$  are 0.97 – 0.98, which means that they are actually indicative about the coefficient of selectivity of the two membranes having too high value of 97–98 %. Using a two-chamber laboratory electrolyser and membrane MA-4, detailed balance is made of the inter-electrode voltage of saturation of the starting  $\text{HBF}_4$  ( $C_{\text{HBF}_4}=400$  g / l) with tin through anodic dissolution. The high anodic density applied is selected based on our previous studies for characterization of the anodic behavior of tin in boron hydrofluoric acid. The roles of the individual components in the voltage balance are assessed and the specific resistance of the membrane is estimated.

Designed is a semi industrial membrane electrolyser with movable membrane module and horizontal anionite membrane MA-4. The electrolyser is functional and mobile and allows working with both monolithic and bulk anodes and cathodes. During the membrane preparation of boron hydrofluoric tin concentrate, kinetic dependencies are build that illustrate the increase of the concentration of tin, the variation of anodic current yield, the variation of inter-electrode voltage, and the variation of temperatures of anolyte and catholyte. Specified are the optimal parameters of the membrane electrolytic process, and namely the ratio of the volumes of anolyte and catholyte, the volumetric current loading and the maximum permissible current loading of the membrane, as well as some other technological requirements: application of circulation, arrangement of the membrane module depending on the type of the anodes used, etc. It is namely in compliance with these requirements that the higher efficiency of the process is achieved, as tin concentrates with very high concentration of tin of 255 g/l are prepared, which do not contain  $\text{Sn}^{4+}$ , and the yield in terms of  $\text{Sn}^{2+}$  amounts to 97-98%, which coincides with the coefficient of selectivity of the membrane. At these optimal parameters the electrolytic saturation is steady, the voltage is low and invariable 2V, and the temperature in the two half-cells increases insignificantly without any need of forced cooling.

*Key words:* boron hydrofluoric tin concentrate, membrane electrolysis, inter-electrode voltage, transport numbers, ohmic resistance, selectivity of membrane.

## Anodic Dissolution of Tin in Boron Hydrofluoric Electrolytes

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Based on the polarization dependencies recorded in potentiostatic and potentiodynamic mode, the anodic behavior of tin in boron hydrofluoric acid is studied in a wide range of concentrations from 50 g/l to 400 g/l, and from 50 g/l до 200 g/l with addition of Sn<sup>2+</sup>. The objective is to identify the maximum permissible anodic current densities ( $i_{a,max}$ ), to which the metal is dissolved only in the form of Sn<sup>2+</sup>, but not to undesired oxidation to Sn<sup>4+</sup>, or to release of oxygen that accompanies both reactions. The values of  $i_{a,max}$  thus specified are a solid ground for further application of the method of membrane electrolysis for preparation of highly concentrated boron hydrofluoric tin solutions for the needs of galvanotechnics. It is found that with the increase of the concentration of HBF<sub>4</sub> to 400 g/l, the anodic polarization decreases. The saturation of HBF<sub>4</sub> (CHBF<sub>4</sub>=400 g/l) with Sn<sup>2+</sup> up to 100 g/l leads to effect of depolarization but at higher concentration C<sub>Sn</sub> = 200 g/l the anodic polarization substantially increases. Moreover, using two independent methods, i.e. gravimetric analysis and ISP, the anodic current efficiency ( $W_a$ ) is determined with simultaneous record of chrono potentiometric dependencies in galvanostatic mode. It is shown that at values of  $i_a$  within the range from 40 A/dm<sup>2</sup> to 80 A/dm<sup>2</sup>,  $W_a=100\%$  and concomitant chemical dissolution is not present.

The activation energy for anodic dissolution at different potentials is determined, and based on the temperature-kinetic analysis, the type of anodic polarization is identified depending on the range of applied anodic current densities or potentials.

**Key words:** tin, anodic behavior, boron hydrofluoric electrolytes, polarization dependencies, current efficiency

## Behavior of Polarizable Dielectric Liquid in Functional Ceramics by Permittivity Spectroscopy

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This work presents results from studies of processes and phenomena associated with the behavior of polar dielectric liquid (water and alcohol) in a non-polar porous matrix of (proton and oxide ion) conducting dielectric ceramic composite material  $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{2.925}$ / $\text{Ce}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$  (BCY15/YDC15) and proton conducting ceramic material BCY15. The investigation was performed by Permittivity Spectroscopy which is a branch of the Impedance Spectroscopy especially tuned for measurements and analysis of dielectrics permittivity properties. This method is based on the relationship between admittance, capacity and dissipative permittivity:

$$Y(i\omega) = i\omega C = i\omega(C' - iC'') = \omega C'' + i\omega C', \quad (1)$$

where the real component  $\omega C''$  represents dielectric losses and  $\omega C'$  is directly related to the dielectric permittivity, i.e. to the polarization ability. The measurements were carried out in large frequency range (from 1 MHz down to 0.01 Hz). Above a certain level of wetting a gigantic enhancement of the effective capacitance was observed at low frequencies. The effect is stronger in the BCY15 matrix and for the more polar water dielectric liquid.

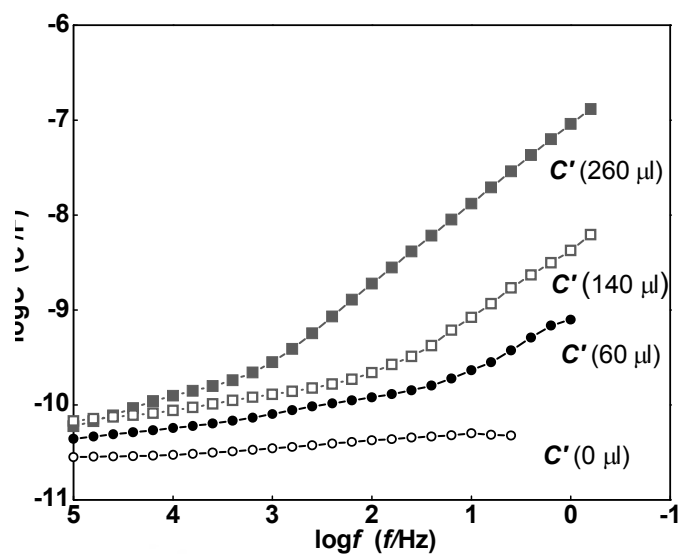


Fig.1. Frequency dependence of  $C'$  at different levels of watering

The phenomenon of gigantic enhancement of the effective capacitance is explained with the formation of dipole volumetric layer which was induced by the external alternating electrical field.

### Acknowledgements

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## Electrocatalysts Incorporating Higher Fullerenes

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This work considers the possibility of using new electro-catalytic materials in chemical and microbial fuel cells.

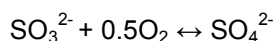
The possibility of using fullerenes as promising catalysts has been considered in the past. In the present study we utilize higher fullerenes as fabricated by Diener & Alford by applying the carbon arc method in a quartz reactor designed for both production and subsequent sublimation [1]. Higher fullerenes are small-bandgap fullerenes currently commercially available from Sigma Aldrich. These include the fairly stable species C<sub>74</sub>, C<sub>78</sub>, C<sub>80</sub>, C<sub>82</sub>, C<sub>84</sub>, C<sub>86</sub>, C<sub>88</sub>, C<sub>90</sub>, C<sub>92</sub>, C<sub>94</sub>, C<sub>96</sub>, C<sub>98</sub>, C<sub>100</sub>. Larger species become unstable as they grow in size. Characteristic of higher fullerenes is that the bonding sites between pentagon atom groups are usually found to be the most reactive.

In this study we have applied a new method to fabricate the electro-catalyst for the fuel cell electrodes. To overcome catalyst agglomeration a process of lyophilization was applied. We used higher fullerenes to maximize the electro-active surface area of the catalyst. Up to 3mg of higher fullerenes were dispersed in 6ml of distilled water in a sonic bath for 15min. Next, (20-40)mg of manganese acetate and (20-100)mg of polypyrrole were slowly added to the aqueous suspension. These ternary components were then baked at 180C<sup>0</sup> for 12h in a Teflon autoclave. Thus, Mn particles were deposited on the higher fullerene lattice structures with polypyrrole binding. The suspension was finally dehydrated by freeze-drying yielding a monolithic three dimensional block composed of carbon networks and MnO<sub>4</sub> nano particles.

X-ray diffraction studies were carried out on a wide range of samples with different quantities of manganese acetate included as the catalyst.

The catalyst was used in the process of oxidation of sulfites to sulfates in solution. The solution was sodium sulfite.

The initial results are encouraging with reactions such as:



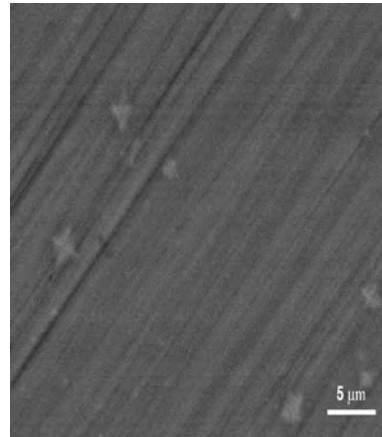
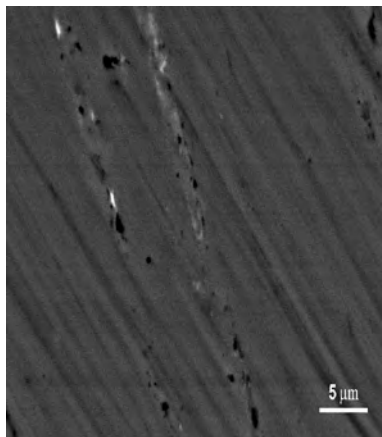
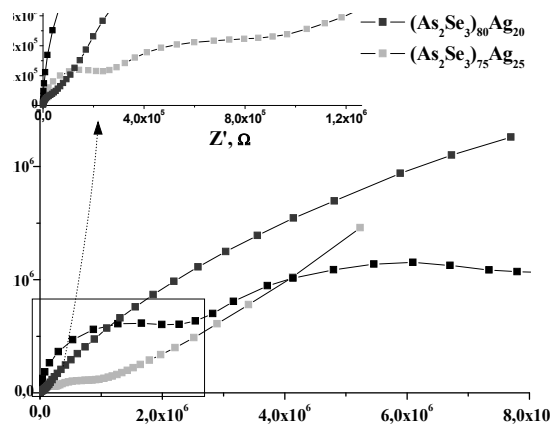
Polarization curves were acquired characterizing the higher fullerene and Mn containing catalyst.

### Acknowledgement

This work was supported by the project "New fuel cells based on chemical and microbial processes", through the Ministry of Education and Science and the Bulgarian National Science Research Fund, contract DFNI E02/15.

### References

- [1] M.D. Diener, J. M. Alford, Isolation and properties of small-gap fullerenes, *Nature*, 393, 668-671(1998).



## Electrochemical Properties of Synthetic Fe<sub>2</sub>O<sub>3</sub> as Electrode Materials for Hybrid Battery-Supercapacitor Systems

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In recent years there is a considerable interest in development of hybrid electrochemical battery-supercapacitor systems involving hybridization of a faradaically rechargeable battery-type electrode with an electrochemical double-layer capacitor-type electrode. Various asymmetric supercapacitors using composite electrode usually with carbon matrix and addition of an electrochemically active oxide are developed.

The objective of the present work is development of hybrid battery supercapacitor based on active carbon and synthetic Fe<sub>2</sub>O<sub>3</sub>.

Fe<sub>2</sub>O<sub>3</sub> oxide is synthesized by solution-combustion method using solutions of Fe(NO<sub>3</sub>)<sub>2</sub> and sucrose as starting materials and the amorphous powder oxide obtained is subjected to thermal treatment (400 °C/1 h). The nanosized hematite thus produced (average particle size about 30 nm) is structurally and morphologically characterized by XRD, SEM and TEM, and tested as electrode material in hybrid lithium battery-double layer capacitors.

The hybrid supercapacitor cell studied is assembled by an electrode of nanosized activated carbon (TDA Research USA - 1600 g/m<sup>2</sup> specific surface area), a composite electrode with activated carbon matrix and additions (20-80 %) of Fe<sub>2</sub>O<sub>3</sub>, and an organic electrolyte - LiBF<sub>4</sub> with solvent ethylene carbonate/dimethyl carbonate mixture (EC/DMC) 1:1. Symmetric supercapacitor cell composed by two identical electrodes of the same activated carbon and the same organic electrolyte is also assembled and tested for comparison.

The supercapacitor cells are subjected to electrochemical charge/discharge cycling test under galvanostatic conditions at different current loads (15 – 450 mA/g). The hybrid supercapacitors developed demonstrate very good cycleability, current efficiency (up to 95%) which increases with the current load and specific capacity higher than the capacity of the basic symmetric capacitor.

The results obtained prove the possibility of application of Fe<sub>2</sub>O<sub>3</sub> as electrochemically active material for hybrid lithium battery – supercapacitor systems.

### Acknowledgement

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## Effect of Dopant Used In Synthesis of Poly(3,4-Ethylenedioxythiophene) for Electrocrystallization of Silver

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Electrochemical deposition of silver is studied on conducting polymer layers of poly(3,4-ethylenedioxythiophene (PEDOT) doped with polystyrenesulfonate (PSS) or dodecyl sulfonate (DDS) ions. Experiments are performed by means of electrodriven and electroless deposition procedures at PEDOT layers with polymerization charge,  $Q_{\text{poly}}$  of 4 mC. Several potentiostatic current transients are obtained at constant potential for both types of PEDOT layers. It is found that for PEDOT/DDS the first several current transients vary within the usual scattering of the experimental data, whereas for PEDOT/PSS there is a consecutive decrease in the currents within the first 4-5 measurements followed by stabilization at relatively low current values. Thus the currents of silver electrocrystallization at PEDOT/DDS layers exceed about four times those obtained at PEDOT/PSS layers. These results are commented in terms of the dopant- based difference in the surface morphology and bulk structure of the polymer layers as well as their different mechanical properties. SEM pictures taken after dissolution of the silver crystals give evidence for the existence of crystal "fingerprints" in the relatively soft PEDOT/PSS polymer matrix.

Series of current transients are obtained at different constant potentials for both types of PEDOT layers. The current transients are tentatively interpreted by the model for nucleation and diffusion-controlled growth developed by Scharifker et al [1]. The experimental data can be easily described by the theoretical equation if using three free parameters (number of active sites for nucleation, nucleation rate at a single nucleation site and product of electrode surface area and diffusion coefficient). Nevertheless the obtained best fit parameters seem to be not always reasonable. Microscopic pictures show marked difference in the characteristic of the metal deposits obtained at the two types of PEDOT – a small number ( $10^5 \text{ cm}^{-2}$ ) of large (several micrometer sized) well faceted silver crystals are observed in the PEDOT/PSS case whereas a larger number ( $10^6 \text{ cm}^{-2}$ ) of bulk crystals and dendrites are found on the PEDOT/DDS surface.

In the case of electroless metal precipitation the reduction of the metal ions is driven at the expense of PEDOT oxidation. (PEDOT layers are pre-reduced in the absence of metal ions in supporting electrolyte.) The electroless deposition process is studied in the presence of two types of silver ionic species: silver cations ( $\text{Ag}^+$ ) and silver anion complex of EDTA ( $[\text{AgEDTA}]^{3-}$ ). It is found that independently on the PEDOT dopant and the type of the silver species the amount of electroless deposited silver remains the same. In all cases electroless deposition of silver results in a larger number ( $10^8 \text{ cm}^{-2}$ ) of sub-micrometer sized silver crystallites that are homogeneously dispersed over the entire electrode surface. There is however a difference in the number, size and size distribution of the silver crystallites depending on the doping agent of PEDOT with smaller crystals observed in the PEDOT/PSS case.

The results obtained demonstrate the significant role of the PEDOT dopant used in the course of electrochemical polymerization for the subsequent process of metal electrodeposition. The main effect in the electrodriven deposition of silver seems to be related to the more permeable and soft polymer matrix obtained in the PEDOT/PSS case in contrast to the PEDOT/DDS layer which is more rigid and hydrophobic thus impeding presumably the metal ions diffusion inside the polymer layer. A major effect of the dopant is observed also in the electroless deposition process. The more hydrophilic and porous PEDOT/PSS layer provides the possibility for the dispersion of a larger amount of smaller sized silver particles.

### References

- [1] B. Scharifker and J. Mostany, J. Electroanal. Chem. 177 (1984) 13.

## Bifunctional Oxygen Electrodes for the Zn-Air Battery

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Rechargeable zinc-air batteries are attractive candidates for applications where the high specific energy and simple design provide significant cost advantages. Unfortunately, improving the basic characteristics of the rechargeable zinc-air battery are still hindered by various technical problems related to the reversibility and lifetime of the electrodes.

The main idea of the proposed Bifunctional Oxygen Electrode (BOE) is to achieve characteristics similar to both state of the art electrolyser and fuel cell electrodes with a high stability. Specifically, this would be obtained through: (i) Non-carbon gas diffusion electrode (GDE) substrates design and fabrication. A variety of gas permeable particles will be teflonized. A critical aspect of successful gas diffusion layer (GDL) fabrication is the sub-micron level mixing of the hydrophobic binder, generally Teflon and the gas diffusion agent, generally a mesoporous particle capable of delivering the requisite oxygen quantities; (ii) Modeling, design, deposition and characterization of disordered amorphous nano-materials as bi-functional electro-catalysts/electrocatalytic layers (ECL). The ECL will have a double layer structure: spots with areas of  $< 1 \text{ mm}^2$ , consisting of nano-sized particles of the catalyst placed on the current collector screen (Ni or Ag), so there will be no losses in conductivity.

The electrochemical properties of BOE in an alkaline electrolyte have been investigated. The GDL was obtain with carbon teflonized (60%) Vulcan XC 72. The catalytic layer was a silver coating (for oxygen reduction) deposited directly on the GDL. On the other hand the current collector which contains various oxides (in the oxygen evolution reaction) was pressed on to the silver coating. The surface area of the electrodes was  $10 \text{ cm}^2$ .

At a current density of  $20 \text{ mA/cm}^2$  the average potential at oxygen reduction and evolution are promising for further investigation of the as prepared BOE.

## Studies on the Selectivity of an Ascorbate Biosensor

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Selectivity of a previously developed enzymatic electrochemical biosensor for Vitamin C [1, 2] has been studied in model aqueous solutions upon addition of organic compounds potentially attending the real samples. Voltammetric studies have shown that in neutral buffer solutions (pH= 7.0) both D- and L- isomers of ascorbic acid are oxidized at the same potential yielding virtually the same current densities, whilst in slightly acidic buffers (pH = 5.6, where the enzymatic activity is maximal) the current density of L-ascorbic acid oxidation is by ca. 30% higher. It has been established that the electrochemical oxidation of Na-ascorbate proceeds identically to the Vitamin C in both neutral and acidic media.

The following substances have been tested voltammetrically as potentially interfering substances of the Vitamin C assay with the biosensor: antocyanes, carotenoids (from paprika extract, orange peel extract, lutein), betanine from beet root, Cu-chlorophylline, saffron extract, gamma- amino butyric acid (GABA), para-amino benzoic acid (PABA); taurine, L-carnitine, and ubiquinone/ubiquinol (Q10).

It has been found that none of the colored food extracts (antocyanes, carotenoids, betanine, Cu-chlorophylline, saffron extract) interfered the electrode response substantially. Slight inhibiting effect on the enzyme activity has been noted for antocyanes and betanine, which is most probably due to their strong adsorption onto the electrode. Similarly, the other tested substances did not contribute to the response of the biosensor. Due to its very limited solubility in physiological solution, ubiquinone/ubiquinol (Q10) did not have effect on the biosensor performance despite it is a potentially oxidizable and reducible over the same range of potentials as the target analyte (Vit. C).

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### References

- [1] N.Dimcheva, T. Dodevska, E. Horozova, J. Electrochem. Soc. 160 (2013) H414.
- [2] N.Dimcheva, E.Horozova, T.Dodevska, Bulg. Patent Application #111733, 2014.

## Effect of the Surface Structure of the Electrochemically Deposited ZnO Films on the Quartz Crystal Microbalance on Its Response to NO<sub>2</sub>

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The influence of the quartz roughness on the ZnO sorption properties is investigated. AT-cut quartz plates with different treated surface - flat polished and rough ones are used. The frequency of used Quartz Crystal Microbalance (QCM) is 10 MHz. The nanostructured ZnO layers are deposited by electrochemical method on the Au electrodes of the quartz resonators. Thin ZnO nanostructured films are deposited by an electrochemical process from slightly acid aqueous solution of ZnCl<sub>2</sub> (5. 10<sup>-3</sup> M) and KCl (0.5 M) with pH 4.0 at 80°C and -1000mV (vs SCE) using a three-electrode electrochemical cell [1]. The electrolyte is agitated by magnetic stirrer. The quartz crystal resonator with Au electrode is used as a cathode. Spectrally pure graphite plate electrode is used as an anode. The deposition is carried out controlling the redox potential of the system. The total oxygen content in solution is controlled in addition by a DO&T meter Hanna Instruments 9146. Duration of the ZnO deposition is 60 min. The thicknesses of the prepared ZnO films are in the range of 0.5-0.7 μm. The structure of the ZnO layers deposited on the polished and rough QCM surface is studied by SEM and the optical spectroscopy - by the spectra of specular and diffused reflection. The results are compared to the corresponding data obtained for the QCM before ZnO growing. The specular reflection of the QCM on the polished substrate decreases from 70% to 20% after ZnO deposition while these values for the rough quartz surface slightly decrease from 20% to 10% (Fig. 1 a and b). The values of the diffused reflection increase in the case of deposition on flat polished QCM surface and decrease in the case of deposition on the rough quartz surface. These changes correlate with the surface structures of the deposited ZnO films.

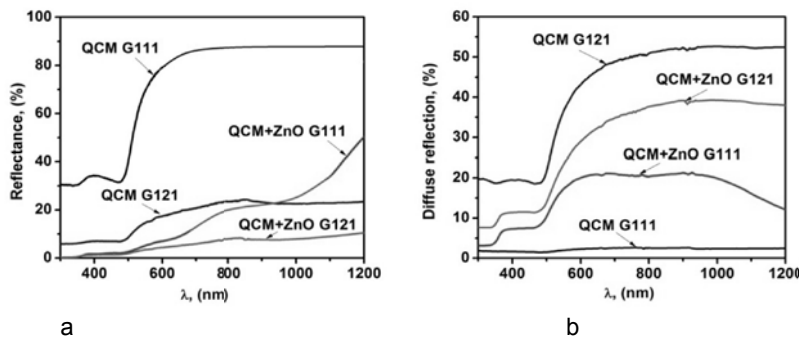


Fig.1. Spectra of reflectance (a) and diffused reflection (b) of QCM with polished quartz surface before (QCM G 111) and after ZnO layer deposition (QCM+ZnO G 111) and with rough quartz surface before (QCM G 121) and after ZnO layer deposition (QCM+ZnO G 121).

The sorption properties of ZnO layers deposited on different kind of surfaces are estimated by QCM method.

The measured changes of the QCM frequency as result of the ZnO mass loading are 60-70 kHz. The sorption ability of the ZnO thin layers is defined by measuring the resonant

frequency shift ( $\Delta f$ ) of the QCM-ZnO structure in the presence of different  $\text{NO}_2$  concentration. The measurements are based on the correlation between the frequency shift of the QCM and additional mass loading ( $\Delta m$ ) on the resonator calculated using Sauerbrey equation for the AT-cut quartz plate [2].

In the present work the Frequency – Time Characteristics (FTCs) of the sample are measured on QCM with differently treated quartz surface - polished one and deliberately rugged one before Au electrodes and ZnO NS films deposition. The experiments are carried out on a special laboratory set up in dynamically regime. From FTCs the response and the recovery times of the QCM-ZnO structure are measured (Fig. 2 a and b). The study is carried out in the  $\text{NO}_2$  concentration interval of 50 - 5000 ppm.

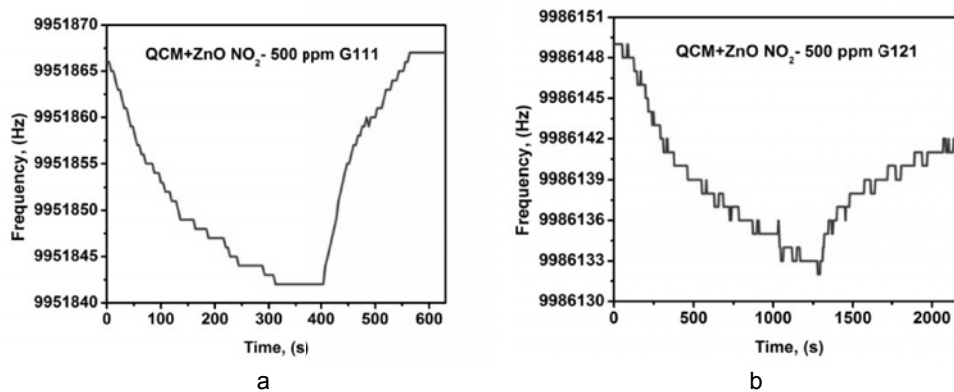


Fig.2. Frequency-time characteristics of QCM with ZnO layer deposited on polished (a) and rough (b) quartz surface measured at 500 ppm  $\text{NO}_2$  concentration.

The correlation between the sorption ability of the ZnO and the different state of the quartz surface is obtained from the QCM response. The QCM with ZnO deposited on the polished quartz demonstrate better sorption ability compared to QCM fabricated on rough quartz surface.

## References

- [1] Doriانا Dimova-Malinovska, Konstantin Lovchinov, Maxim Ganchev, Orlin Angelov, Joachim Seland Graff and Alexander Ulyashin, *Phys.Stat.Sol. A* 210 (2013) 737.
- [2] Sauerbrey G *Zeitschrift für Physik* 155 (1959) 206.

## **Synthesis and Characterization of $\text{LiV}_3\text{O}_8$ as a Negative Electrode Materials for Li-Ion Battery with Water Electrolyte**

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$\text{LiV}_3\text{O}_8$  was synthesized via “wet” chemistry followed by SSR method and alternatively by melting process. The initial syntheses compounds were  $\text{LiOH}$  and  $\text{V}_2\text{O}_5$  for both syntheses. The SSR method was consisted at three temperatures ( $450^\circ$ ,  $550^\circ$  and  $590^\circ\text{C}$ ) for 24 h each treatment. The “melting” material was heated at  $400^\circ\text{C}$  for 24 h and than at  $640^\circ\text{C}$  for few hours. The obtained lithium vanadates were characterized physico-chemically by XRD, SEM and BET analyses. The melted sample was grinded few hours in a ball mill to obtain relatively small particles from the melt. Further, part of the sample was treated in autoclave at  $250^\circ\text{C}$ . The electrochemical performance of the materials were investigated using three-electrode cells in aqueous solution of  $\text{LiNO}_3$ , with  $\text{Ag}/\text{AgCl}$  reference electrode.  $\text{LiMn}_2\text{O}_4$  was used as a counter electrode. The working electrodes were made by mixture of 50% active material and 50% TAB2 (teflonized acetylene black) and than pressed on the Ni-mesh under a pressure of 3 tones.

The aim of this work is characterization of  $\text{LiV}_3\text{O}_8$  as a negative active material for reversible Li intercalation in  $\text{LiNO}_3$  water electrolyte.

The SSR sample possessed the best electrochemical characteristics from all of three samples.

## Hydrogenation and Cracking of Nickel Electrodeposited in the Presence of Brighteners

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During cathodic polarization in an acidic media containing hydrogenation-enhancing additives, nickel absorbs large quantities of hydrogen [1]. A new crystal phase, nickel hydride ( $\beta$ -NiH<sub>x</sub>, where  $0.7 \leq x \leq 0.8$ ) with a f.c.c. lattice is formed, the lattice parameter being approximately 6% larger than that of nickel [2]. For a very short time strongly stressed layers are formed [3] that lead to lasting structural alterations.

The conversion of nickel into nickel hydride in bright nickel electrodeposits is more complete than that of matt ones obtained from an additive-free electrolyte [4]. The hydride phase is unstable and disintegrates under normal conditions. In contrast to matt coatings where the disintegration follows an equation inherent to first-order reactions [5], the disintegration of the hydride phase in the bright coatings begins after a certain period of time after the end of hydrogenation [4]. When the hydrogenation is over above a certain degree, a process of crack formation in the bright nickel deposits starts [6]. The cracking process proceeds at a rate which offers a possibility for a direct observation of the initiation and propagation of the cracks by using a metallographic microscope. A part of the cracks shows a shape close to that of the Archimedes spiral.

However, bright coatings can be obtained in the presence of at least two organic additives – each one of the two classes of additives for nickel electrodeposition, which are usually added in order to improve the properties of the layers such as their appearance, internal stresses, etc. [7]. The present research shows the effect of saccharine and butyndiol - typical representatives of the two classes of additives to the process of phase transformation, as well as on the subsequent cracking of the nickel coatings after the end of cathodic hydrogenation. The investigation showed that both additives in the nickel electrolyte contribute to a more complete phase transformation of nickel into nickel hydride. This is assisted by the fine structure of the nickel deposits with a higher density of defects as well as the incorporated compounds containing sulphur as a product of electrochemical transformation of the saccharine. The type of the additives influences both the tendency of the nickel layers to form cracks and the shape of the cracks.

### References

- [1] B. Baranowski, M. Smialowski, Bull. Acad. Pol. Sci., Ser. Sci. Chim., Geol. Geogr., 7 (1959) 663.
- [2] A. Janko, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 8 (1960) 131.
- [3] Z. Szklarska-Smialowska, M. Smialowski, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 6 (1958) 427.
- [4] St. Rashkov, M. Monev, I. Tomov, Surf. Technol., 16 (1982) 203.
- [5] A. Janko, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 10 (1962) 617.
- [6] M. Monev, St. Rashkov, R. Kaishev, Surf. Technol., 17 (1982) 315.
- [7] Yu. Yu. Matulis: "Blestjashtie elektroliticheskie pokritija", 1969, Vilnius, Mintis.

## Palladium-Poly(3,4-Ethylenedioxythiophene) Composite Layers for Electrooxidation of Glycerol in Alkaline Medium

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In the recent years glycerol was investigated intensively for its possible application in direct alcohol fuel cells, converting the free energy of the alcohol into electrical energy. The anode catalyst and the corresponding matrix for the deposition of the catalyst are crucial for the efficiency of the fuel cell.

In the present investigation composite layers of catalytically active Pd particles deposited on pre-synthesized layers of the conductive polymer poly-3,4-ethylenedioxythiophene (PEDOT) are used as an anode material for electrocatalytic oxidation of glycerol. The Pd particles are obtained by electroless deposition occurring at the expense of the oxidation of the PEDOT layers that are reduced in a former step of the experiment. The polymer matrix is not electroactive for electrooxidation of glycerol and serves only as support for dispersing the catalytic metal phase.

The oxidation of glycerol is studied by cyclic voltammetry in alkaline electrolyte. It is found that the use of several sequential palladium deposition steps of on the same PEDOT layer provides the possibility to increase the amount of deposited metal and thus the electrocatalytic response. Fig. 1 shows the first and the fifteenth voltammetric curves obtained in the course of continuous voltammetric cycling in 0.1 M glycerol and 0.5 M KOH solution. The gray line denotes the measurement in the absence of glycerol. The composite Pd/PEDOT layers exhibit good stability for glycerol electrooxidation reaction upon further cycling in the glycerol containing solution.

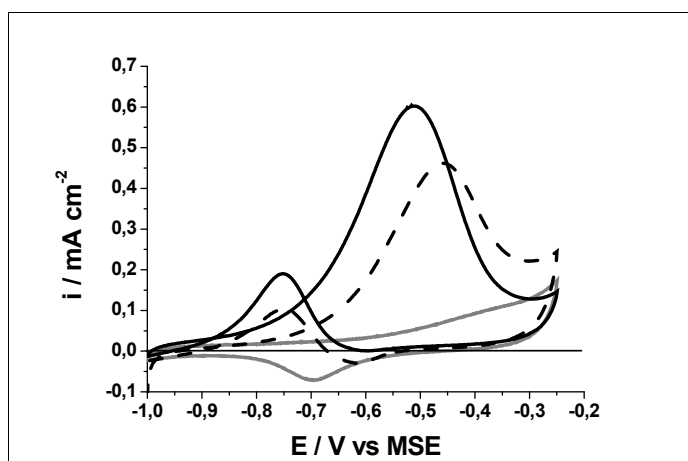


Fig.1. Cyclic voltammometric curves measured in 0.5 M KOH and 0.1 M glycerol at Pd/PEDOT: First scan (dashed line), fifteenth scan (full line). The gray line is measured in supporting electrolyte. Scan rate  $\nu = 0.02 \text{ V s}^{-1}$

## Glassy Carbon Modified With Zr, Ce And Y Oxides as Cathode in Hypochlorite Production

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Zr, Ce and Y – oxides were coated on glassy carbon (GC) by electrolysis of ethanol solutions. The surface morphology and elemental analysis of electrode were examined by means of SCE and XPS. The electrochemical behaviour was characterized by CVA and potentiodynamic polarization curves. The effect on the current efficiency (CE) of the electrodes was also investigated. The highest CE for hypochlorite production occurred on the ZrO<sub>2</sub> - 60 - 65 %. This electrode possessed the maximum apparent activity for HER ( the side reaction) and optimal apparent activity for hypochlorite(the main reaction), respectively. Deposition of Cu - sublayer onto the glassy carbon in the regime of reverse current effects positively onto the layer of ZrO<sub>2</sub> in the relation of its selectivity of the hydrogen reaction and simultaneously the rate of reduction of Cl<sup>+</sup> do not increase..

The major conclusion of the investigation is the GC modified with ZrO<sub>2</sub> can be considered as an alternative to chromate additions in the hypochlorite electrolyte .

### References

- [1] J.Wulff, An Cornell, J .Appl.Electrochem.37(2007)181.
- [2] TMarinova,A.Tsanev,D,SToychev,Mater. Sci.and Eng.B 130(2006)1.
- [3] N.Vesuderan,Res.J. of Cmem.Sci.. 2(2012)55.

## Electrocatalytic Properties of Polypyrrole-Based Composite Layers for Oxidation of Bioactive Compounds

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Polypyrrole (PPy) layers are potentiostatically synthesized on glassy carbon substrate in the presence of two different anionic species – perchlorate ( $\text{ClO}_4^-$ ) and polystyrenesulfonate (PSS). Electrocatalytic and redox properties of the polymer layers are studied at two different values of the polymerization charge. It is established that in comparison to PPy/ $\text{ClO}_4^-$  the PPy/PSS layers have a broader potential region corresponding to the high conducting, oxidized state of PPy.

Electrooxidation of ascorbic acid and epinephrine (pH=6.9, 1 mM analyte concentration) are used as model reactions to elucidate the electrocatalytic properties of the PPy layers. It is found that for PPy/PSS layers the oxidation current of epinephrine is higher than for PPy/ $\text{ClO}_4^-$ . Furthermore the main epinephrine oxidation peak is shifted to more negative potentials by about 100 mV (Fig. 1). In the case of ascorbic acid oxidation, the effect of the doping anion results in a slight shift of the oxidation peak towards more negative potentials when using PPy/PSS layers.

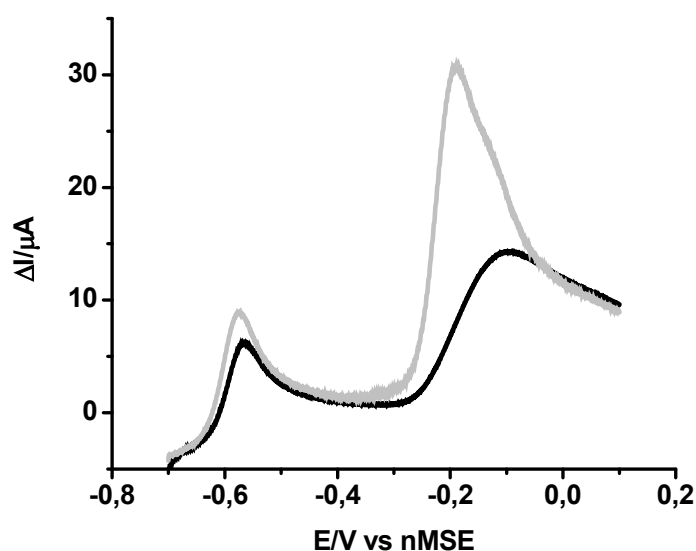


Fig. 1 Anodic parts of the voltammetric curves (after subtraction of the buffer curves) corresponding to the electrooxidation of epinephrine for PPy/PSS (gray line) and PPy/ $\text{ClO}_4^-$  (black line) coated electrodes. ( $Q_{\text{poly}}=7 \text{ mC.}$ )

## Electrodeposition of Sn-Co Alloys from Gluconate Electrolytes in The Presence of Glycine

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During electrodeposition of Ag-Sn, Ag-In и In-Co alloys formation of wave, spiral and target structures on the electrode surface can be observed [1-3].

According to the phase diagram of the Sn-Co alloy different intermetallic compounds can be formed depending of the metal content. Possibility to obtain heterogeneous coatings gives us the opportunities to study the self-organization phenomena [4].

The influence of glycine on the electrochemical processes of deposition and dissolution of tin, cobalt and tin-cobalt alloy from a gluconate electrolyte are studied by means of cyclic voltammetry.

The addition of glycine to the weak acid electrolyte for deposition of Sn-Co alloy has no significant influence on the deposition of tin and relatively strong influence on the deposition of cobalt, with a strong effect on the deposition of Sn-Co alloy. The addition of the glycine and the increase of its concentration lead to a strong increase in the cobalt percentage in the coatings at pH=3.

Dull coatings with high cobalt content can be deposited from the investigated electrolyte. Depending on the pH and glycine addition the deposition of coatings with cobalt content in the whole range from 0 up to 60 wt. % is possible.

Under certain conditions instabilities in the electrochemical system and resulting potential oscillations could be observed.

### References

- [1] A. Hrussanova, I. Krastev, *J. Appl. Electrochemistry* 39 (7) (2009) 989
- [2] Ts. Dobrovolska, L. Veleva, I. Krastev, A. Zielonka (2005) *J Electrochem Soc* 152, C137
- [3] I. Krastev, Ts. Dobrovolska, U. Lacnjevac, S. Nineva, (2012) *J. Solid State Electrochem.*, 16, 3449
- [4] Brenner, *Electrodeposition of alloys, Principles and Practice. Band I. Von A.. Academic Press, New York-London 1963*

## **Optical Characterization of CDB SnS Thin Films**

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Tin sulfide thin layers were deposited by Chemical Bath Deposition on glass or on TiO<sub>2</sub> covered glass substrates in acidic medium. The morphology, crystal structure and optical properties of the thin films have been investigated using X-ray diffraction, Atomic Force Microscopy, Vis-NIR spectroscopy and Scanning Electron Microscopy with EDAX. The influence of the bath composition, plating time and solution temperature on the growth and optical characteristics of the films were established. The as deposited films are smooth and uniform and improve crystallinity after annealing at 250 °C. The optical band gap of thin SnS films were calculated for the case of the direct transitions to be between 1.23 - 1.28 eV.

## Novel Cost Efficient Corrosion Resistant Catalytic Carrier for PEMWE Applications

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Polymer electrolyte membrane water electrolysis (PEMWE) is an attractive method to produce pure hydrogen for various energy clean stationary and transport applications. The choice of efficient catalysts dispersed on high surface area stable catalytic supports has important role for the reliable operation and durability of the membrane electrode assembly (MEA) - the main PEMWE component where the energy conversion (electrical to chemical) takes place.

In this work the phyllosilicate mineral Montmorillonite (MMT) has been investigated in regard of its properties as catalytic support for hydrogen generation via electrochemical water splitting. MMT is a cheap natural product, main constituent of the volcanic ash. Chemically, it is a complex mixture of hydrated hydroxides with general formula  $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$ . Potassium, iron, and other cations are common substitutes as the exact ratio of cations varies with source. Morphologically, MMT consists of plate-shaped nano-crystallites which form clay with high surface area and thermo-mechanical properties of a polymeric matrix. MMT possesses low electrical conductivity and by now has not been investigated as catalytic support.

In the present research MMT has been loaded with noble metal nanoparticles (Ir and Ru) with proven high catalytic activity towards the oxygen evolution reaction. Ir has been deposited by the well established sol gel technique, while Ruthenium montmorillonite was prepared by the following procedure: a mixture of 1g montmorillonite Na<sup>+</sup> and 10 ml solution of ruthenium (III) chloride was irradiated with ultrasound for 2h. The solution is obtained by dissolving 0.1g ruthenium (III) chloride in 10 ml of 50:50% ethanol-water system. The slurry were used as received. The obtained MMT-supported catalysts have been characterized by EDX, SEM, and XRD techniques. Their electrochemical performance and OER catalytic efficiency have been investigated by cyclic voltammetry and steady state polarization curves in aqueous acid solutions (0.5 M H<sub>2</sub>SO<sub>4</sub>) and in proton conductive polymer electrolyte (Nafion 117, DuPont). The results obtained showed superior performance of Ir/MMT in regard to both activity and stability as well as a good correlation with the previously reported data about Ir supported on commercial ceramic supports with excellent electrical conductivity such as Magnelli phase titania (Ebonex, Atraverda and N82, Ti-Dynamics).

The results obtained proved that the MMT can be considered as potential catalytic support for hydrogen generation via water Energy System.

## Phosphating of Zinc Surfaces by Modifying Zinc-Phosphate Solutions

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The communication presents results about the effects of a zinc-based phosphating agent KAF-101-ZT modified by calcium, nickel and manganese on the processes of phosphating film formation onto zinc substrate surfaces.

The results from the gravimetric, chemical, electrochemical and physical test revealed data about the density, conductivity, the total and free acidity as well as those of the produced coatings (thickness, phase and chemical compositions, structure, corrosion resistivity, protection ability).

The phosphating processes with modified solutions of the agents KAF-90ZN(Ni), KAF-90ZM(Mn) и KAF-90ZK(Ca) result in films with thicknesses finer than those obtained with the basic agent KAF-101ZT, irrespective of the operating conditions (concentration range 5-15 %, temperature range (20-60°C).

The phosphate coatings consist mainly of the phases hopeite with a partial replacement of Zn in it by Ca, Ni and Mn, but not enough to lead to formation of a new phase. The modification of the hopeite could be classified as quasi-hopeite of the calcium, nickel and manganese, respectively.

The modification of the phosphate coatings by nickel, calcium and manganese leads to shifts in a positive direction of their corrosion potentials in model NaCl solutions with about 25-10 mV. In case of 0.6M  $\text{NH}_4\text{NO}_3$ , the corrosion potentials are positive with high corrosion currents greater than the ones observed in the NaCl solutions.

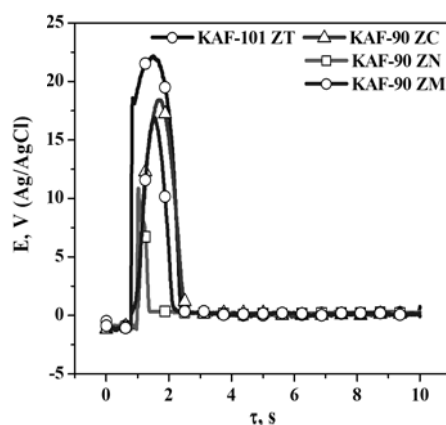


Fig.1. Relationships "potential – time" ( $E, V - \tau, s$ ) during galvanostatic polarization of phosphate coatings

The electrochemical methods determining the protective characteristics of the coatings are related to measurements of the time evolution of anodic potential  $E_{Amax}$  in course of galvanostatic polarization in a suitable electrolyte ( $\text{NaCl} + \text{Na}_2\text{SO}_4; 6 + 94 \text{ g l}^{-1}$ ) as it is illustrated by Fig. 1. Each sample was tested in triple experiments in order to assure acceptable accuracy and reproducibility of the measured characteristics. The anodic behaviours of the coatings reveal that better corrosion-protection properties correspond to higher maxima of the anodic potential.

### References

- [1].Rausch D., "The Phosphating of Metals", Finishing Publications Ltd, Teddington, Middlesex, England, 1990
- [2].Freeman D. B., Phosphating and Metal Pretreatment, Woodhead-Foulkner, Cambridge, 1986
- [3] Donofrio J., Metal Finishing, 98, 2000, p.57, 60
- [4].T.Sugama, T. Takahashi, "Surface modification of electrogalvanized steels by zinc phosphate conversion coatings", J.of Mater. Science, **30**, 1995, p. 809

## Corrosion Behavior of Anodically Formed Oxide Films on Aluminum, Sealed in Cerium-Ions Containing Solutions

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The corrosion behavior of anodically deposited oxide films on Al-1050 has been studied in 0.1M NaCl solutions. The Al<sub>2</sub>O<sub>3</sub> films have been formed in an electrolyte containing H<sub>3</sub>PO<sub>4</sub> – 40 g/l under voltostatic conditions of anodization. The sealing has been carried out in 0.5M CeCl<sub>3</sub> solutions at temperatures 25°C and 60°C. The thickness of the coatings was 3-5µm.

The surface morphology and the composition of the sealed nano-porous anodic films have been studied by means of scanning electron microscopy (SEM) and energy dispersive analysis (EDS). It has been established that depending on the conditions of sealing the concentration of cerium inside the pores of the oxide films is growing up from 5.3 up to 10.4 wt.%. On the basis of the XPS spectra of the studied systems the chemical state of cerium in the nano-pores of the oxide film has been defined.

Potentiodynamic investigations have been carried out and the corrosion currents from polarization (E-i) curves have been determined for non-sealed and sealed in solutions containing Ce<sup>3+</sup> ions anodic oxide coatings on aluminum. It has been shown that the filling up of the nano-pores of the formed Al<sub>2</sub>O<sub>3</sub> anodic film with Ce (OH)<sub>3</sub>/Ce<sub>2</sub>O<sub>3</sub> is promoting its corrosion protection ability.

## Ni Based Multicomponent Electrodeposited Alloys for Hydrogen Evolution Reaction

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One of the most common electrode materials is based on nickel and its alloys because of their good catalytic activity for hydrogen evolution reaction (HER). These electrodes play an important role in various electrochemical processes. In order to improve the properties of these materials and increase their electrocatalytic activity various methods are applied such as alloying with other elements, incorporation of composite components and other changes with the aim to obtain electrodes with well-developed, rough or porous surface. Codeposition on nickel with transition metals, which have better catalytic activity compared with the pure metal is one of the most popular methods. In this study, based on Ni-Fe-Co alloys with the addition of Mo and P, were electrodeposited. The morphology and component distribution were characterized by SEM and EDX analyses. These materials were investigated by galvanostatic steady-state curves in 6 M KOH for HER. It is shown that in dependence of the electrolysis process conditions rich of nickel, molybdenum or iron alloys can be obtained. The hydrogen overvoltage is reduced when the alloys contain more Fe and Co than Ni in the layers without phosphorus. The presence of phosphorus (2 to 4%) in the alloys significantly reduces the content of molybdenum in them. Polarization dependences of these alloys show better catalytic characteristics for HER than the deposits without phosphorus content. The amorphous systems NiFeCoP alloys show the lowest polarization for HER. The reason for such result is probably the synergism between Ni and Co, Fe from one hand, and the reduction of the crystal grain size, from the other hand, which determines a more developed surface.

**Acknowledgment:** This study was funded by the National Science Fund of Bulgaria through contract E 02/9.

## Study of LiNaSO<sub>4</sub> as Electrolyte Material

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With the advancement of technology, requirements for the efficiency and stability of chemical power sources increase. Lighter, providing with high energy density and longer life materials are being sought. The interest in highly conductive lithium compounds is dictated by their potential use as a solid electrolyte in various energy systems. In particular, our interest is directed to LiNaSO<sub>4</sub> compound which is used as a solid electrolyte and as a supplement in a functional layer in a medium temperature fuel cells [1,2]. It is famous for its ionic superconductivity in the range of 500-700 oC (~ S cm<sup>-1</sup>) [1,2].

The purpose of this work is investigations of this compound as a potential solid electrolyte in lithium batteries. Samples were prepared by the mechano-chemical method. This method is cheap and easily accessible. It allows the managing of the atmosphere and the synthesis at room temperature. The performed X-ray investigations confirmed that all characteristic peaks of LiNaSO<sub>4</sub> are present. The samples are homogenous and all of the starting materials have reacted. The claim was confirmed by the SEM images. The samples were tested for total conductivity by means of impedance spectroscopy method. The results are very promising. Further investigations are in progress.

### Acknowledgement

The research leading to these results has received funding from Bulgarian NSF under grant No E02/3/2014

### References

- [1] Weiming Lv, Z. Tong, Yi-Mei Yin, J. Yin, Zi-Feng Ma, Nano-Micro Lett., DOI 10.1007/s40820-015-0038-4
- [2] Yu Feng, Jingli Luo,\*,z and Karl T. Chuang, J. Electrochem. Soc., 153 5 A865-A868 2006

## Methanesulfonate and Pyrophosphate Electrolytes for Deposition of Copper-Antimony Alloys

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The main reason to alloy copper with antimony is two-fold: once, to obtain very thick copper bright coatings (with up to 3-5 wt. % of antimony) for the purpose of microrobotics and second, to obtain colored coatings – some phase of Cu-Sb alloys are purple [1].

One more reason – the possibility to obtain periodical spatio-temporal structure onto the electrodeposited surface of alloy due to the presence of intermetallic compounds in the phase diagram of the alloy.

Recently was presented that the copper-antimony alloys could be deposited from acid methanesulfonate electrolytes and optical heterogeneity could be observed onto the cathode surface [1]. Investigations of some other alloys (Ag-Sb, In-Co, Ag-In) allows to summarize that the optical heterogeneity in a form of waves, spirals and structures are closely connected with a phase heterogeneity [2]. The present investigation aimed to find out the appropriate electrolyte for the deposition of copper-antimony alloy in a wide range of antimony content and to investigate the possibility to observe spatio-temporal structures onto the electrode surface. Some comparative experiments for the deposition of copper-antimony alloys from acid as well as from alkaline electrolytes with equal content of metal ions ( $2.5 - 7.5 \text{ g dm}^{-3}$  Cu and  $3 - 9 \text{ g dm}^{-3}$  Sb) are performed. The substrates are brass and the anodes – platinum.

It is established, that from methanesulfonic electrolytes at the low current densities ( $0.1 - 0.4 \text{ A dm}^{-2}$ ) the coatings are copper like (up to 2 wt. % of Sb) and with increasing current density onto the pink base the spots and lilac shadows appear (after  $0.5 - 1 \text{ A dm}^{-2}$ ). The ordered pattern could also be observed. At the antimony content in the alloy about 70 wt. % the coatings are purple.

The electrodeposition from pyrophosphate electrolytes at low current densities ( $0.1 - 0.3 \text{ A dm}^{-2}$ ) leads to the obtaining of grey coatings, rich of antimony (with more than 80 wt. % Sb). The co-deposition of copper starts at higher current densities. The pyrophosphate ions, being strong complex forming agents for the copper ions shift the deposition potential of copper to more negative potentials. It is obvious, that in the methanesulfonate electrolytes for the alloy deposition the copper deposits predominantly and vice versa in the alkaline electrolytes. Composition and the morphology of the obtained coatings are also presented.

### References

- [1] A. Hrusanova, I. Krastev, A. Zielonka, Effect of electrolyte composition on the electrodeposition of Cu-Sb alloys from methanesulfonate – tartrate electrolytes, *Zastita materijala* 52 (2011), 3, 145-151.
- [2] I. Krastev, T. Dobrovolska, Pattern formation during electrodeposition of alloys, *J. Solid State Electrochem.* 17 (2013) 481-488,

## Superconductive BSCCO Ceramics as Additive to the Zinc Electrode Mass in the Nickel-Zinc Rechargeable Batteries

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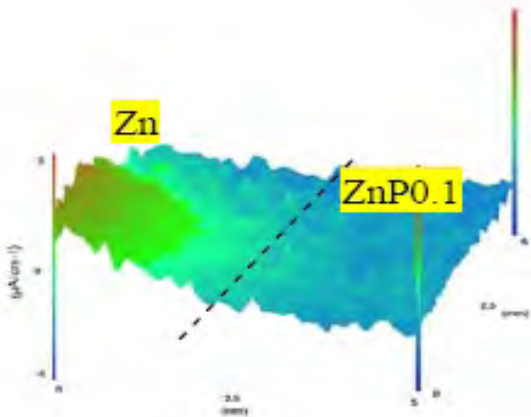
The interest to the rechargeable alkaline nickel-zinc batteries in recent years is determined by the advantages offered by this type of battery – high both specific energy density and power density, high voltage, relatively low-cost materials and environmental friendly chemistry. The battery life is largely determined by the life of the zinc anode, usually a paste type composite electrode with main component - electrochemically active ZnO powder and various additives for improving electrochemical performance of the electrode. The electronic conductivity of ZnO however is rather poor and this is the main reason for the electrochemical heterogeneity of the anode mass and the loss of active surface area during charge/discharge cycling with a corresponding negative effect on zinc electrode characteristics. In order to improve the conductivity of the zinc electrode mass a carbon powder additive (e.g. acetylene black) is usually applied but this may result in an increase of the hydrogen gas evolution during charging. The main objective of the present work is a study on the possibility of application of superconductive cuprate Bi-Pb-Sr-Ca-Cu-O (BSCCO) ceramics as a multifunctional conductive additive to the zinc electrode mass.

Powder samples of cuprate superconducting ceramics  $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{8-x}$  ( $x \leq 0.2$ ) are produced by conventional solid-state synthesis. The ceramics samples are structurally and morphologically characterized by XRD, SEM and EDX analysis. The X-ray diffraction patterns and phase identification as well as the SEM observation reveal a well crystallized single phase of superconducting 2212 system BSCCO with an average crystallite size 2-5  $\mu\text{m}$ . The chemical stability of the obtained BSCCO ceramics in alkaline medium is studied by analyzing polycrystalline samples before and after prolong exposure (96 h) to an alkaline solution (7M KOH), normally used as a basic electrolyte in alkaline nickel-zinc batteries. The high chemical resistance of the ceramics in strong alkaline media is confirmed by structural and surface morphological observations [1].

The electrochemical behavior of zinc electrodes with addition of BSCCO powder (7 w%) to the active electrode mass based on ZnO (89 w%) are studied and compared to the behavior of zinc electrodes with an active mass with similar composition but containing acetylene black (2 w%) as a conductive additive instead of BSCCO ceramics. The electrochemical tests are carried out by a specially designed prismatic Ni-Zn battery cell with conventional sintered type nickel electrodes. The study show that the cells with BSCCO superconducting ceramic additive to the zinc electrode exhibit very good cycleability and remarkable capacity stability at charge/discharge cycling as well as much higher specific capacity at prolong cycling in comparison to the cells with zinc electrode with “classic” carbon conductive additive. It is suggested that the addition of BSCCO ceramics improves not only conductivity of the zinc electrode mass and reduces the gas evolution but also stabilizes its porosity structure. The results obtained prove definitely the positive effect of application of superconducting BSCCO ceramics as a multifunctional additive to the active mass of the zinc electrodes for alkaline battery systems.

### References

- [1] G. Ivanova, L. Stoyanov, S. Terzieva, A. Stoyanova-Ivanova, M. Mladenov, D. Kovacheva, R. Raicheff, Nanoscience and Nanotechnology 14, Eds. E. Balabanova, E. Mileva, Publ. BPC Ltd., Sofia (2014) p. 33



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## Implementing ScSZ electrolyte SOFC for Combined Heat and Power Production

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Zirconia (ZrO<sub>2</sub>) doped with 10-mol. % Sc<sub>2</sub>O<sub>3</sub> and 1-mol. % CeO<sub>2</sub> (1Ce10ScSZ) is considered now as a promising highly conductive alternative to widely used yttria stabilized zirconia (8YSZ) ceramic electrolyte and studied now extensively. 600 °C Ceramic Fuel Cell is a promising technology for reliable and environmentally safe power generation.

The project is directed on

Further development of zirconia powders to be produced in Ukraine and validated at the partnering institutes;

Further development of EB-PVD towards larger cell areas;

Development of a stack design optimized for low temperature operation;

SOFC prepared by EB-PVD and traditional techniques will be compared and tested at least for 2000 hours of operation;

These activities will constitute a major step towards the industrial implementation of new powder sources.

Ukrainian SOFC team has achieved:

Zirconia powders; EB-PVD technique for electrolyte; LSCF cathode for 600 °C operation.

The state of the proposed:

Laboratory technologies. As result, specific resistance at 600 °C of Zirconia Ukraine FC is ~0.6 ohm·cm<sup>2</sup>. Typical is >2.0 ohm·cm<sup>2</sup>. Sample of portable 10 W FC battery is demonstrated.

FC equipment of \$500 per kW is expected.



IPMS SOFC team, 2014. From the left: Ye. Brodnikovskiy, O. Kyrpa, N. Lysunenکو, M. Brychevskiy, D. Brodnikovskiy, I. Bykov, I. Brodnikovska, O. Vasylyev

Potential participants:

*EU*

- University of Birmingham
- Jülich Research Center
- Warsaw Technical University
- Sofia Institute of Electrochemistry & Energy Systems

*Ukraine*

- Institute for Problems of Materials Science
- Physical-Mechanical Institute
- Ukrainian Chemical Technology University
- Institute for Physical Chemistry

## **RIGEL, a Reversible and Innovative fuel cell based system for Grid balancing and Energy storage from Large green hydrogen production**

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RIGEL will study, explore in depth and develop a radically new, efficient, simple, robust high-performance reversible solid-oxide electrochemical device able to quickly switch from fuel cell (FC) to electrolyzer (EC) mode. This concept of a totally new electrochemical device follows the EERA policy for long-term breakthrough research in support of the Hydrogen Economy establishment.

The RIGEL reversible cell derives from a novel dual membrane high-temperature FC designed and patented by key consortium members in a successful FP7 project (IDEAL-Cell)[1, 2, 3, 4]. RIGEL goes well beyond this original idea and the current state of the art, boosting the concept to a reversible cell coupled with a renewable energy source (RES) as a stand-alone single system able to provide grid balancing services through hydrogen production using momentary electricity over-capacity.

In the RIGEL cell, water, oxygen and hydrogen are produced/consumed in three separate chambers, which ensures considerable advantages compared to existing technologies (no dilution of gases, easy pressurization, fast switching from FC to EC modes, no severe interconnect corrosion, simple auxiliaries, excellent aging resilience).

The project will bring the RIGEL concept from TRL2 to TRL4 in 4 years via 3 successive steps of increasing levels of integration through a high degree of basic science, ensuring: i/ optimization of the reversible cell through an Integrated Computational Materials Engineering approach, combining novel materials and microstructure architectures, microscopic reaction kinetics and 3D modeling of the cell components microstructure, ii/ integration of the cells into a specifically designed innovative 3-chamber short stack, and iii/ evaluation of the RIGEL technology as a means combined to weather-dependent RESs. The dissemination activities aim at attracting industrial partners for further development of the RIGEL concept in FCH JU, as well as towards increased public awareness of hydrogen technologies.

The consortium that will contribute to this project gathers renowned experts in complementary fields (materials science, electrochemistry, modeling, metallurgy, solid state physics and chemistry, powder metallurgy, impedance spectroscopy, renewable energy management and systems, communications) from Bulgaria, Italy, Serbia, Norway, France.

We are looking for partners who are interested in the concept and its realization, who have experience in proton conducting SOFC and can contribute to the scaling up and fabrication of a stack.

### **References**

- [1] Thorel A., Abreu J., Ansar S.A., Barbucci A. et al. *J.Electrochem. Soc.* (2013) 160 (4) : F360-F366
- [2] Ou T., Delloro F., Bessler W., Thorel A., Nicoletta C., *J.Electrochem. Soc.* (2013) 160 (4): F367-F37
- [3] Viviani M., Canu G., Carpanese M-P., Barbucci A., Sanson A. et al., *Energy Procedia* 28 (2012) 182-189
- [4] Viviani M., Thorel A.S., Barbucci A. et al. *Proceedings of SOFC XIII (ECS transactions)*, Japan, (2013)

## Project for Hydrogen Fuel Cell Forklift

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Fuel cell powered forklifts have numerous benefits against battery powered forklifts including: increased productivity through quick refueling and constant power across the operation and 3-shift operation with one energy system. The main disadvantages of the fuel cell drives are: high cost of the fuel cell system, expensive and complicated storage of hydrogen in high-pressure cylinders, limited number of charging stations for hydrogen.

The project's background is the accumulated experience of Bulgarian companies and research organizations in batteries electric forklifts and involvement in the development of hydrogen technologies.

The concept of the proposal is based on the following ideas:

Hybridization of the drive – fuel cell and battery. This is one of the main questions in a hydrogen fuel cell forklift development, because the system cannot be built only on fuel cell concept. Energy is needed to start the cell, to assistance in peak power consumption when the dynamics of the cell is insufficient. It is convenient to have a backup power in the case of hydrogen depletion.

One problem that arises when replacing batteries with fuel cells is the lower system weight, which brings to insufficient mass of the counterweight or higher center of gravity. We offer a solution – metal hydrides for hydrogen storage which on the one hand compensate the lower weight and on the other hand increase the safety of the system.

The conversion will be performed on standard battery forklift, produced by the Bulgarian company "Balkancar Records" Co (Fig. 1);

Software for optimization of the hybrid power units will be developed.

The design will be based on the real driving cycle.



Fig. 1. The Project idea for hybrid fuel cell power system is based on a standard 2.5 or 3.5 tons battery forklift on the Balkancar Records manufacturer.

Current IEES partners:

"Balkancar Records" Co., Plovdiv, Bulgaria – forklifts producer;

ADVENTURE AD, Sofia, Bulgaria – producer of Hydrogen generators by oxy-steam reforming.

We are looking for:

Fuel cells producer;

Metal hydrides producer;

Other partners interested in that topic.

*Participation of B. Burdin in RSE-SSE 5 has been made possible with the financial support of Bulgarian Ministry of Education and Science*



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ISE STUDENT SATELLITE REGIONAL  
SYMPOSIUM ON  
ELECTROCHEMISTRY  
SOUTH-EAST EUROPE

June 7, 2015  
IEES-BAS, Sofia, Bulgaria



## ISE SSRSE-SEE5 PROGRAM

### SUNDAY, June 7, 2015

08:30-08:45 Opening Institute of Electrochemistry and Energy (IEES-BAS)  
10 Acad. G. Bonchev Str., 1113 Sofia, Bulgaria

#### Session 1 / Chair: Marin Pandev

09:10-09:50 Oleksandr Vasylyev, Y. Brodnikovskiy and M. Brychevskiy

**SS-KN-01 Structural optimization of solid oxide fuel cells**

09:50-10:05 Marius Pelmuș, Michaela Dina Stănescu, Eleonora-Mihaela Ungureanu,  
Georgiana-Luiza Arnold, Laszlo Tarko

**SS-O-01 Electrochemical and QSPR investigations of some phenols and aromatic amines**

10:05 -10:20 Gavrilo Šekularac, Aleksandar Dekanski, Milica Košević and Vladimir Panić

**SS-O-02 Microwave synthesis of crystalline RuO<sub>2</sub> supercapacitor materials**

10:20-10:35 Athanasios Papaderakis, S. Sotiropoulos, S. Balomenou and D. Tsiplakides

**SS-O-03 Electrochemical impedance studies of IrO<sub>2</sub> catalysts for oxygen evolution**

10:35- 10:50 Coffee Break

#### Session 2 / Chair: Athanasios Papaderakis

10:50-11:05 Elitsa Chorbadzhiyska, Y. Hubenova and M. Mitov

**SS-O-04 New electrocatalysts for bioelectrochemical hydrogen production**

11:05-11:20 Ivo Bardarov, Yolina Hubenova and Mario Mitov

**SS-O-05 Freshwater Sediment Microbial Fuel Cells as remote area power sources**

11:20-11:35 Georgiana-Luiza Arnold, Catalina Negut (Cioates), and Eleonora-Mihaela Ungureanu

**SS-O-06 On the electrochemical behaviour of oleamides**

11:35-11:50 Ivana Jevremović, Marc Singer, Srđan Nešić, Vesna Mišković-Stanković

**SS-O-07 Talloil diethylenetriamine imidazoline as corrosion inhibitor for mild steel for both continual immersion and top of the line conditions**

13:00-14:00 Lunch

#### Session 3 / Chair: Mykola Brychevskiy

12:50- 13:30 Tsvetina Dobrovolska

**SS-KN-02 Electrochemical methods of analysis. Phase identification by anodic linear sweep voltammetry**

13:30-13:45 Denis Sačer, Marijana Kraljić Roković

**SS-O-08 Materials based on reduced graphene oxides for supercapacitor devices**

13:45-14:00 Alice Giuliano, M. P. Carpanese and A. Barbucci

**SS-O-09 Characterization and electrochemical measurements of impregnated cathodes for solid oxide fuel cells**

16:00-16:35 Coffee Break

#### Session 4 / Chair: Alice Giuliano

14:15-14:30 Barbara Volarič, Ingrid Milošev

**SS-O-10 Conversion coatings based on lanthanide salts and their mixtures as a corrosion protection of 7075-T6 aluminium alloy in chloride solution**

14:30-14:45 Katja Fröhlich, Atanaska Trifonova and Peter Blaha

**SS-O-11 Understanding of electrochemical processes in lithium nickel manganese cobalt oxide using density functional theory**

14:45-15:00 Marin Pandev

**SS-O-12 Opportunities and Services for Researchers and Research Units. Technology Transfer. Enterprise Europe Network.**

15:00-15:15 Mykola Brychevskiy

**SS-O-13 Structural Dependence of 1Ce10ScSZ Electrolyte Strength**

15:15-15:30 Yegor Brodnikovskiy

**SS-O-14 Zirconia Powder for SOFC Anode**

15:30 -15:40 Conclusions & Closing

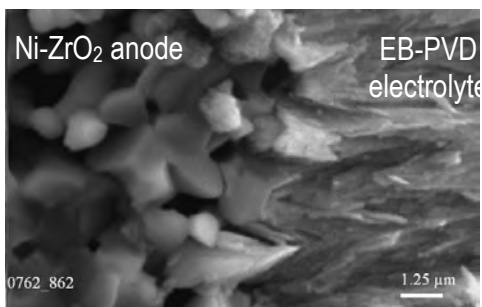


Fig. 1. Cross-section with fracture of 10Sc1CeSZ film deposited on Ni-8YSZ anode with EB-PVD [1].

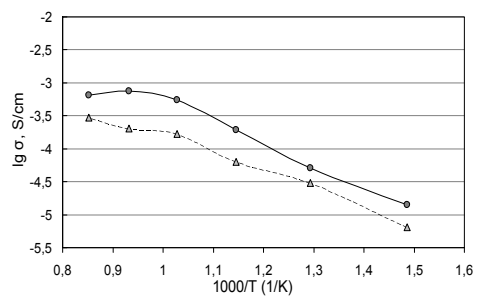


Fig. 2. The total conductivity of 10Sc1CeSZ films deposited on Ni-8YSZ anodes with EB-PVD (●) and screen printing (▲) techniques [1].

## **Electrochemical Methods of Analysis. Phase Identification by Anodic Linear Sweep Voltammetry**

Tsvetina Dobrovolska

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In the present lecture the short coverage of fundamentals for electrochemical methods, widely used is given. The potentials and thermodynamics of cells, kinetics of electrode reactions, double-layer structure, mass transfer by migration and diffusion, potentials sweep methods polarography and pulse voltammetry are briefly presented. The very convenient experimental tools of electrochemical methods are presented with emphasis made toward their application.

The lecture includes numerous problems and examples especially in the field of noble metals deposition processes as well in the electrodeposition of alloys.

The anodic linear sweep voltammetry (ALSV) is an appropriate in situ technique for electrochemical characterization of the phase composition of an electrodeposited alloy [1-5]. This technique is based on the electrochemical principle, that each phase in the coating has its own equilibrium potential, i.e. dissolution potential and therefore the anodic linear sweep voltammetry (ALSV) can successfully be applied as a method for anodic dissolution of thin alloy layers in a specially chosen electrolyte and determination of their phase compositions. In the present lecture an attempt was made to summarize the methods of using the ALSV technique and to compare the results with those obtained by the conventional techniques, such as X-ray analysis and scanning electron microscopy.

### **References**

- [1] A.R. Despic, V.D. Jovic, in: R.E. White, J.O'M. Bockris, B.E. Conway (Eds.), *Modern Aspects of Electrochemistry*, vol. 27, Plenum Press, New York, 1995 (Chapter 2)
- [2] V.D. Jovic, R.M. Zejnilovic, A.R. Despic, J.S. Stevanovic, *J. Appl. Electrochem.* 18 (1988) 511–520
- [3] V.D. Jovic, B.M. Jovic, A.R. Despic, *J. Electroanal. Chem.* 357 (1992) 357–372
- [4] Ts. Dobrovolska, V. D. Jovic, B. M. Jovic, and I. Krastev, *J. Electroanal. Chem.*, 611 (2007) 232-240
- [5] T. Dobrovolska, I. Krastev, B.M. Jovic, V.D. Jovic, G. Beck, U. Lacnjevac, A. Zielonka, *Electrochim. Acta* 56 (2011) 4344-4350

## ORAL PRESENTATIONS

### Electrochemical and QSPR Investigations of Some Phenols and Aromatic Amines

Marius Pelmuș<sup>1,2</sup>, Michaela Dina Stănescu<sup>1\*</sup>, Eleonora-Mihaela Ungureanu<sup>1</sup>, Georgiana-Luiza Arnold<sup>1</sup>, Laszlo Tarko<sup>2</sup>

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#### 1. Introduction

Oxidation reactions of phenols and aromatic amines in aqueous solution are of great interest for wastewater remediation [1]. Laccases (benzenediol:oxygen oxidoreductases) have proved to be an excellent choice as biocatalyst for the oxidation of aromatic derivatives due to their large substrate diversity (phenols, methoxyphenols, aromatic amines, etc.), as well as the use as co-substrate of oxygen from air. The oxidation potential ( $E_{ox}$ ) of the substrates, together with the working pH, play an important role in the bioremediation of wastewater with laccases [2]. The pH values for good enzymatic activity and stability for most of the laccases are in the range: mild acidic – weak alkaline [3]. Therefore, we consider of interest to investigate some representative phenols and aromatic amines by electrochemical methods to determine how the  $E_{ox}$  value is influenced by the pH value in a range suitable for laccases. Theoretical quantitative structure–property relationships (QSPR) studies were performed to identify the molecular characteristics of the substrates that are significant for the value of the  $E_{ox}$ .

#### 2. Experimental

The studied compounds were: catechol, resorcinol, hydroquinone, pyrogallol, phloroglucinol, gallic acid, *p*-aminophenol and *p*-phenylenediamine. All chemicals were of reagent grade quality from commercial sources and used without further purification.

*Electrochemical experiments* have been carried out in a conventional three-electrode cell using an Autolab-PGSTAT12 potentiostat. The working electrode was a glassy carbon electrode (GCE) ( $\varnothing = 3$  mm). As reference electrode, Ag/AgCl electrode in saturated KCl was used. A platinum wire was the counter electrode. Before each experiment the active surface of the GCE was polished with diamond paste (0.25  $\mu\text{m}$ ) and subsequently washed with distilled water. The  $E_{ox}$  values were determined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). For resorcinol the square wave voltammetry (SWV) was also used. The aromatic compounds were dissolved in a Britton-Robinson (BR) buffer to make 1 mM solutions with pH between 3 and 8. CV curves were recorded at 0.1 V/s, DPV curves were recorded at 0.01 V/s with a pulse height of 0.025 V and a step time of 0.2 s, and SWV curves were recorded at a frequency of 25 Hz with the amplitude of 20 mV.

#### 3. Computation method

*QSPR calculations* were performed for the pH dependent neutral and cationic species of the substrates. The PCModel program was applied for virtual building and optimization of geometry of the studied compounds. Based on the MOPAC program and the PM6 semi-empirical method the geometries of the studied molecules were more rigorously optimized and a number of molecular descriptors (computable features of the molecules) were calculated. Nearly 500 global descriptors and the percentages of molecular weight fragments for each species were calculated using the statistical program PRECLAV. The aromaticity descriptors were calculated by DESCRIPT program.

#### 4. Results and discussions

All the previously mentioned compounds were analyzed by the CV and DPV methods. As an example Fig. 1 shows how the pH value influenced the voltammetric curves for *p*-aminophenol.

For resorcinol a comparison of results obtained by the three voltammetric methods (CV, SWV, DPV) was performed (see Fig. 2). For the three methods, a similar variation of the  $E_{ox}$  values with the modification of the pH was observed.

Fig. 3 shows a similar pattern,  $E_{ox}$  decreases with the increase of pH, for the  $E_{ox}$  variation with the pH for all compounds. The substitution position is also of importance. Thus, the *meta* substituted phenols (resorcinol and phloroglucinol) have the highest value for  $E_{ox}$ , while the aromatic amines (*p*-aminophenol and *p*-phenylenediamine) have lower values.

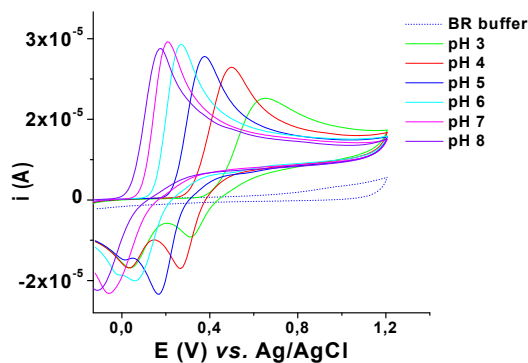


Fig. 1. CV curves for *p*-aminophenol at different pH values.

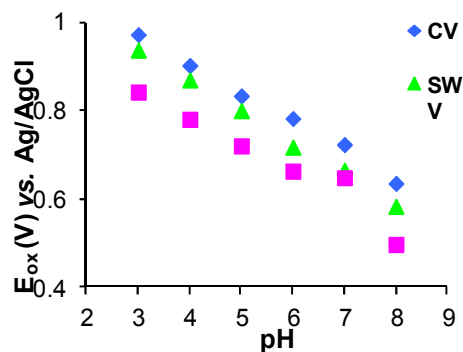


Fig. 2. Variation of the  $E_{ox}$  with pH for resorcinol – using 3 different methods of voltammetry.

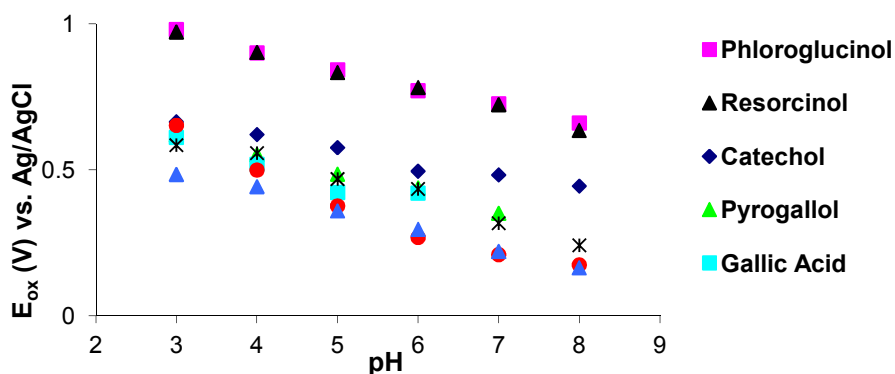


Fig. 3. Variation of the  $E_{ox}$  with pH for all tested substrates – using CV (0.1 V/s).

The QSPR calculations reveal that the value of the  $E_{ox}$  of the species (neutral and cationic) correlates with the net charge of the hydrogen atoms and aromaticity of the cycle (influenced by the type, number and position of substituents). This is in agreement with the results obtained by the electrochemical study: the *meta* substitution deactivates the aromatic ring which explains the high  $E_{ox}$  value. The amino group present in the aromatic amines, being a better electron donor than the hydroxyl from phenols, leads to low  $E_{ox}$  values.

## 5. Conclusions

By electrochemical methods (CV, DPV, SWV) a decrease of the oxidation potential with the increase of pH, for all the studied aromatic compounds was evidenced. Thus, performing the oxidation in neutral or alkaline conditions leads to better results in the wastewater remediation. However, by using laccase as biocatalyst, the choice of the working pH depends also of the enzyme optimal pH. The QSPR calculations demonstrate the influence of the substituent on the  $E_{ox}$  value.

## 6. References

- [1] E. Valero, M.-I. González-Sánchez, M.-T. Pérez-Prior, in: Environment, Energy and Climate Change I, E. Jiménez, B. Cabañas, G. Lefebvre (eds), The Handbook of Environmental Chemistry vol. 32, Springer International Publishing, 2015, pp. 317-339.
- [2] B. Viswanath, B. Rajesh, A. Janardhan, A. P. Kumar, G. Narasimha G. Fungal laccases and their applications in bioremediation. *Enzyme Res.* 2014 (2014), <http://dx.doi.org/10.1155/2014/163242>.
- [3] BRENDA (BRaunschweig ENzyme Database) / Laccases (EC 1.10.3.2) <http://www.brenda-enzymes.org/enzyme.php?ecno=1.10.3.2#pH%20RANGE> (accessed March 30, 2015).

## Microwave Synthesis of Crystalline RuO<sub>2</sub> Supercapacitor Materials

Gavrilo Šekularac\*, Aleksandar Dekanski, Milica Košević and Vladimir Panić  
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One-step simple temperature-controlled microwave synthesis was applied to prepare nanocrystalline RuO<sub>2</sub> dispersion from aqueous RuCl<sub>3</sub>. RuO<sub>2</sub> samples were synthesized at temperature 120, 150, 200, 220 and 250 °C in closed vessel. Reaction time was 5 min. Capacitive properties of RuO<sub>2</sub> was investigated by cyclic voltammetry and electrochemical impedance spectroscopy in 1 M H<sub>2</sub>SO<sub>4</sub> and standard three-electrode cell, with ink-type working electrode on glassy carbon substrate. The specific capacitance of 320, 550, 750, 750 F/g was obtained for samples synthesized at temperature 150, 200, 220 and 250 °C respectively, cyclic voltammetry curves are shown in (Fig.1). The best capacitive performance was obtained for sample synthesized at temperature of 200 °C, specific capacitance of 750 F/g which negligibly depend on sweep rate in 5–500 mV/s range. RuO<sub>2</sub> dispersion was subjected to dynamic light scattering in order to analyze the synthesized particles, whereas structural and morphological properties of the solid phase are investigated by AFM, SEM, EDAX and XRD techniques. The ordered unusual shape of ca. 100 nm native particles, as well as highly-ordered prismatic agglomerate sheets are observed for sample synthesized at temperature 200 °C. These findings are quite unusual for this kind of material consisted of rather large particles [1], and makes it excellent candidate for both low and high power applications.

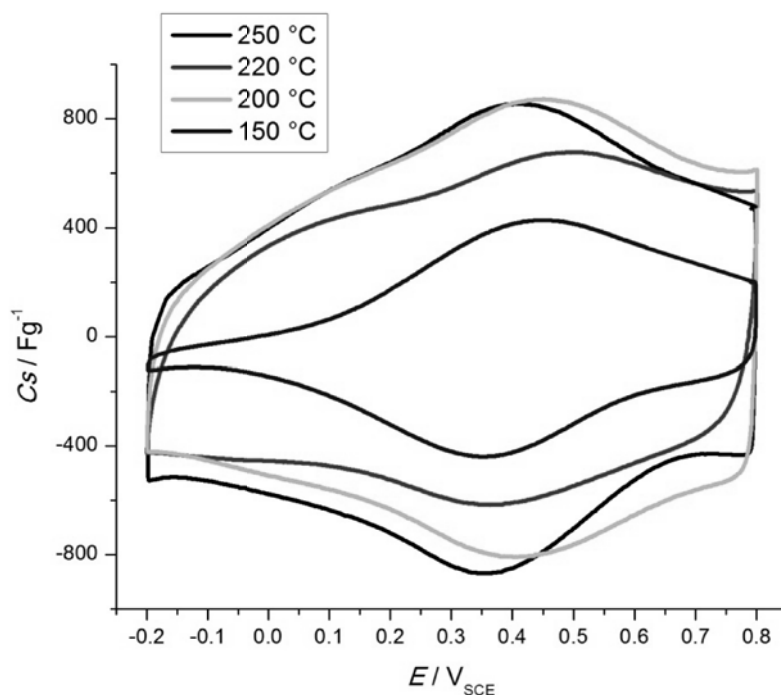


Fig.1. Cyclic voltammograms of RuO<sub>2</sub> synthesized in microwave at temperature 150, 200, 220, 250 °C in 1 M H<sub>2</sub>SO<sub>4</sub>, scan rate 50 mV/s.

### References

- [1] J. P. Zheng, P. J. Cygan, T.R. Jow, J. Electrochem. Soc. 142 (1995) 2699

# Electrochemical Impedance Studies of IrO<sub>2</sub> Catalysts for Oxygen Evolution

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IrO<sub>2</sub> electrodes used as oxygen evolving anodes were studied by electrochemical impedance spectroscopy (EIS) to establish criteria for the assessment of their electroactive surface area and their intrinsic catalytic activity. Two types of IrO<sub>2</sub>-coated electrodes were used: anodically grown oxides on an Ir substrate and commercially available IrO<sub>2</sub> nanoparticles, dispersed in a Nafion<sup>®</sup> polymer electrolyte layer on a glassy carbon substrate. EIS data obtained at potentials outside and within the oxygen evolution reaction (OER) range, indicate that both formulations behave as porous electrodes and their AC response can be described by variants of the classic transmission line model [1]. In order to obtain an independent estimate of electrochemically active surface area (EASA) based on the total capacitance of the electrode, an alternative approach (free from the assumptions and geometric formulations of a model) has been adopted comprising the construction of  $-1/(\omega Z_{im})$  vs.  $Z_{re}$  plots. The latter acquire or approach a limiting value at low or intermediate frequencies which can be related to the total electrode capacitance  $C_t$  [2].  $C_t$  values scale well with the charge associated with IrO<sub>2</sub> surface electrochemistry and with oxide layer thickness or oxide particle loading. Fig. 1a presents such plots for anodic IrO<sub>2</sub> at potentials outside (inset) and in the OER potential range. An attempt has been made of decoupling the intrinsic catalytic activity for OER and surface area effects (assessed by the values of total electrode capacitance during OER,  $C_{t,OER}$ ) from the overall catalytic activity (assessed by the values of  $R_p$  for each electrode). We propose that  $R_p$  should be normalized for the electroactive area by multiplication with  $C_{t,OER}$ , since the latter is proportional to the surface area.  $C_{t,OER}$  can also be used to correct direct current vs. electrode potential OER data for electroactive surface area effects (Fig. 1b).

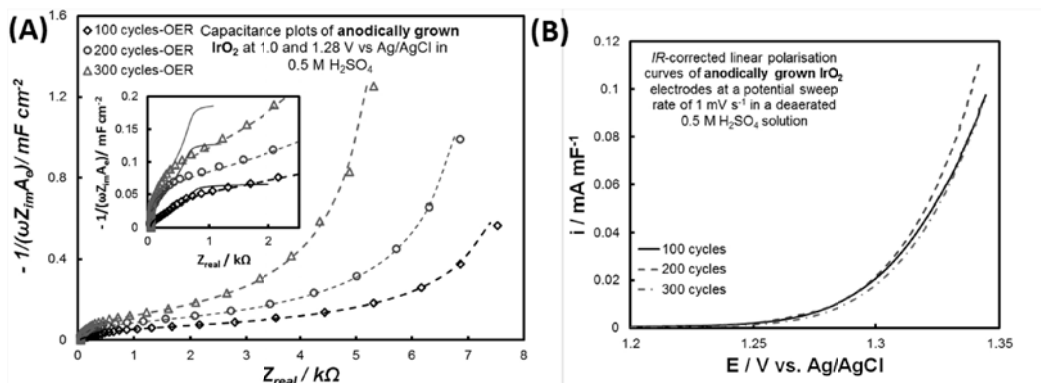


Fig.1. a) Plots of  $-1/(\omega Z_{im})$  vs.  $Z_{re}$  (where  $A_e$  is the electrode substrate area) obtained in deaerated 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions at +1.28 V vs Ag/AgCl at anodically produced IrO<sub>2</sub> electrodes (by 100, 200, 300 potential cycles). Inset: Plots of  $-1/(\omega Z_{im})$  vs.  $Z_{re}$  at +1.00 V vs Ag/AgCl from the same EIS data described above.

(The lines correspond to simulated AC responses based on the classic transmission line model [1]). b) Linear sweep voltammographs for OER at anodically produced IrO<sub>2</sub> electrodes (by 100, 200, 300 potential cycles), recorded in deaerated 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions at a 1 mV s<sup>-1</sup> potential scan rate. Currents are normalized per total capacitance,  $C_{t,OER}$  as obtained from data in Fig.1a.

## References

- [1] Lasia, A., in *Electrochemical Impedance Spectroscopy and its Applications*, Springer, New York, 2014.  
 [2] Reid, O., Saleh, F.S., Easton, E.B., *Electrochimica Acta*, 114 (2013) 278-284.

## New Electrocatalysts for Bioelectrochemical Hydrogen Production

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Microbial electrolysis cells (MECs) are an innovative technology for hydrogen production [1]. Although the cathode process in MEC is the same as that of a water electrolyzer, the operational conditions in both systems are completely different. As MECs typically operate at neutral pHs and ambient temperatures (20–30°C) suitable for microbial growth, the development of cost effective cathodes at mild conditions is the most critical challenge for the practical application of the technology. In this study, new supported electrocatalysts were produced and investigated as cathodes for HER in neutral phosphate buffer solution (PBS) with respect of their possible application in MECs. Two methods were used for preparing the materials: chemical reduction and electrochemical deposition on different support materials: carbon felt (SPC-7011, 30g/m<sup>2</sup>, Weißgerber GmbH & Co.KG), Ni-foam (RCM-Ni-4753.016) and porous graphite (GMZ, Russia). Depends on the catalyst elemental content, the produced materials may be divided into three groups: i) Pd-Au modified electrodes in different ratio of both metals; ii) CoB, NiB, CoNiB modified electrodes; iii) NiW and NiMo modified electrodes. Scanning electron microscopy and energy-dispersive X-ray spectroscopy investigations were performed to explore the morphology and the elemental composition of the prepared catalysts. The electrocatalytic activity of the newly produced materials towards HER in PBS was examined by means of linear voltammetry. In all cases the modified electrodes possess much higher electrocatalytic activity compared to that of the non-modified support materials [2-6]. The quantities of the produced hydrogen gas with different electrocatalysts were calculated from data obtained by chronoamperometry. The highest hydrogen production rate of 26 ml.mg<sup>-1</sup>.cm<sup>-2</sup>.h<sup>-1</sup> (at -1.2 V vs. Ag/AgCl) was achieved with Pd<sub>50</sub>Au<sub>50</sub>/Ni-foam [4]. NiMo and NiW electrodeposited on Ni-foam were explored as non-precious metal electrocatalysts for hydrogen production in a tubular membrane-free MEC. The obtained values of hydrogen recovery with these cathodes are 80±8%.

### References

- [1] E. Chorbadzhiyska, Y. Hubenova, G. Hristov, M. Mitov, In: Proc. of the Fourth International Scientific Conference FMNS-2011, Blagoevgrad, p.422.
- [2] E. Chorbadzhiyska, M. Mitov, G. Hristov, N. Dimcheva, L. Nalbandian, A. Evdou, Y. Hubenova, *Int. J. Electrochem.*, 2014, Article ID 239270, 6 pages (2014). <http://dx.doi.org/10.1155/2014/239270>.
- [3] E. Chorbadzhiyska, Y. Hubenova, G. Hristov, L. Nalbandian, M. Mitov, *Bulg. Chem. Comm.*, in press.
- [4] E. Chorbadzhiyska, M. Mitov, L. Nalbandian, Y. Hubenova, *Int. J. Hydrogen Energy* (2015). doi: 10.1016/j.ijhydene.2015.04.029
- [5] E. Chorbadzhiyska, M. Mitov, Y. Hubenova, L. Nalbandian, In: Proc. of the Fifth International Scientific Conference FMNS-2013, Blagoevgrad, p.88.
- [6] M. Mitov, E. Chorbadzhiyska, L. Nalbandian, Y. Hubenova, *Bulg. Chem. Comm.*, in press.

## **Freshwater Sediment Microbial Fuel Cells as Remote Area Power Sources**

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<sup>1</sup> *South – West University “Neofit Rilski”, Blagoevgrad, Bulgaria*

<sup>2</sup> *Plovdiv University “Paisii Hilendarski”, Plovdiv, Bulgaria*

\* *ivobardarov@gmail.com*

Microbial Fuel Cells are a rapidly evolving technology, which utilizes the natural electrogenic properties of specific bacterial species. Sediment Microbial Fuel Cells (SMFCs) utilize the natural potential gradient existing in the benthic zone to allow bacteria to generate current by the oxidation of organic and inorganic matter contained in the sediment. SMFCs are inexpensive and easy to construct, which makes them suitable for power sources in remote areas. The current article summarizes the results from a 3-years study of twelve freshwater SMFCs in laboratory conditions. The electrical outputs achieved by fuel cells using river sediment and soil were compared and discussed. Their long-term reliability as power sources was proved using statistical evaluation of the data collected from continuous and periodical polarizations. Several ultralow voltage power management systems were explored in order to determine their ability to power different sensors using the developed SMFCs as power sources.

## On the Electrochemical Behaviour of Oleamides

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### 1. Introduction

This work is devoted to the electrochemical characterization of two oleamides (Fig. 1): 1 phenoxy-2-propanol-3-izopropyleamide (**1**) and N-(4-hydroxyphenethyl)oleamide (**2**). The compounds were synthesized from oleic acid and 1,1 - carbonyldiimidazole to give the oleyl-imidazol intermediate which reacted with the corresponding amines, according to the procedure described in [1]. The new oleamides were characterized by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR spectra.

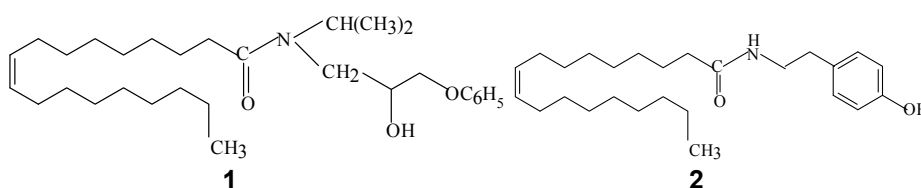


Fig. 1. Structure of investigated compounds

Electrochemical investigations were performed by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and rotating disk electrode (RDE).

### 2. Experimental

All compounds used for synthesis were purchased from Merck and used without further purification. For electrochemical investigations acetonitrile and tetrabutylammonium perchlorate (TBAP) from Fluka were used (as received) as solvent and supporting electrolyte, respectively.

The electrochemical experiments were carried out using a PGSTAT12 AUTOLAB potentiostat coupled to a three-compartment cell. The CV curves were generally recorded at 0.1V/s or at various rates (0.1 - 1V/s) when studying the influence of the scan rate. DPV curves were recorded at 0.01V/s with a pulse height of 0.025V and a step time of 0.2 s. The RDE curves were recorded at 0.01V/s. The working electrodes were glassy carbon disks (diameter of 3mm). Their active surface was polished before each determination with diamond paste (200  $\mu$ m). Ag/10 mM AgNO<sub>3</sub> in 0.1 M TBAP, CH<sub>3</sub>CN was used as reference electrode. The potential was referred to the potential of the ferrocene/ferricinium redox couple (Fc/Fc<sup>+</sup>) which in our experimental conditions was +0.07V. A platinum wire was used as auxiliary electrode. The electrochemical experiments were performed at 25°C under argon atmosphere.

### 3. Results and Discussion

The electrochemical behavior of compound was studied in acetonitrile (CH<sub>3</sub>CN) containing tetrabutylammonium perchlorate (TBAP) as supporting electrolyte, using stationary or rotating glassy carbon electrodes. The results of electrochemical experiments carried out by CV, DPV and RDE are shown in Fig. 2. Anodic curves were recorded individually, starting from the stationary potential. No cathodic process can be evidenced. The anodic processes (1a - 5a) are denoted in the order in which they appear in the voltammograms. Two main anodic processes (1a and 2a) are observed in all kind of curves (Fig. 2). The influences of the scan rate and scan domain on the CV curves showed that all processes are irreversible.

By cycling the potential in the range of the first anodic peak a decrease of the current has been seen showing the formation of a film or accumulation of insoluble products on the electrode surface. The cycling led to a modified electrode which was characterized by CV. The transfer of this modified electrode in ferrocene solutions in supporting electrolyte showed altered CV curves for the redox probe. The ferrocene signal is smaller in intensity and very flat, confirming the electrode covering with an insulating layer (film or insoluble products). The electrode modification can be performed also by controlled potential electrolysis.

The results obtained for both oleamides are in agreement with the previous characteristics obtained for a similar compound [2]. However, the two investigated compounds show different electro activities evidenced by different domains of potential for anodic processes. Compound 2 is oxidized easier than 1. This behavior could be explained by the

differences in their structures. The presence of an aromatic moiety connected to the amide in **2** is expected to give it better adsorption on the electrode and, consequently, **2** is oxidized easier.

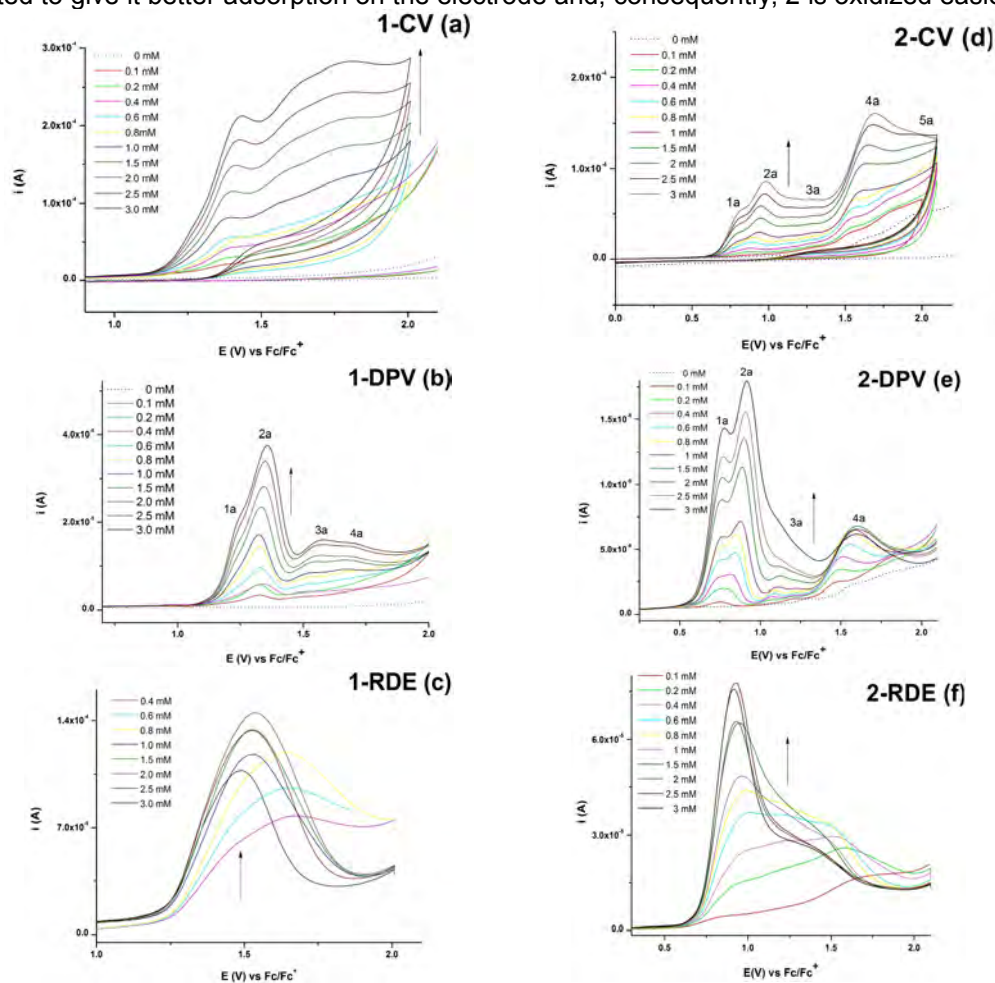


Fig. 2. CV (a,d), DPV (b,e) and RDE (c,f) curves for **1** (a,b,c) and **2** (d,e,f) obtained for different concentrations of each compound

#### 4. Conclusions

Two main anodic irreversible processes were identified by cyclic and differential pulse voltammetry. Scanning the potential in the range of the first anodic peak led to the coverage of the electrode with an insulating layer. Its formation was confirmed by rotating disk electrode curves.

#### Acknowledgments

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#### References

- [1] C. Tanase, C. Negut (Cioates), D. I. Udeanu, E.-M. Ungureanu, M. Hrubaru, C. Munteanu, S. P. Voicu, F. Cocu, A. C. Ionita, *Revista de Chimie*, 65 (7), (2014), p. 768-773.
- [2] C. Negut (Cioates), E.-M. Ungureanu, F. Cocu, C. Tanase, C. Draghici, C. Munteanu, *Scientific Bulletin, Series B, Chemistry and Materials Science*, 76 (4), (2014), p. 173-182.

## Talloil Diethylenetriamine Imidazoline as Corrosion Inhibitor for Mild Steel for both Continual Immersion and Top of the Line Conditions

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The use of corrosion inhibitors is one of the most practical and cost effective methods for combating CO<sub>2</sub> corrosion in oil and gas wells and flow lines [1]. Carbon dioxide (CO<sub>2</sub>) top-of-the-line corrosion (TLC) occurs in wet gas flow where a significant temperature gradient between the outside environment and the inner pipeline surface leads to high condensation rates. The presence of various corrosive species such as CO<sub>2</sub> and acetic acid (CH<sub>3</sub>COOH) causes a severe corrosion problem [2]. Conventional mitigation methods can fall short in protecting the top of the line since the conditions do not allow the inhibitor to reach the top sections of the wall. New inhibitor delivery method is being investigated as an alternative to conventional batch treatment. A novel idea consists of injecting the corrosion inhibitor within a foam matrix and delivering the corrosion inhibitor to locations where condensation occurs.

The objective of this research was to investigate the inhibitor efficiency in liquid phase and to prove if the corrosion inhibitor can be carried by the foam matrix and provide sufficient corrosion inhibition on the top of the line. The inhibition effect of talloil diethylenetriamine imidazoline (TOFA/DETA imidazoline) on corrosion of mild steel in CO<sub>2</sub>-saturated 3 wt. % NaCl solution was investigated by electrochemical impedance spectroscopy (EIS), potentiodynamic sweep (PDS), cyclic voltammetry (CV) and scanning electron microscopy (SEM). Corrosion rate was monitored under condensing conditions, in the vapor phase, using electrical resistance (ER) measurements.

The investigated organic compound TOFA/DETA imidazoline exhibited high inhibition efficiency against mild steel corrosion in 3 wt. % NaCl solution saturated with CO<sub>2</sub>. The protection efficiency increased with increasing inhibitor concentration from 50 ppm<sub>v</sub> to 90 ppm<sub>v</sub>, up to 92 %. PDS measurements shown that TOFA/DETA imidazoline can be considered a mixed-type corrosion inhibitor with the predominant anodic effect. The addition of TOFA/DETA imidazoline decreased the corrosion current density for more than one order of magnitude. The results of CV measurements indicated inhibited electrode processes in the presence of TOFA/DETA imidazoline due to the adsorption of inhibitor molecules on mild steel electrode active sites (Fig.1).

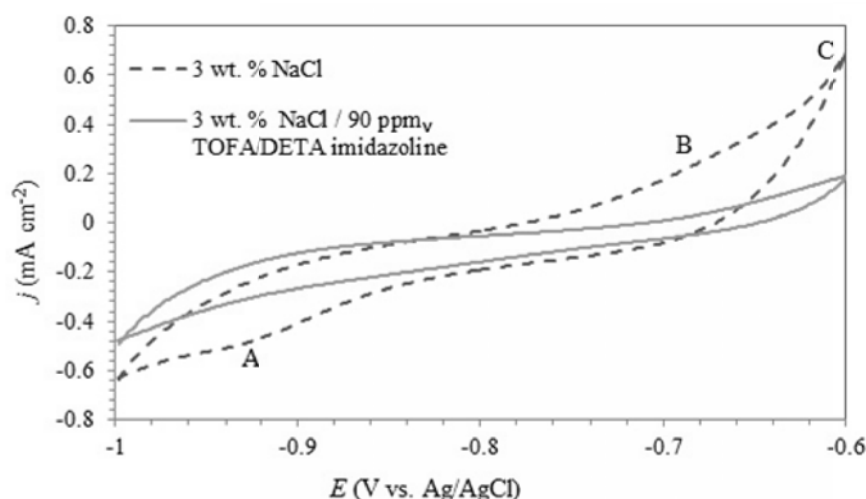


Fig. 1. Cyclic voltammograms obtained in CO<sub>2</sub>-saturated 3 wt. % NaCl solution at mild steel electrode with and without 90 ppm<sub>v</sub> of TOFA/DETA imidazoline, 20°C, scan rate 20 mV s<sup>-1</sup>.

EIS measurements revealed that the thickness of TOFA/DETA imidazoline protective layer increases with increase in inhibitor concentration resulting in a decrease in double layer-

capacitance. The SEM measurements revealed that the appearance of steel surface was significantly improved after the introduction of TOFA/DETA imidazoline to the corrosive solution suggesting that TOFA/DETA imidazoline forms an inhibitive film on the mild steel surface which is very stable and protective even at elevated temperatures after 24 h exposure to the aggressive solution.

The TLC rate of mild steel, calculated from metal loss, which was measured in the vapor phase using the ER probe, was reduced effectively by periodic treatment by the foam, sodium C14-16 olefin sulfonate, concentration 20 vol. % in deionized water containing 1000 ppm<sub>v</sub> TOFA/DETA imidazoline corrosion inhibitor. Fig. 2 shows the time dependence of metal thickness loss in vapor phase for contact times of 15 s indicating that the corrosion rate remained below 0.1 mm·yr<sup>-1</sup> for at least 15 h. Consequently, it can be considered that the TOFA/DETA imidazoline carried by the foam matrix was effective and significantly decreased the TLC rate.

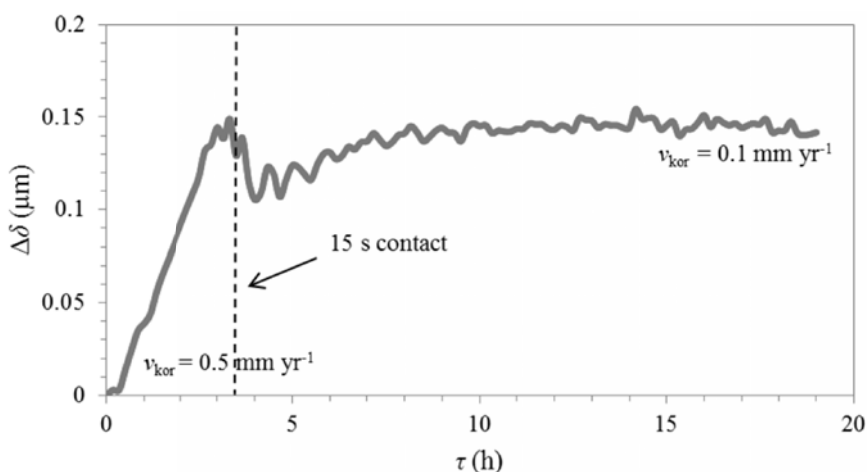


Fig. 2. Time dependences of metal thickness loss in vapor phase when 1,000 ppm<sub>v</sub> TOFA/DETA imidazoline was added in the foam, 3 wt. % NaCl solution at 70°C, pH 4 with acetic acid in a concentration of 0.02 mol·dm<sup>-3</sup> for contact time of 15 s.

The electrochemical study confirmed the efficiency of the TOFA/DETA imidazoline in the CO<sub>2</sub>-saturated 3 wt. % NaCl solution while the measurements in the vapor phase confirmed that the foam matrix containing 1000 ppm<sub>v</sub> TOFA/DETA imidazoline can be used to effectively apply batch inhibition at the top of the line.

## References

- [1] I. Jevremović, M. Singer, S. Nešić, V. Mišković-Stanković, *Corros. Sci.* 77 (2013) 265–272.
- [2] I. Jevremović, M. Singer, M. Achour, D. Blumer, T. Baugh, V. Mišković-Stanković, S. Nešić, *Corrosion*, 69, 2 (2013) 186-192.

## Materials Based on Reduced Graphene Oxides for Supercapacitor Devices

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Materials based on carbon are important because of its low price and abundance, many potential applications in various fields of science and engineering. Graphene<sup>1</sup> is carbon based material consisting of atomic layer of graphite, organized into a hexagonal lattice in which carbon atoms are connected using sp<sup>2</sup> hybridisation resulting in unique electrical properties of zero bandgap semiconductor with both holes and electrons as charge carriers. Its excellent electrical and mechanical properties combined with optical and thermal ones, make it the one of the most investigated material in recent years. One of the possible applications of graphene is based on its high surface area which together with high conductivity opens up the possibility for its application as active electrode components in supercapacitors. Till today a lot of efforts have been made to create the best method for providing graphene in bulk quantities. Most frequently used methods were mechanical or thermal exfoliation of bulk graphite, chemical vapor deposition or epitaxial growth. However, until now only chemical<sup>2</sup> synthetic methods proved capable of production of graphene with relatively good properties in bulk quantities. In chemical methods first step is oxidation and exfoliation of graphite into graphene oxide (GO), product that contains high quantities of different oxygen functionalities, followed by its reduction into the compound usually termed reduced graphene oxide (rGO). However, rGO are far away from theoretical predictions due to agglomeration of rGO sheets and also due to residual defects from oxidation step which highly disrupts the conductivity of such materials and consequently limits its application properties.

The aim of this work was the synthesis of rGO starting from different precursors and using different experimental conditions in order to determine the optimal conditions for production of rGO with the best capacitive properties. Two precursors were used: natural graphite flakes and synthetic graphite. Both materials were subject to the oxidation and exfoliation by Staudenmaier method followed by treatment with either sodium borohydrate<sup>2</sup> or hydrazine hydrate as reducing agents. Obtained GO and rGO were characterized using SEM, AFM, XPS and UV spectroscopy. Supercapacitive properties of resulting materials were investigated by cyclic voltammetry. In addition, the influence of rGOs on the pseudocapacitive responses of pseudocapacitive materials such as MnO<sub>2</sub> and polypyrrole was also investigated.

Using cyclic voltammetry method it was shown that GO layer on Pt support had poor conductivity and that it was not electrochemically active, while rGO had much better conductivity and reversible capacitive response due to the charging/discharging process at electrode/electrolyte interface. Capacitive values of rGO varied from 10-100 F g<sup>-1</sup> depending on choice of graphite precursor in the oxidation step, the type of reducing agents as well as on the pH value and reaction temperature during synthesis.

### References

- [1] A. K. Geim, K. S. Novoselov, *Nature Materials* 6, 2007, 183 - 191
- [2] D. R. Dreyer, Sungjin Park, C. W. Bielawski, R.S. Ruoff, *Chem. Soc. Rev.*, 2010, 39, 228-240

## Characterization and electrochemical measurements of impregnated cathodes for solid oxide fuel cells

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Efforts in the domain of solid oxide fuel cells (SOFCs) are focused on devices capable of operating within an intermediate temperature (IT) range (500-700 °C) for an acceptable period. In this range one of the main polarization losses occur on the cathode considering hydrogen as fuel [1].

La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-δ</sub> (LSM), a commonly used cathode material, exhibits high polarization resistance below 800 °C [2], [3].

For this reason, many mixed electronic and ionic conducting perovskite cathode materials have been developed. Mixed conductors with both electronic and ionic conductivity (MIEC) [4] can be considered as promising cathode materials because of their extended electrochemically active area. In MIECs the reaction sites for oxygen exchange reaction occurs in the whole electrode volume [1]. The iron-cobalt-based perovskite are good candidates for intermediate-temperature SOFCs (IT-SOFCs), in particular Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> (BSCF) and La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> (LSCF) are proposed as cathode materials because of their sufficiently high electronic conductivity and high catalytic activity for the oxygen reduction reaction, unfortunately their use in IT-SOFCs has been hindered by performance degradation.

Interdiffusion between the cathode and the electrolyte and strontium segregation have been reported to be responsible for the performance degradation of LSCF cathode [8]. Efforts to improve the LSCF stability by infiltration with LSM, SSC and GDC [5], [6] have been performed.

On the other hand BSCF is not stable because enrichment of Sr<sub>2</sub>O<sub>3</sub> and BaO on the surface leads to the formation of carbonates in the presence of CO<sub>2</sub> [7].

The aim of this study is to enhance and stabilize performance of BSCF and LSCF for the use as cathode materials in IT-SOFCs combining the high electronic conductivity and stability of LSM with the high ionic conductivity and electrochemical activity of BSCF and LSCF. Then, a BSCF or LSCF cathode scaffold were impregnated with LSM nanoparticles in order to form a composite structure.

To reach this goal, a Samaria-doped ceria (SDC) electrolyte supported half-cell with three-electrode configuration was performed.

BSCF and LSCF electrode scaffolds were prepared using commercial powders (Treibacher and Marion Technology respectively) and in lab synthesized by a novel autocombustion method that use sucrose like complex agent. A fine tuning of electrode decoration was performed by LSM infiltration with a simple sol-gel synthesis that allows the production of nanoparticles.

XRD measurements were applied to investigate the phase composition; Scanning Electron Microscope (SEM) was used to observe the microstructure of obtained cell.

The cathode performances, durability, and long-term stability were evaluated by electrochemical impedance spectroscopy (EIS) measurements. Impedance measurements were carried out at OCV and under applied overpotentials at different O<sub>2</sub> partial pressures and temperatures.

In table 1, R<sub>p</sub> values at 700 °C, OCV and 21% O<sub>2</sub> partial pressure, for impregnated and non-impregnated cathodes, are reported, together with the apparent process activation energies.

	R <sub>p</sub> (Ω·cm <sup>2</sup> )	E <sub>a</sub> (kJ/mol)
LSCF	0.76	138.94
LSM-impregnated LSCF	0.65	138.76
BSCF	0.081	111
LSM-impregnated BSCF	0.06	100.38

Table 1. Polarization resistance and activation energies for LSCF, LSM-impregnated LSCF, BSCF and LSM-impregnated BSCF cathodes.

Electrochemical measurements demonstrate that, for BSCF and LSCF based cathodes, the polarization resistance ( $R_p$ ) decrease when LSM impregnation was carried out. Moreover the impregnation successfully increases the long-term performances of cathodes.

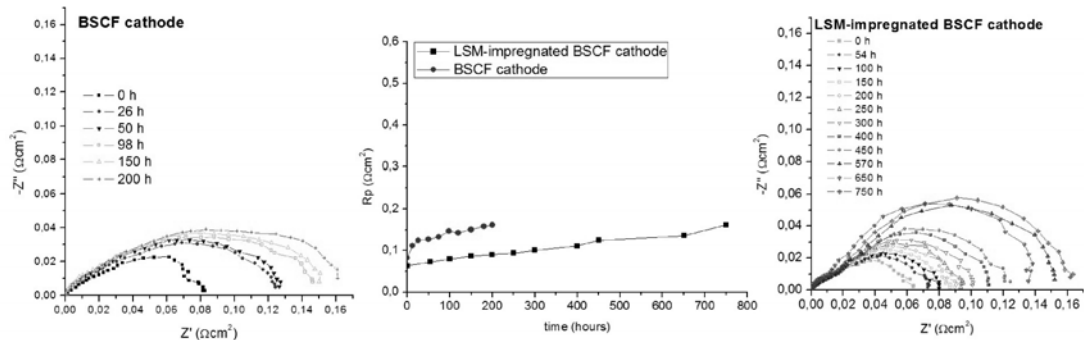


Fig. 1. Nyquist plots for BSCF and LSM-impregnated BSCF cathodes and polarization resistance in function of time. Measurements were performed under an applied current voltage of  $200 \text{ mA}\cdot\text{cm}^{-2}$ , at  $700^\circ\text{C}$  and  $21\% \text{ O}_2$  partial pressure.

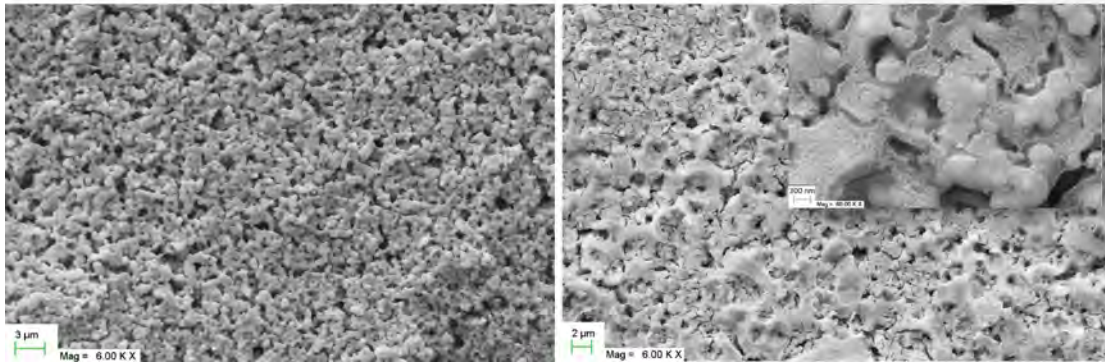


Fig. 2. SEM micrograph for LSCF and LSM-impregnated LSCF cathodes.

## References

- [1] S. B. Adler, "Factors Governing Oxygen Reduction in Solid Oxide Fuel Cell Cathodes," 2004.
- [2] J. Nielsen and M. Mogensen, "SOFC LSM:YSZ cathode degradation induced by moisture: An impedance spectroscopy study," *Solid State Ionics*, vol. 189, no. 1, pp. 74–81, 2011.
- [3] J. Nielsen and J. Hjelm, "Impedance of SOFC electrodes: A review and a comprehensive case study on the impedance of LSM:YSZ cathodes," *Electrochim. Acta*, vol. 115, pp. 31–45, Jan. 2014.
- [4] A. Petric, P. Huang, and F. Tietz, "Evaluation of La-Sr-Co-Fe-O perovskites for solid oxide fuel cells and gas separation membranes," *Solid State Ionics*, vol. 135, p. 719, 2000.
- [5] X. Lou, S. Wang, Z. Liu, L. Yang, and M. Liu, "Improving  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  cathode performance by infiltration of a  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$  coating," *Solid State Ionics*, vol. 180, no. 23–25, pp. 1285–1289, Oct. 2009.
- [6] L. Nie, M. Liu, Y. Zhang, and M. Liu, " $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  cathodes infiltrated with samarium-doped cerium oxide for solid oxide fuel cells," *J. Power Sources*, vol. 195, no. 15, pp. 4704–4708, Aug. 2010.
- [7] A. Yan, M. Cheng, Y. Dong, W. Yang, V. Maragou, S. Song, and P. Tsiakaras, "Investigation of a  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$  based cathode IT-SOFC. I. The effect of  $\text{CO}_2$  on the cell performance," *Appl. Catal. B Environ.*, vol. 66, pp. 64–71, 2006.
- [8] S. P. Simner, M. D. Anderson, M. H. Engelhard, and J. W. Stevenson, "Degradation Mechanisms of La-Sr-Co-Fe-O SOFC Cathodes," *Electrochem. Solid-State Lett.*, vol. 9, no. 10, p. A478, 2006.

## Conversion coatings based on lanthanide salts and their mixtures as a corrosion protection of 7075-T6 aluminium alloy in chloride solution

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Aluminium alloy 7075-T6 is due to good physical and chemical properties commonly used material in different applications in industry. To protect the metal surface against corrosion phosphate and various organic polymer coatings were often used. Some of the components used for their production include toxic organic solvents harmful to the environment. Chromate coatings have been for many decades extremely effective and easy way to improve corrosion resistance on aluminium alloy.  $\text{Cr}^{6+}$  has very good mobility and solubility in solutions, so it can be transported to the parts, where the process of corrosion started. Reduction of  $\text{Cr}^{6+}$  to form  $\text{Cr}^{3+}$  leads to a formation of protective layer of solid chromium hydroxide on the metal surface.  $\text{CrOOH}$  represents the "backbone" of the protective layer. Within this structure is formed islands  $\text{Cr}^{6+}$  and connections  $\text{Cr}^{3+}\text{-O-Cr}^{6+}$ . This process is referred to as a self-healing process [1] and results in the protection of the material in different corrosive media [2]. Six-valent form of chromium is well soluble in water, it also has good permeability through biological membrane, so it is very toxic and carcinogenic [3]. Due to health and environmental problems the use of chromate coatings has become increasingly controlled in the early 90s. Today is the use of chromate conversion coatings severely restricted [4].

As an alternative, various new approaches, which are more environmentally acceptable, are used today to protect metals and their alloys. These include the conversion coatings based on titanium or zirconium [5], sol-gel coatings [6] and conversion coatings based on rare earth salts [7, 8]. Lanthanide compounds are environmentally friendly, their price is reasonable and are available in natural sources. Among lanthanide salts, especially cerium has been identified. Cerium is the most active and the only lanthanide, which can be oxidized in a stable salt with a higher oxidization state [5]. The mechanism of surface protection includes the formation of a protective layer of hydroxide and/or oxide. Due to reduction of oxygen, pH increases, and in the case of cerium forms  $\text{Ce}(\text{OH})_3$ , which is then oxidized to  $\text{Ce}_2\text{O}_3$ . According to another theory, the first step is oxidation of Ce(III) in Ce(IV), which is then precipitated as insoluble  $\text{CeO}_2$  [9]. This reaction is carried out on metal inclusions (Zn, Cu, Mg), which are electrochemically more negative compared to remaining surface of aluminium alloy, and act as a cathode site. Generally, the sites of nucleation coating are cathode inclusions in aluminium alloy [10].

The aim of this study was to investigate various lanthanide salts as potential corrosion inhibitors of technologically important aluminium alloys and may be suitable as replacements of chromate coatings. Conversion coatings are expected to provide equivalent corrosion protection and to be environmentally friendly at the same time. Conversion coatings based on various lanthanide compounds, as well as their mixtures were investigated [11]. Conversion coatings were prepared using 0.01 M nitrate lanthanide salts, i.e., cerium nitrate, lanthanum nitrate and mixtures of cerium and lanthanum nitrate in ratio 1 : 3 and 3 : 1. Coatings were prepared at different times of immersion in lanthanide solutions with the addition of 30 % hydrogen peroxide at the room temperature.

The corrosion properties of bare substrate and substrates modified by conversion coatings were studied by electrochemical measurements in 0.1 M NaCl. Linear polarization (LP) ( $dE/dt = 0.1$  mV/s) and potentiodynamic polarization (PD) curves ( $dE/dt = 1$  mV/s) were performed in 0.1 M NaCl solution using an Autolab PGSTAT12 instrument. The stabilization time at the open circuit potential was 1 hour. Polarization resistance ( $R_p$ ), corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $j_{\text{corr}}$ ) and inhibition effectiveness ( $IE$ ) were determined. The surface morphology and composition of the coatings were analysed using a field-emission scanning electron microscope (FEGSEM) Joel JSM-7600F and energy dispersive x-ray spectrometer (EDS). Roughness of conversion coatings surface was also analysed by profilometer (Bruker). Corrosive resistance of the conversion coatings were tested up to 24 hours in the salt spray chamber (Ascott) in 5 wt. % NaCl at 35 °C.

Nitrate lanthanide salts and their mixtures achieved good protection of 7075-T5 aluminium alloy. Conversion coating of  $\text{Ce}(\text{NO}_3)_3$  is formed over the entire surface with occasional cracks. On the contrary, conversion coating of  $\text{La}(\text{NO}_3)_3$  results in the formation of deposits

preferentially at the intermetallic inclusions. Mixtures of Ce and La nitrate conversion coatings are formed at the entire surface and also on inclusions (Fig. 1).

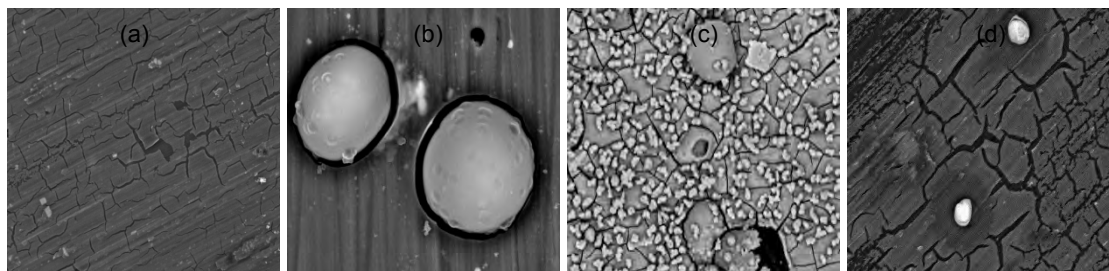


Fig. 1. SEM images of conversion coatings: (a)  $\text{Ce}(\text{NO}_3)_3$ , (b)  $\text{La}(\text{NO}_3)_3$ , (c)  $\text{Ce}(\text{NO}_3)_3 + \text{La}(\text{NO}_3)_3$  1:3, (d)  $\text{Ce}(\text{NO}_3)_3 + \text{La}(\text{NO}_3)_3$  3:1. Conversion coatings were prepared by immersion for 1 hour at room T.

Substrates coated by conversion coating of  $\text{Ce}(\text{NO}_3)_3$  and by mixture of  $\text{Ce}(\text{NO}_3)_3$  and  $\text{La}(\text{NO}_3)_3$  in ratio 3 : 1 prepared by 1 hour immersion achieve the best inhibition effectiveness (Fig. 2). Longer immersion time degrades the effectiveness of inhibitors, except that of  $\text{La}(\text{NO}_3)_3$ .

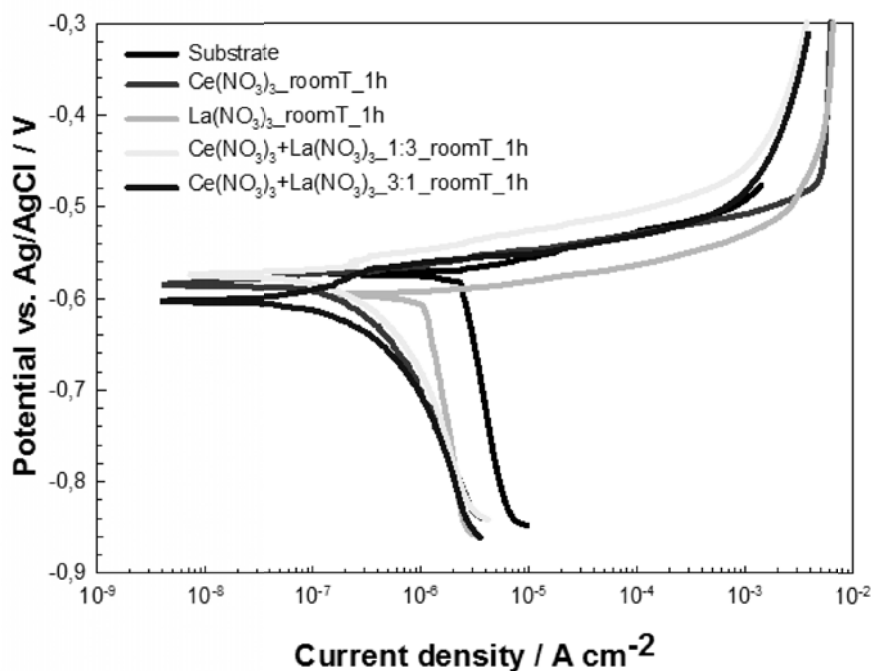
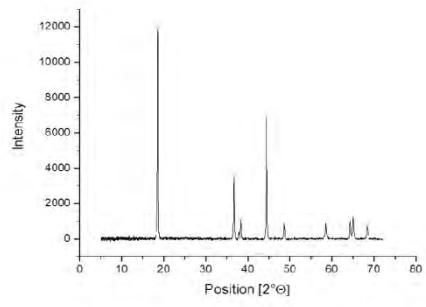


Fig. 2. PD curves measured in 0.1 M NaCl for bare substrate and for substrates modified with conversion coatings prepared by immersion for 1 hour at room T.

## References

- [1] R. Grilli, M.A. Baker, J. E. Castle, B. Dunn, J.F. Watts, *Corros. Sci.* 53 (2011) 1214.
- [2] M. W. Kendig, R. G. Buchheit, *Corrosion* 59 (2003) 379.
- [3] S. Ono, Y. Nishi, *J. Am. Ceram. Soc.* (2001) 3054.
- [4] R. L. Twite, G. P. Bierwagen, *Prog. Org. Coat.* 33 (1998) 91.
- [5] D. Zhao, J. Sun, L. Zhang, Y. Tan, J. Li, *J. Rare Earths* 28 (2010) 371.
- [6] J. H. Osborne, *Prog. Org. Coat.* 41 (2001) 280.
- [7] B. Valdez, S. Kiyota, M. Stoytcheva, R. Zlatev, J. M. Bastidas, *Corros. Sci.* 87 (2014) 141.
- [8] T. G. Harvey, *Corros. Eng. Sci. Technol.* 48 (2013) 248.
- [9] S. B. Brachetti-Sibaja, M. A. Dominguez-Crespo, A. M. Torres-Huerta, W. de la Cruz-Hernandez, E. Onofre-Bustamante, *J. Electrochem. Soc.* 159 (2012) C40.
- [10] A. Boag, A. E. Hughes, A. M. Glenn, T. H. Muster, D. McCulloch, *Corros. Sci.* 53 (2011) 17.
- [11] T. H. Muster, H. Sullivan, et.al, *Electrochem. Acta* 67 (2012) 95.



## Structural Dependence of 1Ce10ScSZ Electrolyte Strength

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The influence of structure on mechanical behavior of 1Ce10ScSZ (1-mol. % CeO<sub>2</sub>, 10-mol. % Sc<sub>2</sub>O<sub>3</sub>, 89-mol. % ZrO<sub>2</sub>) electrolyte ceramics made of powders of various types was studied. Assuming that consolidation of powders and refinement of ceramic structure with sintering are thermally activated processes, the analytical equations, which are describing the relationships between strength, structural sizes, porosity and quality of interfaces are invented.

Strength of ceramics  $\sigma$  is dependent on the sintering temperature  $T_s$  too and might be described as some complex function of structural components, primary porosity  $P$ , effective size of structural elements  $d$  and some effective surface energy  $\gamma$ , which describes quality of boundaries between all structural components and depends on amount and state of impurities.

Generally, the named dependence might be expressed as some complex function  $\sigma(T_s)=f\{d(T_s), P(T_s), \gamma(T_s)\}$ . It requires numerous structural parameters. Traditional ones, like grain size, porosity, are obtained easily. Parameter describing state of inner interfaces might be obtained from fractography, e.g., as strong or weak boundaries resulting in transgranular or intergranular failures, which reflect cleavage and intergranular fracture micromechanisms.

The detailed study of structure and mechanical behavior shows that the fullest set of structural parameters suitable for a sophisticated analysis might be obtained from structural and fractographical data on ceramics made of three different types of zirconia powders, which differ by properties of initial particles and their agglomerates [1]. The data show dramatical difference of structure that is dependent on both the powder type and sintering temperature (Fig. 1).

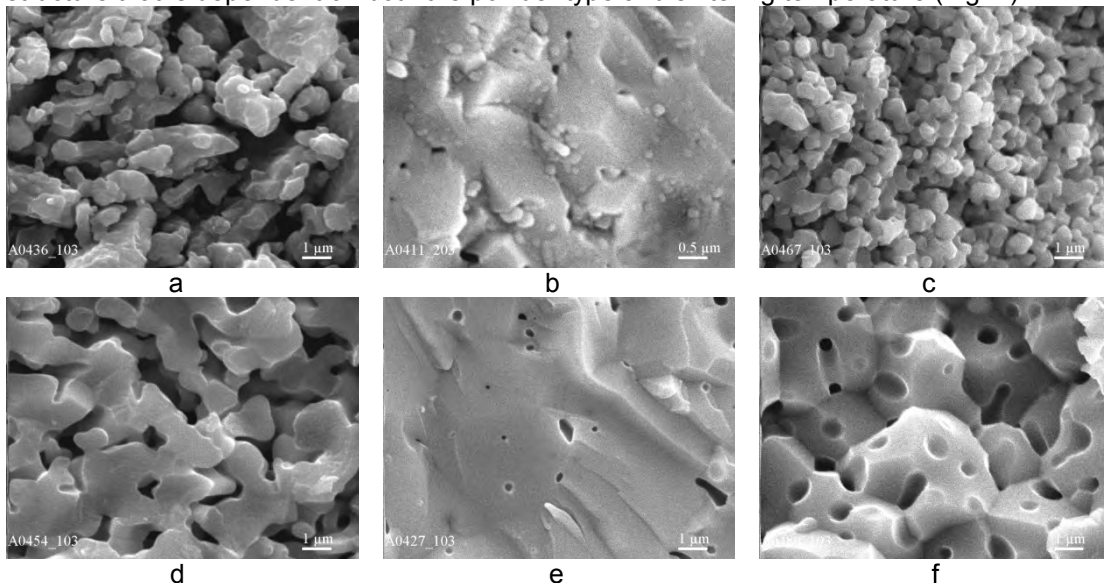


Fig. 1. Fracture surfaces revealed with scanning electron microscopy of 1Ce10ScSZ ceramics made of I - III powder types and sintered at 1350 and 1550 °C, respectively: I - a and d; II - b and e; III - c and f.

Finally, for intergranular and cleavage fracture micromechanisms, ceramic strength is described in above mentioned terms as

$$\sigma = (\sigma_0 + kd^{-1/2}) \cdot (1 - P)^n \cdot \gamma, \quad (1)$$

where  $\gamma$  - the normalized coefficient that determines the boundary quality.

### References

- [1] M. Brychevskiyi, O. Vasylyev, Ye. Brodnikovskiyi at al. Electron microscopy and strength of materials. Vol. 19, Proceedings of IPMS NAS of Ukraine, Kyiv, 2013, p. 169-183.

## Zirconia Powder for SOFC Anode

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Solid oxide fuel cell (SOFC) is the device for direct transformation of chemical energy of fuel in electricity and heat [1,2]. Its anode is the SOFC's component, which provides passing of main electrochemical reaction and provides mechanical stability of all SOFC as a supporter of SOFC. Therefore, strength is one of the basic requirements for anode. Anode should provide strength not less than 100 MPa and have high porosity (>25%) for venting gases.

The most widespread anode material is a composite on the basis of stabilized in a cube phase zirconia (further  $ZrO_2$ ) and nickel. Usually, anodes are made from mixture of powders of  $ZrO_2$  and NiO. Nickel is reduced at operating condition of SOFC.

Influence of zirconia powder morphology on structure formation of anode NiO- $ZrO_2$  sintered at different temperatures (1300-1450°C) and its mechanical behavior was studied. Type 1 – agglomerated powder with initial nanoparticles; Type 2 – dense plane agglomerates consist of uniform initial particles; Type 3 – practically non-agglomerated powder with uniform initial particles (Fig. 1).

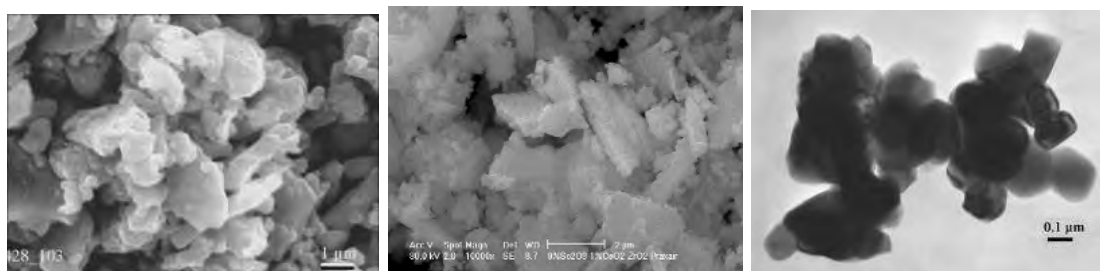


Fig. 1. Structure of different types of  $ZrO_2$  powders: a – type 1, b – type 2, c – type 3.

The size of the initial particles (crystallites) of powders  $ZrO_2$  and NiO were estimated from TEM images of the powder. 20 mm dia, 1.5-2 mm thick disc shaped samples were pressed uniaxially at 20 MPa and then sintered at different temperatures 1300-1450°C for 2h in air. The porosity of the sintered NiO- $ZrO_2$  samples were measured by means of the Archimedes method. The samples were tested for the mechanical strength with biaxial bend test and their fracture surfaces were analysis by means of SEM.

It was found that for formation suitable porosity level (~30 %) and temperature stable structure of anode with strength of 100 MPa, the agglomerated zirconia powder with nanosized initial particles (type 1) is the most suitable.

### References

- [1] S. C. Singhal, K. Kendall (eds.): High-temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications. Elsevier: Oxford, U.K., 2003. (ISBN 13: 978-1-85617-387-2).
- [2] F. Tietz, H.-P. Buchkremer, D. Stover: Components manufacturing for solid oxide fuelcells. Solid State Ionics 152, 153 (2002) 373–381.

## Highly Effective Pd-Au Catalyst for Borohydride Electrooxidation

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In this study, Pd-Au catalysts were prepared by chemical co-deposition on Ni-foam from mixed solutions, containing Pd(II) and Au(III) in different proportions. The morphology and elemental content of the newly synthesized catalysts were characterized by using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively. The electrocatalytic properties of the developed electrodes towards borohydride electrooxidation reaction were explored by means of polarization at variable resistances and chronopotentiometric measurements in stabilized alkaline solution of sodium borohydride. The comparison of the achieved power and discharge capacity values with those obtained with the previously investigated Co-based catalysts reveals a big potential for practical application of the examined materials as highly effective anodes in Direct Borohydride Fuel Cells.

Keywords: Pd-Au catalyst, borohydride electrooxidation, Direct Borohydride Fuel Cells.

## **Opportunities and Services for Researchers and Research Units. Technology Transfer**

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The work presents different opportunities and services for researchers and research units supported by the European Commission, as well as, the model and organisations working in Bulgaria on that field, including the specialised horizontal unit of the Bulgarian Academy of Sciences.

The whole partnership process between science-science and science-business units is explained with aim to assist researchers in achieving business, technological or research partnership agreements.

The Services comprise different tools and approaches, taking into consideration:

Finding international business partners

Finding new technologies

Access to new markets

Information on funding opportunities

Advise on various issues such as intellectual property rights or European legislation and standards

Three specific types of instruments for collaboration are discussed:

Technology Profiles

Business Cooperation Profiles

Project Partner Search Profiles

The drafting of each profile has specific elements since they are for different purposes. Stress is put on explaining the different collaboration types, partners sought and providing targeted information.

### **References:**

- [1] European Commission. (2015, February 3). Partnership Process. Retrieved May 11, 2015, from <http://een.ec.europa.eu/node/4961>
- [2] European Commission. (2015, February 3). Partnership Agreements Guidelines. Retrieved May 11, 2015, from <http://een.ec.europa.eu/node/2012>
- [3] European Commission. (2015, February 3). Additional documents on Profile Drafting and the POD database. Retrieved May 11, 2015, from <http://een.ec.europa.eu/node/2012>
- [4] Enterprise Europe Network. (2015, February 3). Sources of Finance. Retrieved May 11, 2015, from <http://een.ec.europa.eu/my/intranet/sources-finance>
- [5] Enterprise Europe Network. (2015, February 3). Technology Transfer. Retrieved May 11, 2015, from <http://een.ec.europa.eu/my/intranet/tt/technology-transfer-1>

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## NOTES

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ПЕТИ РЕГИОНАЛЕН  
СИМПОЗИУМ ПО ЕЛЕКТРОХИМИЯ  
НА ЮГОИЗТОЧНА ЕВРОПА

ПРОГРАМА И СБОРНИК С РЕЗЮМЕТА НА ДОКЛАДИ И ПОСТЕРИ

ИЗДАТЕЛ

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