11th International Symposium on Electrochemical/Chemical Reactivity of Metastable Materials

"Chemistry for Materials Science"

12 - 14 September 2012

AGH University of Science and Technology

Faculty of Non-Ferrous Metals

Krakow, Poland

The idea of organizing periodic international symposia on the Electrochemical and Chemical Reactivity of Amorphous Alloys was born in Sendai in 1993.

The Symposium arises as an answer to strong demand from the Scientific Community to hold meetings that would bring together the community of researchers interested in the chemistry of amorphous metals. From the beginning the Symposium focused on the chemical properties of non-equilibrium materials of disordered or nanocrystalline structure. Each time both fundamental and applied aspects of research were discussed.

Non-equilibrium processing techniques should provide new potential for producing compositionally and structurally graded materials with optimized properties.

The scope of 11th Symposium belongs to the general topic "Chemistry for materials science" and is aimed at promoting various opportunities for interdisciplinary collaboration of scientists from around the world in addition to presentation of new results, ideas and technologies in the field of chemical properties of new materials including amorphous and nanocrystalline alloys obtained by different kinds of chemical and physical methods.

This Symposium is aimed at following the tradition already established by the previous Symposia in Warsaw (1993, 1996, 2003, 2007, 2010), Szeged (1995, 2005), Dresden (1997), Sendai (1998) and Mt.Tremblant (2001). The last symposium in 2010 was held in Warsaw as a part of the Annual European Materials Research Society (EMRS) Fall Meetings in order to extend the necessary collaboration of chemists and physicists with material scientists. Since the last symposium organized by Prof Maria Janik–Czachor was very successful, the Scientific Committee of these cyclic Symposia has decided to organize next Symposium also in Poland, but this time in Krakow.

Topics covered by the symposium:

- amorphous and nanocrystalline materials with high corrosion resistance and superior catalytic, electrocatalytic and hydrogen storage properties
- surface modification of advanced materials for improved chemical and electrochemical properties
- electrochemical and chemical fabrication of functional amorphous and nanocrystalline oxide films on metals and alloys and their applications
- characterization of novel materials at nano-scale level
- fabrication, characterization and chemical properties of nano-composite materials, including organic-inorganic hybrid materials
- mechanism of chemical and electrochemical processes on advanced materials

PLENARY LECTURES

PL 1

The use of renewable energy in the form of methane via electrolytic hydrogen generation

K. Hashimoto[1], N. Kumagai[2], K. Izumiya[2], H. Takano[2] and Z. Kato[1]

[1] Tohoku Institute of Technology, Sendai, 982-8577 Japan

[2] Daiki Ataka Engineering Co., Ltd., Kashiwa, 277-8515 Japan

Department of Energy, USA is posting energy-related world data from 1980 to 2009 on the website. The world energy consumption has increased by a factor of 1.01946 every year since 1990. If the increase in the world energy consumption continues at this rate, the world petroleum reserves will be completely exhausted by 2041. If we continue to consume remaining fuels, natural gas, uranium and coal reserves will be completely exhausted by 2044, 2048 and 2054, respectively.

In order to avoid the situation of no fuels and intolerable warming, we have been proposing "global carbon dioxide recycling", in which we will supply renewable energy in the form of methane via electrolytic hydrogen generation to the world.

For realization of global carbon dioxide recycling, we needed to establish the technologies of seawater electrolysis for hydrogen production and methane synthesis by the reaction of carbon dioxide with hydrogen,

The energy-saving nickel alloy cathodes with a similar activity to platinum for hydrogen production were created by electrodeposition. Because of remarkable acceleration of proton discharge by the addition of iron and carbon, the rate-determining step became recombination of adsorbed hydrogen atoms. This is the ideal case of the highest rate of hydrogen formation.

The most difficult subject was the anode. Toxic chlorine formation is not allowed for the production of a large amount of hydrogen even in seawater electrolysis. We succeeded in creating multiple oxide anodes with manganese and other cations on which only oxygen evolution occurs without forming chlorine.

Remarkably active catalyst with almost 100% selectivity of methane formation by the reaction of $CO_2 + 4H_2 = CH_4 + 2H_2O$ was created from amorphous Ni-Zr alloys. During the reaction, the alloys were transformed to Ni supported on ZrO_2. The active catalyst is Ni supported on tetragonal ZrO_2. At the construction of the ZrO_2 lattice by oxidation of zirconium in Ni-Zr alloys, Ni^{2+} ions were also included in the oxide lattice. The inclusion of Ni^{2+} ions in the lattice stabilized the tetragonal ZrO_2 structure, accompanying by the formation of oxygen vacancies. The strong interaction between the oxygen vacancy and oxygen in CO_2 seems to weaken the C-O bond strength and to enhance the hydrogenation of CO_2 to form CH_4 and H_2O.

Using the knowledge obtained from the study of amorphous alloy precursors we established the mass production method of the catalysts without using amorphous alloys.

Based on the construction of a prototype plant in 1995 and industrial scale plants in 2003, joint R & D for industrial applications is in progress with Japanese and foreign companies.

PL 2

Corrosion/degradation and passivation processes as the methods of functionalization of new materials

Maria Janik-Czachor[1], Marcin Pisarek[1] & Agata Roguska[1,2]

[1] Institute of Physical Chemistry PAS, Warsaw, Poland, e-mail: maria@ichf.edu.pl

[2] Faculty of Materials Science and Engineering, Warsaw University of Technology, Warsaw, Poland

To meet extreme demands of the modern technology, functionalized materials of enhanced specific properties are required. Non-equilibrium processing techniques provide potential for producing compositionally and structurally graded materials with optimized properties. Moreover, strictly controlled corrosion/degradation processes or anodic passivation/oxidation may be successfully applied to modify further their chemical activity/reactivity, including their durability, and/or selectivity for catalytic applications. In particular, the biocompatibility and bactericidal properties of Ti-based composites may also be enhanced. The modified materials may also provide active substrates for SERS investigations of adsorbate-substrate interaction; the knowledge gained from such investigations is crucial for corrosion inhibition or heterogeneous catalysis. High resolution methods of characterization of new, modified materials are necessary to identify factors responsible for their unique properties.

In this lecture the activity of the Physical Chemistry of Materials Center (a common initiative of the Institute of Physical Chemistry PAS and the Faculty of Materials Science WUT) during the recent years of interdisciplinary research of new materials is summarized. The following topics will be briefly presented:

- effect of hydrostatic extrusion leading to *nanostructurisation* of austenitic stainless steels on stability of their passive state
- effect of cathodic hydrogen charging on functionalization of Cu- based *amorphous alloys precursors* for catalytic applications
- effect of alkali leaching on functionalization of ternary Ni-Al-Cr(Co) *rapidly quenched alloy precursors* for catalytic applications
- effect of *porous anodic oxide films* partly covered by Ag metal nano-particles on adsorption ability of Ag/TiO_2–*n/Ti* and Ag/Al_2O_3-*n/Al* composite substrates and on intensity of SERS signals
- effect of *nanotubular anodic oxide film on Ti* and/or *Ag nano-particles* on biocompatibility and bactericidal properties of Ag/TiO_2–*n/Ti* composite substrate

The above examples provide a basis: for understanding of the role of high resolution methods in characterization of local phenomena in electrochemistry and in chemistry of materials, in general, as well as for identification of the factors responsible for their specific functions. On the other hand, they visualise the extended possibilities of modification of properties of metastable amorphous and nanostructurized materials by chemical or electrochemical pre-treatments.

Acknowledgement

This work was financially supported by the Polish Ministry of Science and Higher Education (Grant No. N N507 491 138), the National Science Center (Decision No. DEC-

2011/01/B/ST5/06257) and by the Institute of Physical Chemistry PAS (Warsaw, Poland). Surface characterizations (AES, XPS) were performed using a Microlab 350 located at the Physical Chemistry of Materials Center of the Institute of Physical Chemistry, PAS and of the Faculty of Materials Science and Engineering, WUT.

PL 3

Nanostructured Hybrid Electrocatalytic Materials: Activation of Noble Metal Centers through Modification with Metal Oxo Species

Pawel J. Kulesza, Iwona A. Rutkowska, Sylwia Zoladek, Krzysztof Miecznikowski, Malgorzata Glowienka, Anna Wadas, Karolina Klak, Diana Marks

Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland
pkulesza@chem.uw.edu.pl

Recently, there has been growing interest in development of the direct alcohol fuel cells as alternative technology to hydrogen based electrochemical energy systems. For example, ethanol can be ideally oxidized to carbon dioxide thus delivering 12 electrons. But realistically the reaction is rather slow at ambient conditions. Obviously, there is a need to develop novel electrocatalytic materials.

Platinum has been recognized as the most active catalytic metal towards oxidation of ethanol at low and moderate temperatures. But Pt anodes are readily poisoned by the strongly adsorbed intermediates, namely by CO-type species, requiring fairly high overpotentials for their removal. To enhance activity of Pt catalysts towards methanol and ethanol oxidation, additional metals (one or two), such as Ru, Sn, Mo, W or Rh, are usually introduced as the alloying component. More recently it has been demonstrated that catalytic activity of platinum-based nanoparticles towards electrooxidation of ethanol has been significantly enhanced through interfacial modification with ultra-thin monolayer-type films of polyoxometallates, particularly heteropolymolybdates. Also gold in combination with platinum has been demonstrated to produce novel high performance bimetallic catalysts.

We are going to describe a concept of utilization of functionalized titanium dioxide, tungsten oxide or zirconium oxide matrices (by admixing them with polyoxometallate-modified gold nanoparticles) for supporting and activating noble metal nanoparticles (Pt, Pt-Ru or Pt-Rh) during electrooxidation of ethanol. Remarkable increases of electrocatalytic currents measured under voltammetric and chronoamperometric conditions have been observed. The most likely explanation takes into account improvement of overall conductivity (due to the presence of nanostructured gold) at the electrocatalytic interface (formed by metal oxide support), as well as and possibility of specific Pt-metal oxide or Pt-Au electronic interactions and existence of active hydroxyl groups on transition metal oxo species.in the vicinity of catalytic Pt sites. Further, the capping layers of Keggin-type phosphomolybdates, which are known to undergo fast stepwise multi-electron redox processes as well as to activate Pt-based electrocatalysts during ethanol oxidation, may also contribute to the overall enhancement effect.

PL 4

Heterogeneous catalysis – where to go?

Árpád Molnár

Department of Organic Chemistry, University of Szeged, Dóm tér 8, 6720 Szeged, Hungary, e-mail: amolnar@chem.u-szeged.hu

Catalysis, in general, and heterogeneous catalysis, in particular, has come a long way from being a "black art" to be a major contributor of many industrial processes. The trial-and-error approach in the discovery of new catalysts and developing new catalytic processes has been superseded by a combination of a vast array of techniques and catalysis has become an interdisciplinary science. Today, it is a mature discipline, which is due mainly the successes of the surface science approach providing a better understanding of the mechanisms of catalytic reactions. Nevertheless, there are still possibilities for further progress. In this respect, technology that is the application of catalysis in industry is without doubt a major driving force. Collaboration between industry and fundamental research is also an obvious necessity. An integrated approach is required including

i) the design of new catalyst materials at the nanostructure level,
ii) fabrication of new, more selective catalysts,
iii) the use of new techniques for characterization of catalysts at the molecular level,
iv) characterization of the catalysts under reaction conditions, and
v) application of computational chemistry.

Possibilities for further advancement will be illustrated by selected successful examples such as single-site catalysts, development of selective catalysts for carbon–carbon coupling reactions, and enantioselective catalysis.

PL 5

Raman analysis of surfaces using silica-covered silver nano-resonators

Andrzej Kudelski[1], Sebastian Wojtysiak

[1] Faculty of Chemistry, University of Warsaw, ul. Pasteur 1, 02-093 Warsaw, Poland
e-mail: akudel@chem.uw.edu.pl

In this contribution applications of silica-protected silver and gold electromagnetic resonators for Raman analysis of various surfaces will be discussed. Silica-protected silver and gold nano-resonators have been synthesized by coating of respective nanoparticles with ultrathin (ca. 5 nm) layer of silica. Ag@SiO_2 and Au@SiO_2 nanoparticles significantly enhance the electric field of incident electromagnetic radiation of certain wavelengths, hence leading to a very large increase of the Raman signal from species being in the close proximity to them. Layers of Ag@SiO_2 and Au@SiO_2 nanoparticles have been spread over model surfaces that were further probed using Raman spectroscopy. Spreading the silica-covered electromagnetic nano-resonators over the analyzed surfaces allows for identification of well visible contributions in the measured spectra from very small amount of species present on the surface, even though the contribution from these compounds could not be observed in the standard Raman spectra of analyzed samples. We showed that Ag@SiO_2 nano-resonators allows for significantly easier combination of the SHINERS (shell-isolated nanoparticle-enhanced Raman spectroscopy) with the standard resonance Raman effect than previously used Au@SiO_2 nanoparticles. Since silver provides stronger plasmons resonance than gold, sensitivity of SHINERS analysis with Ag@SiO_2 nanoparticles is higher than when using Au@SiO_2 nanoparticles. The problem of diffusion of the molecules of the analyte via the silica layer will be also discussed.

Acknowledgement

This project was financed from the funds of the National Science Centre (Poland) allocated on the basis of the decision number DEC-2011/01/B/ST5/03870.

PL 6

Status of radioactive contamination by nuclear accident in Japan Our efforts for decontamination

Naokazu Kumagai, Yoshihiko Nishizaki, Seigo Ichikawa and Koichi Izumiya

Daiki Ataka Engineering Co., Ltd., Kashiwa, 277-8515 Japan

The earthquake and tsunami on March 11, 2011 have caused the catastrophic damage on Nuclear Power Station in Fukushima. Radioactive substances had been scattered widely particularly in northern and central parts of Honshu Island. Radioactive I-131 and 133 are particularly dangerous for infants because of causing thyroid dysfunction, but their half-lives are short as 8.06 days and 20.8 h, respectively. The scattering of radioactive substances from the power station was shortly ended, and hence the risk by taking I-131 and 133 into bodies had not continued longer. In contrast, the exposure to the strong radioactivity of Cs-137 cannot be avoided. The radioactivity and half-life of Cs-137 are 3,215 Bq/ng and 30.17 years, respectively. The radioactive substances have been staying on buildings, grounds, fields, trees and mountains. About 103,000 residents of Fukushima Prefecture had to take refuge from their residential area. Other residents who have not been asked to take refuge by government had to be staying at their houses and exposed to relatively strong radiation. Decontamination had to be performed urgently.

Decontamination of individual houses has been carried out by washing with pressurized water, mostly by volunteers, which results in the formation of large volumes of contaminated water and waste. On the grounds, the radioactive substances exist mostly in the surface of a few cm deep. Decontamination of ground has been carried out by stripping contaminated soil from the ground surface. About 3 cm stripping from the surface generally leads to about 80 % decrease in radioactivity. In grassland, about 30 cm removal from the surface had been known to obtain radiation free soil. However, for decontamination of most of farming fields and mountains, we need to rely on the growth of vegetable. In residential area, farming fields and mountains radioactive substances are going to be contained in growing grasses and fallen leaves. Incineration of those has resulted in accumulation of radioactive substances mostly in fly ash to the value of several tens of thousand Bq/kg. Today, canned fly ash with high radioactivity has been piled up in incinerators.

We need to remove radioactive substances from fly ash although administrators and citizens have not been wanting to increase the radioactivity by concentration. Nevertheless, the capture and concentration of radioactive substances from fly ash via fallen leaves and grown grasses have to be done several tens of years because this is only the way to decontaminate nature. We also need to purify the contaminated water used for decontamination. Because of difficulty to find the place for storage of radioactive soil stripped from the ground, the soil has been mostly piled up in a corner on the spot. We need to establish the technology to decontaminate the soil.

We have succeeded to capture and concentrate radioactive substances after dissolving them into water.

PL 7

The magnetic field effects on the electrodeposited Co-Cu binary alloy onto copper seed-layer

Agnieszka Franczak[1], Alexandra Levesque[1], Piotr Żabiński[2], Remigiusz Kowalik[2], Maciej Czapkiewicz[3], Donggang Li[4], Qiang Wang[4], Frederic Bohr[1] and Jean-Paul Chopart[1*]

[1] Laboratory of Engineering and Material Science LISM, University of Reims Champagne-Ardenne, BP 1039, 51687 REIMS Cedex 2, France

[2] Faculty of Non-Ferrous Metals, AGH University of Science and Technology, Krakow, Poland

[3] Department of Electronics, AGH University of Science and Technology, Krakow, Poland

[4] Key Laboratory of Electromagnetic Processing of Materials (Ministry of Education), Northeastern University, Shenyang, China

The electrochemical deposition of magnetic multilayers as well as granular alloys exhibiting GMR still finds a great deal of attention to both scientific and technological communities, because of the low fabrication costs and high-production rate. In granular alloys, the alternate magnetic-nonmagnetic regions similar to multilayer structures are mimicked via phase separation tendencies between magnetic and nonmagnetic components. The resulting structure consists of embedding nanometric ferromagnetic or superparamagnetic granules in nonmagnetic matrix. Among the various possibilities, the Co-Cu binary alloy is one of the natural choices for such a heterogeneous alloy due to magnetic (Co) and nonmagnetic (Cu) combination along with immiscibility at ambient temperatures [1]. The microscopic process of growth strongly affects magnetic and electrical properties of materials. Superimposing an external magnetic field offers possibilities to influence the deposition process mainly by magnetohydrodynamic (MHD) effects, which cause a change in the microstructure of grown layers in correlation with the above mentioned properties. Furthermore, magnetic fields applied during the electrodeposition induce an orientation of particles in the direction of easiest magnetization in the case of multilayered system such as Co-Cu/Cu [2]. This explains the importance of investigation on the relationship between microstructure and magnetic properties in these materials. The present work shows the magnetic field effects on the magnetic properties of electrodeposited Co-Cu binary alloys onto Cu seed-layer and the relation between nanoscale structure and magnetic properties.

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Acknowledgement

The authors would like to thank Dr Eng. Tomasz Tokarski from Department of Structure and Mechanics of Solids at AGH Univeristy of Science and Technology in Krakow, Poland for SEM analyses as well as Champagne-Ardenne Region Council, ANR Agency and Materalia for the financial support provided by a University Research Grant n°2010-INTB-903-01.

LECTURES

L 1

Methanation of hydrocarbons
In relation to methanation of CO_2 and CO with hydrocarbons

Hiroyuki Takano[1], Koichi Izumiya[1], Naokazu Kumagai[1] and Koji Hashimoto[2]

[1] Daiki Ataka Engineering Co., Ltd., Kashiwa, 277-8515 Japan

[2] Tohoku Institute of Technology, Sendai, 982-8577 Japan

For the use of renewable energy in the form of methane via electrolytic hydrogen generation we have been studying the effective catalysts for the formation of methane by the reaction of CO_2 with H_2. The effective catalysts for CO_2 methanation we have found are Ni supported on tetragonal $Zr^{4+}_{1-x-y}Ni^{2+}_{x}M^{n+}_{y}O^{2-}_{2-x-0.5ny}V^{\cdot\cdot}_{x+0.5ny}$, where M is the cation(s) with lower valence than Zr^{4+} and effective in stabilizing the tetragonal ZrO_2 type structure, and $V^{\cdot\cdot}$ is the oxygen vacancy effective for oxygen removal from CO_2 [1,2].

Depending upon the CO_2 source, CO_2 contains CO, alkanes, alkenes and sometimes even aromatic hydrocarbons. It is desirable for methanation to convert CO_2 and CO without removal of these hydrocarbons. Our preliminary experiments using the gas mixture of CO_2, CO and aliphatic and aromatic hydrocarbons imitated the natural gas from a gas field revealed the preferential methanation of almost all hydrocarbons and CO being accompanied by conversion of CO_2 to methane using remaining hydrogen. This is especially attractive for methanation of synthetic gas from wood, coal and other biomass because there is a possibility for methanation without contamination by the deposition of tar on the catalyst. In this connection, if steam reformation of long chain and aromatic hydrocarbons occurs on our catalysts in the environment for methanation, all hydrocarbons along with CO_2 and CO can be converted to methane as far as H_2 and H_2O are sufficient.

The present work aimed to clarify the hydrogenation behavior of aliphatic, branched aliphatic, aromatic and bicyclic aromatic hydrocarbons. Our methanation, $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ is practically performed in two stages. Because of the reverse reaction of the methanation products CH_4 and H_2O, the conversion in the first reactor is about 90%, and after removal of H_2O, the remaining reactant gas and methane is passed to the second reactor for 99% or higher conversion. For enhancement of methanation using two stage reactors the addition of water vapor to the reactant gas mixture of hydrocarbons and hydrogen was also examined for reformation of hydrocarbons which is effective for subsequent methanation in the second stage reactor.

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L 2

High hydrogen pressure treatment of selected intermetallic compounds: novel hydrides, novel phenomena

Stanisław M. Filipek

Institute of Physical Chemistry of PAS, ul. Kasprzaka 44, 01-224 Warsaw, Poland, sfilipek@ichf.edu.pl

The increasing hydrogen pressure results in increase of hydrogen fugacity what in consequence enhance hydrogen solution in the metallic lattices exposed to gaseous H2.

Particularly, intermetallic compounds reacting with compressed hydrogen can form hydrides with high hydrogen content and interesting properties. Systematic investigations of AB2 Laves phases (where A=Zr, Y or rare earth; B is transition metal like Fe, Co or Mn) under pressures ranging 1 GPa(H2) lead to discovery of a number of novel hydrides formed by three different mechanisms:

- by expansion of metallic lattice without change of symmetry like in systems considered before as non-hydride forming ($ZrFe_2$, $ZrCo_2$) [1,2]

- by expansion and anisotropic distortion of metallic lattice; this was found for YFe_2, $ErFe_2$ or $HoFe_2$ for which novel isostructural hydrides with concentration 5 H p.f.u. were found [3,4]

- by radical restructurisation of the former metallic lattice with formation of a complex deuteride AMn_2D_6 (A=Y or rare earth)[5]. This type of transformation has never been observed before for any Laves phases and seems to be limited only to intermetallics containing Mn and rare earth or yttrium. Unexpectedly such hydride was formed also in the case of Y_6Mn_{23} [6]. Finally let us mention the recent discovery of hydrogen induced semimetal-metal transition observed for Tb_7Rh_3 and Dy_7Rh_3[7].

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Acknowledgement

The support by the MNiSW under Grant No. N N204 527939 is gratefully acknowledged.

L 3

Direct Formic Acid Fuel Cells on Nanocrystalline Catalysts: Basics, Current State and Possible Applications.

P. Kędzierzawski, A. Borodziński, A. Mikołajczuk i L. Stobiński,

Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland

Direct formic acid fuel cells (DFAFC) are promising candidates for a power supply for portable applications.

DFAFC has a number of advantages over other direct liquid fuel cell including DMFC. Athough it has lower energy density (only two hydrogen atoms, compared to four for methanol), it does not pose serious catalytic problems. Other advantages are high thermodynamic electromotive force, small fuel crossover flux and low toxicity.

In the presentation, current state of the DFAFC will be summarized including the progress in palladium base anodic catalysts synthesis. Possible applications areas will be outlined. DFAFC anode deactivation mechanisms will be described. Attempts to overcome the problem of catalysts poisoning by fuel impurities will be addressed.

L 4

Biomimetic calcium-phosphates coatings on Ti: formation, physicochemical surface characterization, biological response

Marcin Pisarek[1], Agata Roguska[1,3], Lionel Marcon[2], Mariusz Andrzejczuk[3]

[1] Institute of Physical Chemistry PAS, Warsaw, Poland

[2] Interdisciplinary Research Institute, Lille, France

[3] Faculty of Materials Science and Engineering, Warsaw University of Technology, Warsaw, Poland

Recently, various surface modifications have been applied to form a bioactive layer on a Ti surface, which is known to accelerate osseointegration. Chemical/electrochemical processes for modifying surfaces of Ti and its alloys are widely employed to increase the biocompatibility of those materials and appeared also highly suitable pre-treatments for apatite-like coating deposition [1,2]. Using a two-step procedure (etching in an alkaline and acidic solution or anodic oxidation of Ti followed by soaking in Hanks' medium), biomimetic calcium phosphate coatings were deposited on porous TiO_2 layers [3-5]. Electrochemical processes (direct electrodeposition of calcium-phosphates coatings from Hanks' solution) were also applied for modifying surfaces of Ti [6]. The combined effects of surface topography and chemistry on the formation of the calcium phosphate layer are presented. Such layers can provide very promising substrates which increase biological tolerance [7]. To evaluate the potential use of the coatings obtained for biomedical applications, the adsorption of serum albumin, the most abundant protein in the blood, and the attachment of living cells (osteoblasts, U2OS) were studied.

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Acknowledgement

This work was financially supported by the National Science Center (decision No. DEC-2011/01/B/ST5/06257), and by the Institute of Physical Chemistry PAS and Interdisciplinary Research Institute.

L 5

Evaluation of biological activity of Ag loaded TiO_2 nanotubes

Agata Roguska[1,2], Marcin Pisarek[1], Anna Belcarz[3], Lionel Marcon[4], Maria Janik-Czachor[1] & Małgorzata Lewandowska[2]

[1] Institute of Physical Chemistry PAS, Warsaw, Poland, e-mail: aroguska@ichf.edu.pl

[2] Faculty of Materials Science and Engineering, Warsaw University of Technology, Warsaw, Poland

[3] Department of Biochemistry and Biotechnology, Medical University of Lublin, Lublin, Poland

[4] Interdisciplinary Research Institute, Lille, France

To date, studies of modified Ti surfaces for biomedical purposes have focused on observations of morphology and on identifying their physicochemical properties which influence the biological response. However, for implant materials, also an antibacterial property is of high importance. The aim of this work was to create nanoporous oxide layers on Ti with loaded Ag nanoparticles in order to obtain coatings for biomedical applications ensuring both biocompatibility and antibacterial properties. TiO_2 nanotubes (NT) were grown on a Ti substrate via electrochemical oxidation at constant voltage in a mixture of glycerol, deionized water and NH_4F. Silver particles with a size of 2 – 50 nm were deposited on the surface using the sputter deposition technique). The fabricated composite layers were characterized by high-resolution SEM and surface analytical techniques: local AES, XPS, For the biomedical applications, the layers were tested with the use of *S. epidermidis* cells (antibacterial tests), as well as in U2OS cell culture (to study living cell adhesion and alkaline phosphatase activity, ALP). Our results have shown that Ag nanoparticles can be incorporated into the biomaterial surface in a simple and economic manner suitable for the fabrication of new types of bactericidal materials. The presence of TiO_2 NT layer significantly reduced the *S. epidermidis* cells adhesion and biofilm formation on modified surfaces; the deposition of Ag nanoparticles enhanced the anti-adhesive properties of TiO_2 NT layer. Additionally, the Ag/TiO_2 NT composite layers were shown to have a positive effect on the adhesion and differentiation of the osteoblast-like cells (U2OS).Thus, the Ag/TiO_2 NT composite layers may be promising for combating post-operative infection for applications in hard tissue replacement procedures.

Acknowledgement

This work was financially supported by the National Science Center (decision No. DEC-2011/01/B/ST5/06257), and by the Institute of Physical Chemistry PAS and Interdisciplinary Research Institute.

L 6

Nanoporous anodic metal oxides for applications in nanotechnology

G.D. Sulka[1], L. Zaraska[1], J. Kapusta-Kołodziej[1], K. Hnida[1], A. Brzózka[2], M. Jarosz[1],
E. Kurowska[1]

[1] Department of Physical Chemistry and Electrochemistry, Jagiellonian University
Ingardena 3, 30060 Krakow, Poland, sulka@chemia.uj.edu.pl

[2] Faculty of Non-Ferrous Metals, AGH University of Science and Technology
Al. Mickiewicza 30, 30059 Krakow, Poland

Nanoporous anodic metal oxides have received significant attention due to a successful combination of functional chemical/physical properties with a well controllable nano-architecture. Among different approaches used for fabricating nanoporous oxides, anodization is one of the best, inexpensive and simple method. By controlling parameters of the electrochemical oxidation a variety of unique oxide structures with different morphologies and characteristic parameters can be obtained.

Well-organized nanoporous anodic aluminum oxide (AAO) membranes formed by anodization have become the most popular templates used for fabrication of diverse nanomaterials. Recently, AAOs with more complex-shaped nanopores, including templates with modulated pore diameter, Y-branched pores and with a few levels of branched pores, were successfully synthesized by anodization [1, 2]. Here, we present a template-assisted fabrication of various metal (e.g., Ag, Cu, Sn, Sb, Au-Ag) and polymer (e.g., polystyrene, polypyrrole) nanowire arrays [3, 4]. Anodic titanium oxide (ATO), fabricated by electrochemical anodization under well-controlled conditions, exhibits high-ordered, close-packed and hexagonally arranged pores [5]. On the other hand, porous tin oxide layers with a random pore distribution can be formed by anodization of metallic tin.

There are several potential technological applications of these nanomaterials in energy storage systems (anode materials for high-power lithium-ion batteries), electrocatalysis and as novel thermoelectric materials, chemical and biochemical sensors as well as biocompatible materials for bone implants. Moreover, modern nanodevices with exceptional performance can be also fabricated on a basis of porous anodic alumina [6].

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No N N204 213340) and was carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (contract no. POIG.02.01.00-12-023/08).

This work was also supported by the International PhD-studies programme at the Faculty of Chemistry Jagiellonian University within the Foundation for Polish Science MPD Programme co-financed by the EU European Regional Development Fund.

MJ is indebted to the project Interdisciplinary PhD Studies "Molecular Sciences for Medicine" (supported by the European Regional Development Fund in the framework of the Polish Human Capital Operational Programme) for the fellowship.

L 7

Photoelectrochemistry of lead molybdate – towards information processing at the nanoscale

Przemysław Kwolek[1], Konrad Szaciłowski[1,2]

[1] Faculty of Non-ferrous Metals, University of Science and Technology, Kraków, al. Mickiewicza 30, 30-059 Kraków, Poland, e-mail: pkwolek@agh.edu.pl

[2] Faculty of Chemistry, Jagiellonian University, Kraków, ul. Ingardena 3, 30-060 Kraków, Poland

Constantly growing demand for a fast and powerful information processing requires a permanent development in the field of electronics. Since the silicon-based technology gradually achieves its technological and physical limits, alternative ways of information processing should be developed [1], for example application of semiconducting electrodes exhibiting the Photoelectrochemical Photocurrent Switching Effect (the PEPS effect). Such a system behaves like an AND gate or 1:2 demultiplexer and in principle can work at the nanoscale [2].

Photoelectrochemical characterization of lead molybdate by pulsed photocurrent spectroscopy technique indicated, that this compound exhibits the PEPS effect, therefore, potentially may be employed in information processing. $PbMoO_4$ is an indirect, n type semiconductor [3] and was obtained by the microwave assisted hydrothermal route using lead acetate and molybdic acid as precursors. The PEPS effect occurs due to changes in the electrode polarization. For sufficiently high electrode potential an electron is transferred from the conduction band of the semiconductor to the conducting substrate and the anodic photocurrent occurs. The presence of the electron in the conduction band stems from an intraband transition within $PbMoO_4$ particle. An electron donor in the electrolyte is necessary, to extract a hole from the valence band. Otherwise, a photocorrosion of the material will be observed. On the other hand, cathodic photocurrent occurs for sufficiently negative potential of the working electrode, moreover, the presence of the electron acceptor such as molecular oxygen in the electrolyte is necessary.

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L 8

Effect of nitrogen and carbon species inclusion on dielectric properties and photoresponse of anodic films formed on niobium

Sachiko Ono, Chie Higaki, and Hidetaka Asoh

Department of Applied Chemistry, Faculty of Engineering, Kogakuin University
2665-1 Nakano, Hachioji, Tokyo 192-0015, Japan, sachiono@cc.kogakuin.ac.jp

Anodic oxide film formed on niobium has attracted considerable attention as an alternative dielectric material to tantalum oxide due to its high abundant and high permittivity. Previously, we reported that the capacitance of the film formed in alkaline phosphoric acid with the addition of ammonium hydroxide was significantly higher than that of the film formed in acidic electrolyte. The film formed in alkaline electrolyte is composed of two layers having different resistance: the outer low-resistivity oxide layer containing nitrogen and the inner high-resistivity layer consisted of pure niobium oxide. The peculiar electric property of the film formed in ammonium alkaline electrolyte is caused by nitrogen doping into anodic niobium oxide, i.e., an amorphous n-type semiconductor [1, 2]. In the present study, to clarify the factor controlling dielectric property other than nitrogen doping, we investigated the effect of organic solvent addition to the electrolyte on the structure and semiconductivity of anodic films grown on niobium.

The capacitance of the films formed in phosphoric acid with the addition of organic solvent such as ethylene glycol and ethanol was slightly higher than that of the film formed in phosphoric acid. From impedance measurements, however, it became clear that the films formed in phosphoric acid with the addition of organic solvent were composed of electrical two layers. The outer layer resistances of the films formed in phosphoric acid with the addition of ethylene glycol and ethanol lowered to 1.3 and 0.8 μm^2, respectively. It should be caused by organic species incorporation into the outer layer of the films. Moreover, the leakage current under certain applied voltage of these films was notably increased in the condition of light irradiation. This phenomenon is suggested to be derived from n-type semiconducting property [3]. These results indicate that the semiconductivity of the anodic niobium oxide films is also enhanced by incorporation of organic species into the films as well as nitrogen doping.

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L 9

Photoelectrochemistry of hybrid organic-inorganic materials - influence of geometry of substituents.

Justyna Mech[1], Konrad Szaciłowski[1,2]

[1] Faculty of Non-Ferrous Metals, University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków Poland, e-mail: justyna@agh.edu.pl

[2] Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Kraków, Poland

Hybrid materials based on the titanium dioxide, surface-modified by a dihydroxyanthraquinone derivatives like: 1,2-dihydroksy, 1,4-dihydroxy, 1,5-dihydroxy and 1,8-dihydroxy anthraquinone have been examined in terms of its electrical and photoelectrical properties. Studies on anthraquinone derivatives/TiO_2 hybrid materials indicate an important role of position of substituents in this family of chromophores. Geometry of substituents is responsible for specific binding of chromophore to semiconductor surface. The most common binding mode, described in the literature is covalent binding via oxygen atoms from substituents group of chromophore and defects at TiO_2 surface [1-3]. Surface-modified semiconductor materials synthesized through absorption of organic compounds reveal surprising photoelectrochemical features like photoelectrochemical photocurrent switching effect (PEPS). This phenomenon can be described as photocurrent polarization changing through potential or wavelength tuning. The elementary process in the PEPS effect is fast and efficient electron injection form the donor level of the molecule to the conduction band of semiconductor. The injection process is conditioned by the appropriate interposition of energy levels in semiconductor and molecule and by the strength of the coupling between them. Interaction between both components modify several parameters e.g. density distribution of electron and redox potentials. These parameters can be determined in pure chromophore and in the same molecule attached to TiO_2 by spectroscopy and electrical techniques. The results are supported by DFT calculations which report both geometry and energy level distribution in studied chromophores. Photoelectrochemical measurements indicate pronounced photoelectrochemical photocurrent switching effect. Comparative analysis of photocurrent switching induced by different hydroxyanthraquinone dyes leads to better understanding of photocurrent switching phenomena in wide band gap semiconductors and is relevant for prospective applications of these materials in molecular optoelectronics.

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L 10

Palladium-Gold Multiwall Carbon Nanotubes Supported Anode Catalysts for Direct Formic Acid Fuel Cell

Anna Mikołajczuk 1, Andrzej Borodzński 1, Piotr Kędzierzawski 1, Leszek Stobiński 1,2, H.-M. Lin 3, C.-H. Chen 3, W.-J. Liou 3, S.-H. Wu 3

1. Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland

2. Faculty of Materials Science and Engineering, Warsaw University of Technology, Warsaw, Poland

3. Department of Materials Engineering, Tatung University, Taipei, Taiwan

Fuel cells are classified as one of the ten technologies which will change our life in the near future. Direct formic acid fuel cells (DFAFC) can be a viable power source, particularly for portable applications. The most significant issues in this fuel cells are activity and stability of catalysts used at the electrodes. It is well established that palladium performs particularly well as an anode catalyst [1]. It has been shown that addition of the second metal increases the activity of Pd-based anode catalysts for formic acid electrooxidation [2].

In our studies, we have investigated Pd and Pd-Au supported on multiwall carbon nanotubes (MWCNTs) catalysts, which were synthesized via polyol method followed by heat treatment in H2-Ar at 200°C or Ar at 250°C. The catalysts have been characterized by X-ray diffraction, FE-TEM, EDX, cyclic voltammetry and were tested on the anode of DFAFC.

It was found that the method of heat treatment of the catalysts significantly influenced DFAFC performance. We showed that Pd catalysts annealed in H2-Ar performed better than that annealed in Ar. Also addition of gold improved Pd/MWCNTs catalysts initial activity. We found that the main reason of deactivation of investigated catalysts is poisoning of palladium surface by product of decomposition of impurities present in formic acid (e.g. acetic acid and methyl formate).

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L 11

Efficient proton-conducting amorphous anodic oxide films for intermediate-temperature fuel cells

Hiroki Habazaki[1], Ke Ye[1], Yoshitaka Aoki[1], Etsushi Tsuji[1] and Shinji Nagata[2]

[1] Division of Materials Chemistry, Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido, 060-8628, Japan

[2] Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

Proton-conducting thin films are promising electrolytes for solid-oxide fuel cells that operate at intermediate temperatures (150–400ºC). Intermediate-temperature fuel cells have several advantages over polymer electrolyte fuel cells, which operate below 100ºC under fully hydrated conditions. The former type allows the use of nonprecious-metal electrocatalysts and hydrocarbon fuels and facilitates simpler module assembly by means of anhydrous proton conductors. To obtain a solid electrolyte membrane with a sufficient conductivity below 400ºC, one approach is reducing the thickness of the solid electrolyte to the nanometer scale. The nm-thick proton-conducting films have been prepared by PVD, including ALD, we are interested in electrochemical/chemical processes, such as anodizing of metals and sol-gel spin casting, since these processes are particularly suitable for the formation of dense oxide nanofilms [1, 2]. In this study, proton conductivity of anodic oxide films formed on magnetron-sputtered Zr-W-Si films has been examined.

The anodic ZrO_2-WO_3-SiO_2 films of various thicknesses were formed by anodizing the Zr-W-Si films at several formation voltages in 0.1 mol dm^{-3} phosphoric acid. A gold bottom electrode was deposited on the anodic films, and the conductivity across the anodic films was measured using ac impedance spectroscopy. Prior to the measurements, the specimens were annealed in argon at 250ºC to activate proton conductivity.

Efficient proton conductivity was observed after thermal treatment at 250^{o}C with the conductivity enhanced by reducing the film thickness. The conductivity is enhanced by more than one order of magnitude on reducing the thickness from 300 to 140 nm. The anodic oxide films consist of two layers, comprising a thin outer ZrO_2 layer free from silicon and tungsten species and an inner main layer containing all zirconium, silicon and tungsten species. The thickness-dependent conductivity of the ZrO_2-WO_3-SiO_2 anodic oxide film is associated with the conductivity of the outer ZrO_2 layer, which increases exponentially with reducing the film thickness. The area-specific resistivity of 0.14 Ω cm^2, which is below the minimum requirement (0.2 Ω cm^2) for a practical electrolyte membrane in commercial fuel cells, is achieved at a temperature at 225^{o}C for 100 nm-thick anodic ZrO_2-WO_3-SiO_2 films.

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L 12

Influence of the cathodic cycle on properties of alumina coatings on aluminium produced by plasma electrolytic oxidation

Wojciech Gębarowski, Stanisław Pietrzyk

Faculty of Non-Ferrous Metals, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Cracow, Poland, wojciech.gebarowski@gmail.com

Plasma electrolytic oxidation (PEO) is an effective method to obtain hard ceramic coatings on Al, Mg and Ti alloys. Micro discharges occurring on surface of electrode promotes the creation of oxides crystalline phases which enhance mechanical properties of coating. By using AC or pulse mode instead of DC the process can be conducted in ‘soft’ spark regime. This allows to produce thicker layers, increases growth rate and uniformity, decreases quantity of pores and defects [1]. These facts proof the importance of cathodic cycle in the PEO mechanism, however its role is not well defined [2].

In this work, influence of electrical parameters on kinetics of coating growth, its morphology and composition were investigated. The PEO process was conducted in potassium hydroxide with sodium metasilicate addition. Samples were pure aluminium. The different anodic to cathodic currents ratio and duration of pulses were applied. Electrical equivalent circuits of electrochemical system was proposed by electrochemical impedance spectroscopy tests. Phase composition of coatings were determined by XRD analysis. Morphology of oxides layers were investigated by SEM observations.

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L 13

The instability of silver and silver containing composite cathode materials in the SOFC' environment

Michał Mosiałek[1,2]

[1] Institute of Catalysis and Surface Chemistry PAS, Kraków, Poland,

[2] Institute of Physical Chemistry PAS, Warszawa, Poland, nbmosial@cyfronet.pl

Silver is a cheap noble metal with very low electric resistivity and high catalytic activity in oxygen reduction reaction (ORR). Silver dissolve some amount of oxygen which extends the reaction zone from the triple phase boundary (tpb) line to the two phase contact area. Despite of these advantages silver has not be considered as a component of cathode material in SOFC because of its disadvantages such as: low melting temperature, high vapor pressure and susceptibility to migration in the electric field. Nowadays, when working temperatures of so called Intermediate Temperature (IT) SOFC became lower and lower the application of silver as a component of cathode material can be reconsidered.

In the introduction evaporation and electromigration of silver will be discussed. Various methods of introduction of silver to the cathode material will be presented.

Then author will present his own results. SOFCs with silver containing cathodes showed better performance in comparison to those without silver. Mobility of metallic silver at 600°C were checked at various conditions. Observed electromigration of metallic silver was several orders faster than previously described. The mechanism of the fast transport of metal through gaseous phase will be presented.

Acknowledgement

This work was financially supported by Polish Ministry of Science and Higher Education grant No 6166/B/T02/2010/38

L 14

New technologies for decontamination of radioactive substances scattered by nuclear accident

Yoshihiko Nishizaki, Hiroko Miyamae, Seigo Ichikawa, Koichi Izumiya, Takehiko Takano and Naokazu Kumagai

Daiki Ataka Engineering Co., Ltd., Kashiwa, 277-8515 Japan

Radioactive substances scattered by nuclear accident, which are mostly Cs-137 and 134, have been concentrated in the fly ash of waste incinerators. In particular, in the incinerator with an ash melting system operating at the temperature higher than 1600°C, the radioactivity of the fly ash have been 80,000 Bq/kg or higher.

We examined to dissolve Cs in water from fly ash. After the fly ash with 85,788 Bq/kg in water, where the weight ratio of fly ash to water was 1/10, was agitated for 24 h, filtration with a membrane filter of 0.8 μm resulted in the residue with 4,946 Bq/kg. Thus, most of Cs in fly ash can be dissolved in water, and the residue after filtration, whose radioactivity is lower than 8,000 Bq/kg, can be sent to reclamation

We tried to remove Cs from the filtrate. When a kind of zeolite and commercial prussian blue particles of 11 μm diameter were used to remove Cs from the filtrate, the radioactivity to the weight of zeolite and particles were only 1.61 and 97 times as high as the radioactivity to the weight of fly ash. The adsorption of Cs^+ ion on the zeolite from the filtrate was particularly difficult because of competitive adsorption of K^+ and Na^+ ions, whose concentrations in the filtrate were the 10^9 orders of magnitude as high as that of Cs^+ ions. The surface of prussian blue particle can capture preferentially Cs^+ ions, but it will be more efficient if condensation precipitation occurs after prussiana blue captures Cs^+ ions at the time when prussian blue is formed. Prussian blue, that is, $Fe_4[Fe(CN)_6]_3$ is formed by the reaction of $K_4[Fe(CN)_6]$ and $Fe_2(SO_4)_3$. Considering the fact that $Fe_2(SO_4)_3$ acts as a condensation precipitant in the form of $Fe(OH)_3$ in aqueous solutions, we tried to precipitate Cs^+ ions by adding $K_4[Fe(CN)_6]$ and excess amounts of $Fe_2(SO_4)_3$ into the filtrate. When the amount of $Fe_2(SO_4)_3$ was five times as high as that necessary for the $Fe_4[Fe(CN)_6]_3$ formation, we succeeded to form the precipitate with a high concentration of Cs. The radioactivity/weight ratio in the precipitate was 1,700 times as high as the ratio to the weight of fly ash.

The houses contaminated with mostly Cs have been decontaminated by washing with pressurized water. Because Cs adsorbs on colloidal clay, the decontamination of houses forms a soil suspension contaminated with Cs. Using the knowledge on the condensation precipitation by ferric species we made precipitation of the suspension formed by house washing. The addition of $Fe_2(SO_4)_3$ and an anionic coagulant to the suspension contaminated with about 2000 Bq/kg of Cs led to almost complete removal of Cs, and the radioactivity in the supernatant water was not detected. Water thus treated was used again for decontamination.

We have also succeeded to design a package type adsorbent of zeolite particle for decontamination of water contaminated with Cs, and the decontamination system with the adsorbent package has been practically used for decontamination.

L 15

Electrochemical methods for micro-patterning of bulk metallic glasses

Ralph Sueptitz, K. Tschulik, C. Becker, M. Uhlemann, J. Eckert, A. Gebert

Leibniz Institute for Solid State and Materials Research IFW Dresden
P.O. Box 27 01 16, D-01171 Dresden, Germany, e-mail: r.sueptitz@ifw-dresden.de

A recent trend in bulk metallic glass (BMG) research is the development of suitable techniques for production of micro-parts and micro-patterned surfaces. Thermo-mechanical processing is very promising but has also some limitations [1]. Here pulsed electrochemical micromachining (μ-PECMM) with a micro- electrode is used for micro-patterning of a Fe based BMG. In contrast to previous investigations on actively dissolving metals and alloys [2], the transpassive potential region is exploited for machining the spontaneously passivating Fe-based alloy. The method is described and first results are presented to discuss the advantages and challenges of the localized transpassive dissolution of a multi-component alloy with a high metalloid content.

Micro-holes were machined with a high aspect ratio and depths of up to 100 μm. The effect of process parameters such as electrolyte, pulse voltage and pulse length as well as the bias potential was investigated and their influence on the machined structure morphology is established.

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Acknowledgement

The authors acknowledge financial support of the German Research Foundation

L 16

Self-organization phenomena during electrodeposition of some alloys

Ts. Dobrovolska

“Rostislaw Kaischew” Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria, tsvetina@ipc.bas.bg

Spatio-temporal structure formation is observed during electrodeposition of some indium coatings, alloyed with silver [1] and cobalt [2]. In these special systems pattern like waves, spirals and targets are formed on the electrode surface during electrodeposition under well-controlled electrochemical conditions – Figure 1 and Figure 2. These patterns consist of different phases of the respective alloy.

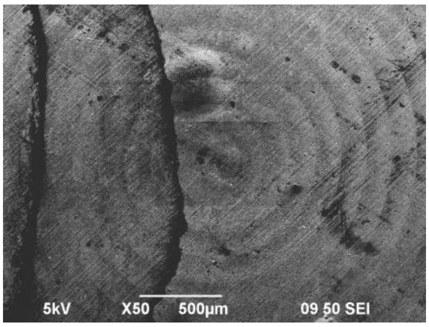

Fig. 1 SEM image of electrodeposited Ag-In alloy

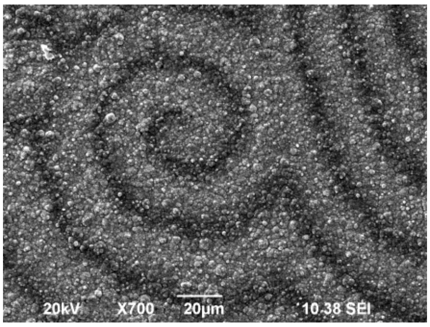

Fig.2 SEM image of electrodeposited In-Co alloy

By appropriate combinations of the electrolysis conditions it is possible to observe significant changes in the composition of the coatings leading not only to the formation of spatio-temporal structures on the electrode surface, but also to the achievement of new properties of the alloy coatings.

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L 17

Electrodeposition of Zn-Mo alloys from citrate solutions.

Honorata Kazimierczak, Piotr Ozga, Zbigniew Świątek

Polish Academy of Science, Institute of Metallurgy and Material Science, 30-059 Krakow,25 Reymonta st., Poland, nmkazimi@imim-pan.krakow.pl

Zinc - molybdenum alloys are interesting as environmentally benign corrosion protective coatings. They can be attractive especially as replacement materials for toxic cadmium coatings and for zinc coatings with Cr(VI)-based conversion layers hence the RoHS EU directive restricts the use of cadmium and hexavalent chromium. The preparation of Zn-Mo alloys is difficult by conventional thermal methods because there are great differences in the melting and boiling temperatures of zinc and molybdenum. Electrodeposition can be the way to obtain such alloys, moreover it is relatively simple and low cost method of coatings production. It is known that the process of molybdenum electrodeposition requires presence of other metal, which causes its co-deposition. This mechanism of the electrodeposition is described as induced co-deposition according to Brenner [1]. The iron-group metals play important roles in the induced codeposition of molybdenum because they may act as a catalyst in the reduction of the intermediate products. However, the possibility of molybdenum with zinc co-depositon was proved and the maximal content of molybdenum was significantly lower than in deposits of molybdenum with iron group metals [2,3].

The purpose of this work was to analyze the mechanism of electrochemical co-deposition of molybdenum with zinc from citrate solutions, characterization of obtained alloy layers and investigation of the corrosion resistance of Zn-Mo layers on steel.

The results of voltammetric studies indicate Zn and Mo interaction during the electrodeposition process. The results of chemical analysis (WDXRF) confirmed the presence of molybdenum in deposit. The highest contents of Mo in the investigated layers was 16,7 wt.%. XPS measurements showed that the content of molybdenum in metallic species (Zn-Mo alloy/compound or Mo) on the surface of deposit is close to 70%. X-ray diffraction analysis carried out in the temperature 25^{o}C (for layers with Mo content from 3,4 to 10,3%wt.) showed the presence of two phases crystallizing in the hexagonal system: Zn and Zn-Mo.

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Acknowledgement

This work was supported by projects: POIG-01.01.02-00-015/09-00; POKL-04.01.01-00-004/10.

L 18

Capacitance Performance and Cycling Stability of Electrodeposited Cobalt Hydroxide in Near-Neutral Electrolytes

Fedor S. Fedorov, Julia Linnemann, Kristina Tschulik, Margitta Uhlemann, Annett Gebert

Department of Chemistry of Functional Materials, Institute of Complex Materials, IFW Dresden, P.O. Box 270016, D-01171 Dresden, Germany, email: f.fedorov@ifw-dresden.de

Cobalt hydroxide-based supercapacitors have an attractively high power density arising from faradaic processes [1]. The cycle stability of the cobalt hydroxide/oxide and its capacitance depend on the reversibility of occurring redox reactions [2].

Conventional alkaline solutions used for capacitive performance of electrodeposited cobalt hydroxides have a number of disadvantages as they are corrosive, environmentally unfriendly and provide a small working potential range.

In this study, the capacitive properties of electrodeposited cobalt hydroxide/oxide were investigated in conventional alkaline (1 M KOH) and, as alternative, near-neutral solutions (1 M Na_2SO_4) by means of cyclic voltammetry, galvanostatic charging/discharging experiments, and electrochemical impedance spectroscopy.

The capacitance of cobalt hydroxide was demonstrated to decrease dramatically in alkaline solution as it is favored to change by the transition of oxidized forms of cobalt species to more reversible redox system in the studied potential range. As a result, the capacitance-responsible redox process is changed.

For near-neutral solutions, the capacitance of the cobalt hydroxide was observed to be 141 Fg^{-1} in 1 M Na_2SO_4 solution comparing with 372 Fg^{-1} for 1 M NaOH at 8 mVs^{-1}. The charge, stored by the system in both cases, is almost the same, 110±5.5 mC. The advantage of using neutral electrolyte is an extended potential window by 0.8 V to 1.3 V vs. Ag/AgCl and improved cyclic stability.

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Acknowledgement -

The authors acknowledge the Leibniz community within the framework of research and innovation for financial support.

L 19

Electrodeposition and properties of nanocrystaline Ni-Mo alloys obtained from citrate-ammonia baths

Agnieszka Bigos[1], Ewa Beltowska-Lehman[1], Paulina Indyka[1] & Marcin Kot[2]

[1] Polish Academy of Sciences, Institute of Metallurgy and Materials Science, 25 Reymonta St., 30-059 Krakow, Poland, nmbigos@imim-pan.krakow.pl

[2] AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland, kotmarc@imir.agh.edu.pl

Electrochemically deposited hard chromium coatings are still widely used in many industrial applications. However, according to the European Union directives (2000/53/WE, 2011/37/UE) they should be eliminated from the manufacturing process due to toxicity of electrolytes (containing carcinogenic hexavalent chromium) used for their preparation [1]. As promising alternative Ni-based alloys, containing refractory metals such as Mo, were proposed. This kind of materials are characterized by high hardness, good wear, friction and corrosion resistance.

In the presented work, the electrodeposition process of Ni-Mo coatings was studied at the aim of the determination optimal plating condition to obtain thick, adherent and crack-free deposits. Characterized alloys were electroplated on the steel substrate, under galvanostatic regime (0.5 – 5 A/dm^2), from an aqueous citrate complex solution containing nickel and molybdenum salts, in a system with a rotating disk electrode (RDE). No detergents, wetting agents or brighteners were used. The effect of cathodic current density, as an operating parameter which controls the efficiency of the electrodeposition process, on microstructure, chemical and phase compositions and crystallite size of the coatings was determined by the scanning and transmission electron microscopy, energy-dispersive X-ray and X-ray photoelectron spectroscopy as well as X-ray diffraction measurements. The influence of microstructure and chemical composition on mechanical properties and corrosion resistance of coatings were determined.

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Acknowledgement

This work was supported by the National Science Centre in the frame of the project No. UMO-2011/01/B/ST8/03974

L 20

Electrochemical behavior of cobalt - ammonium complexes during polarization of Au electrode in alkaline solution.

Krzysztof Mech, Piotr Żabiński, Remigiusz Kowalik, Krzysztof Fitzner

Faculty of Non-Ferrous Metals, University of Science and Technology, Address: Mickiewicza 30 Av., 30-059 Cracow, Poland, e-mail: kmech@agh.edu.pl

The main aim of carried out studies was to analyse mechanism and kinetic of electrochemical reaction accompanying polarization of Au electrode in alkaline solution contained hexaamiecobalt(III) complexes. The voltammetry, electrochemical quartz crystal microbalance (EQCM) and spectroelectrochemical (SEC) measurements connected with the thermodymic analysis of the electrolyte were used to understand the mechanism of electroreduction of hexaaminecobalt(III) complexes. The stability, quantity and numerous of complexes in the electrolyte were examined by the UV – Vis spectrometry method. All potential were determined versus Ag/AgCl reference electrode. Pt thin sheet was used as the counter electrode.

The investigations confirmed that the hexaminecobalt(III) complex electroreduction to Co^0 consist of two steps and deposition occurs only in opd process. The values of electrochemical equivalent shows on formation of $Co(OH)_2$ phase during deposition and chemical dissolution of $Co(OH)_2$ during anodic scan. The reactions corresponding to observed peaks were controlled by the diffusion of complex ions to the surface of the electrode. Using the Randles-Sevcik and Berzins-Delahay equation the diffusion coefficient of complex ions participating in electrode reaction were determined.

Acknowledgements

This work was supported by Polish National Center of Science under grant 2011/01/N/ST5/05509 and 2011/01/D/ST5/05743.

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Phase and electrical behaviour in $Bi_4NbO_{8.5}$

M. Holdynski,1,2 M. Sintyureva,3 X. Liu,3 W.Wrobel,2 J.R. Dygas,2 M. Pisarek,1 R.M. Nix,3 F. Krok,2 and I. Abrahams3

1Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland.

2Faculty of Physics, Warsaw University of Technology, ul. Koszykowa 75, 00-662 Warsaw, Poland.

3Centre for Materials Research, School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London E1 4NS, U.K.

Compounds formed through partial substitution of Bi3+ in bismuth oxide are of interest, as they represent a potential route to stabilising the highly conducting δ-phase of Bi2O3. The structure of δ-Bi2O3 is that of a defect fluorite, with ¼ of the anion sites vacant. It is due to this high vacancy concentration, along with the polarizability of the cation framework, that δ-Bi2O3 exhibits exceptionally high oxide ion conductivity, which is in the order of 1 S cm-1 at temperatures above 730°C.

Substitution of Bi3+ by Nb5+ yields several ordered fluorite phases [1], which have been classified into four basic structural types (I to IV), with several subtypes. This substitution leads to a reduction in the oxide ion vacancy concentration, which is one of the reasons for lower ionic conductivity in the system Bi2O3-Nb2O5, compared to δ-Bi2O3. Vacancy concentration and hence conductivity can be increased through secondary subvalent doping of Nb5+, for example by Y3+, Zr4+ or Er3+ [2].

A study of phase and electrical behaviour in the bismuth niobate, Bi4NbO8.5, using X-ray and neutron powder diffraction, thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) and a.c. impedance spectroscopy is presented. Two polymorphs were identified in this composition, a tetragonal phase (type III), which can appear at temperatures above 800°C and a pseudo-cubic phase (type II) evident at lower temperatures. The defect structure analysis of the type II phase is consistent with the existence of chains of niobate polyhedra, which facilitate electronic conduction at low temperatures. The appearance of the type III phase is very dependent on experimental conditions and TGA and XPS measurements suggest a likely association with change in oxygen stoichiometry.

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POSTERS

Poster 1

Ag/TiO$_2$-n/Ti and Ag/Al$_2$O$_3$-n/Al hybrid materials: role of Ag particles in their behavior as SERS-active and biomedical substrates

Agata Roguska[1,2], Marcin Pisarek[1], Andrzej Kudelski[3], Mariusz Andrzejczuk[2], Maria Janik-Czachor[1], Krzysztof J. Kurzydłowski[2]

[1] Institute of Physical Chemistry PAS, Warsaw, Poland

[2] Faculty of Materials Science and Engineering, Warsaw University of Technology, Warsaw, Poland

[3] Faculty of Chemistry, University of Warsaw, Warsaw, Poland

In this work, we present recent results of investigations of hybrid materials consisting of nanoporous oxides loaded with Ag-nanoparticles: Ag/TiO$_2$-n/Ti and Ag/Al$_2$O$_3$-n/Al, which could be used as active SERS substrates as well as perspective bioactive materials in medicine (implants). Simple electrochemical, chemical and physical methods appeared suitable to fabricate such hybrid materials with different functionalities.

These materials may play a double role, as our investigations have shown: they are active and stable substrates in SERS investigations of adsorbate-adsorbent interactions (Ti- or Al- based materials) as well as biocompatible and bactericidal substrates (Ti-based composites). In both applications – SERS and bio - Ag nanoparticles play an important role, crucial for these two different functionalities.

The new hybrid materials were characterized with high resolution SEM, surface analytical techniques: local AES, XPS and SERS (Surface Enhanced Raman Spectroscopy). For the biomedical applications the hybrid materials were tested with the use of S.epidermis cells (antibacterial test), as well as with U2OS cell culture (living cells behavior and alkaline phosphatase activity-ALP). The tests have shown the highly positive role of Ag nanoparticles in enhancing functionalities of the new hybrid materials.

Acknowledgement

We are most grateful to dr Anna Belcarz from Department of Biochemistry and Biotechnology at Medical University of Lublin (Poland) and dr Lionel Marcon from Interdisciplinary Research Institute, Lille (France) for cooperation and helpful discussions. This work was financially supported by the Polish Ministry of Science and Higher Education (Grant No. N N507 491 138), the National Science Centre (Decision No. DEC-2011/01/B/ST5/06257) and by the Institute of Physical Chemistry PAS (Warsaw, Poland). Surface characterizations (AES, XPS) were performed using a Microlab 350 located at the Physical Chemistry of Materials Centre of the Institute of Physical Chemistry, PAS and of the Faculty of Materials Science and Engineering, WUT.

Poster 2

Nano - porous titania and alumina layers loaded with Ag nano-particles as SERS-active substrates for adsorption studies

M. Hołdyński,[1] M. Pisarek,[1] A. Roguska,[1,2] A. Kudelski[3] and M. Janik-Czachor[1]

[1] Institute Department of Chemistry, University of Warsaw, Pasteur 1, 02-093 Warsaw, Poland.

[2] Faculty of Materials Science and Engineering, Warsaw University of Technology, Woloska 141, 02-507 Warsaw, Poland

[3]Department of Chemistry, University of Warsaw, Pasteur 1, 02-093 Warsaw, Poland.

Silver nanoparticles deposited on various ‘inert’ porous materials (mainly Al_2O_3 and TiO_2) are often used as substrates for surface-enhanced Raman scattering (SERS) measurements. In this study, we used the sputter deposition technique to cover tubular arrays of Al_2O_3 and TiO_2 with Ag nanoparticles. Raman spectra of pyridine (as a probe molecule) and of two selected dyes (5-(4-dimethylaminobenzylidene)rhodanine and 5-(4-(dimethylamino)benzylidene)-3-(3-methoxypropyl)rhodanine) adsorbed on fabrica-ted Ag/TiO_2-n/Ti and Ag/Al_2O_3-n/Al substrates were measured. We found that the SERS spectra of pyridine adsorbed on Ag nanoparticles deposited on an Al_2O_3-n/Al substrate are distinctly different from those measured for an Ag/TiO_2-n/Ti composite. Similar effects were observed for dyes adsorbed on the surface of both composites. The spectral differences between two kinds of composites (Ag/TiO_2-n/Ti and Ag/Al_2O_3-n/Al) are discussed in terms of (1) the modified electronic structure of the Ag nanoparticles due to their interaction with different substrate materials and (2) the different atomic topology of the metal particles thus deposited on the surfaces of the substrates. Composite samples were also studied with the aid of scanning electron microscopy (SEM) and Auger electron spectroscopy (AES) to reveal their characteristic morphological and chemical features.

Acknowledgement

This work was financially supported by the Polish Ministry of Science and Higher Education (Grant No. N N507 491 138), the National Science Centre (Decision No. DEC-2011/01/B/ST5/06257) and by the Institute of Physical Chemistry PAS (Warsaw, Poland).

Poster 3

The effect of formic acid impurities on the performance of palladium-carbon supported catalyst in direct formic acid fuel cells

A. Mikolajczuk[1], A. Borodzinski[1], R. Dziura, P.Kedzierzawski[1], L.Stobinski[1,2] and K.Kurzydlowski[2]

1 Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland

2 Faculty of Materials Science and Engineering, Warsaw University of Technology, Warsaw, Poland

Direct Formic Acid Fuel Cells (DFAFC) with palladium based anode catalysts are promising candidates for a power supply for portable applications such as mobile phones and laptop computers. This type of low temperature fuel cells are close to commercialization and are the most promising alternative power sources. It is known that palladium performs particularly well as an anode catalysts. It is believed that fast deactivation of the catalysts is caused by strongly adsorbed CO on the palladium surface. Organic impurities, present in formic acid, are produced by major industrial method used to synthesize formic acid (e.g. hydrolysis of methyl formate, oxidation of hydrocarbons, hydrolysis of formamide, and decomposition of alkali formate). The most common impurities are methyl formateand acetic acid. The presence of this organic impurities by palladium surface, during electrooxidation formic acid in DFAFC, decrease power output of the fuel cell.

In our studies, the effect of concentration of formic acid and impurities on the performance of palladium carbon supported catalyst have been studied.

Poster 4

Synthesis of Multiwall Carbon Nanotube – Palladium Composite and Its Application in Direct Formic Acid Fuell Cell.

Marta Mazurkiewicz[1], Artur Malolepszy[1], Piotr Kedzierzawski[2], Leszek Stobinski [2], Andrzej Borodzinski[2] , Anna Mikolajczuk[2],

[1] Faculty of Materials Science and Engineering, Warsaw University of Technology, Woloska 141, 02-507 Warsaw, Poland

[2] Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Kasprzaka 44/52, Poland

Fuel cells are classified as one of the ten technologies, which will change our life in the near future, mainly due to the high efficiency. The highest efficiencies have been obtained with hydrogen as a fuel, and the polymer electrolyte membrane (PEM) fuel cell is considered a promising option for future zero-emission vehicles. Conversion of liquid fuels is less efficient in fuel cells, but is still considered an attractive option for certain applications due to the facility of handling liquid fuels compared to that of hydrogen. In fact, direct liquid fuel cells as supply of power to i. e. portable applications are expected to be among the first commercial applications of fuel cells.

So far, the majority of studies concern hydrogen and methanol fuel cells. However, the problem of hydrogen storage has not been resolved yet, and limited supply of platinum limits their applications. Recently published results show, that these problems can be solved by application of formic acid as a fuel, where Pd is a very efficient catalyst.

Metal nanoparticle - CNT composites find numerous applications i. e. as materials for batteries, supercapacitors and as catalysts. In the present work, Pd nanoparticles were deposited on MWCNTs and employed as catalysts of formic acid electrooxidation in a Direct Formic Acid Fuel Cell (DFAFC). MWCNTs coming from two sources: NANOCYL and CNT CO., LTD Korea were used as Pd catalyst support.

Poster 5

Hydrides formed in Zirconium - based intermetallic compounds under high hydrogen pressure

Stanisław M. Filipek[1], Valerie Paul-Boncour[2], Ru-Shi Liu[3] and I. Jacob[4]

1.Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland

2. Laboratoire de Chimie Métallurgique des Terres Rares, CNRS, 2-8 rue H. Dunant, 94320 Thiais, France

3. Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC

4. Department of Nuclear Engineering, Ben-Gurion University of the Negev, Beer Sheva 84105, Israel

Application of high hydrogen pressure technique resulted in syntheses of novel hydrides in a number of zirconium containing alloys. In particular hydrides were obtained for Laves compounds like ZrFe2, ZrCo2 and their pseudobinary alloys, but so far not for ZrPd2 or ZrAl2. Crystalline ZrNi5 forms very unstable hydride which decomposes in a short time at ambient conditions. More stable are “hydrides” formed in Ni-Zr amorphous alloys. Properties of hydrides formed in a group of Zr-based materials are presented and discussed.