



Alfred

Professor Zbigniew Galus

This special issue honors the 70th birthday of Zbigniew Galus, one of the principal figures of Polish electrochemistry and one of the most distinguished Polish chemists.

Zbigniew Galus was born in Szczaworyż near Kielce in 1934. He graduated from the Chemistry Department of the University of Lodz with the *M.Sc.* degree in 1955. He moved to Warsaw to pursue *Ph.D.* study in the Chair of Inorganic and Analytical Chemistry of the University of Warsaw in 1957. Working under the supervision of Professor Wiktor Kemula, Zbigniew Galus participated in the pioneering research on the formation of intermetallic compounds in mercury using newly invented hanging mercury electrode. This project involved collaboration with Zenon Kublik and contributed to scientific foundations of stripping voltammetry. He was awarded the *Ph.D.* degree in 1960.

After graduation, Z. Galus took a two-year long postdoctoral study at the University of Kansas, U.S.A., where he worked with Professor R.N. Adams and collaborated with Prof. P.S. Rowland (Nobel Prize 1997), to elucidate complex mechanisms of electro-oxidation of organic compounds, probably for the first time employing rotating ring-disk electrode, electron spin resonance and radiochemical methods. After his return to the University of Warsaw, his research interests moved towards the intricate problems of electrochemistry of transition metal complexes and, specifically, the mechanisms of electrode reactions involving nickel complexes. This research was the cornerstone of his *habilitation* thesis defended in 1966.

Professor Galus worked at the University of Warsaw for almost five decades. He was appointed to a position of *docent* in 1967, received the scientific title of the *extraordinary professor* in 1973 and the *ordinary professor* in 1981. He has served as the Head of the Inorganic Chemistry and Analytical Chemistry Division of the Chemistry Department for many years. Under his leadership, the division introduced a modern and rigorous curriculum that attracted many brilliant students. Zbigniew Galus created the Laboratory of Electroanalytical Chemistry, and he has been its Head for 35 years. The Laboratory became one of the most vibrant centers of research and education in electrochemistry in Central Europe. Under his supervision, 23 students graduated with *Ph.D.* degrees and 6 received degrees of *habilitated doctors*. Many of his graduates took academic positions in Poland and abroad.

This brief history shows only the milestones of a remarkable career. Scientifically, Professor Galus' interests have ranged across electrochemical kinetics, adsorption processes, inhibition of electrode processes, development of modern electroanalytical techniques, formation of intermetallic compounds in mercury, electrochemical reactions under extreme conditions that include outermost pressures, temperatures or concentrations, chemically modified electrodes, solid electrodes and electrolytes, as well as

ultramicro-electrodes. His scientific achievements are internationally and nationally recognized. He is the author of more than 200 original scientific papers, about ten chapters and review articles, two monographs "Metals in Mercury", (Pergamon, 1986), and "Intermetallic Compounds in Mercury", (Pergamon, 1992), as well as the author of a world famous textbook "Fundamentals of Electrochemical Analysis". This book has got two Polish editions (in 1971 and 1977), two English editions (in 1976 and 1994) and has been translated to Russian (in 1974) and to Mandarin (Chinese edition, 1985). He is one of the few most frequently cited Polish chemists. He has been elected to the editorial boards of the *Journal of Electroanalytical Chemistry* and the *Russian Journal of Electrochemistry*. Professor Galus has been an active member of the Committee for Electroanalytical Chemistry of IUPAC for twelve years and the National Representative of Poland in that committee for the next four years. He has been elected a member of the Polish Academy of Sciences and has also been awarded numerous prestigious prizes such as the Polish Chemical Society Annual Award, J. Zawadzki Medal of the Polish Chemical Society and the prestigious Maria Curie-Sklodowska Medal of the Polish Academy of Sciences.

For his students, friends and co-workers Professor Galus is a modest and altruistic person with exemplary enthusiasm, optimism and devotion to science and education. He is a mentor and a leader able to identify unique research opportunities, helping young scientists to forge their independent career path. Professor Galus has made a tremendous contribution to Polish chemistry throughout his many years of service in the Polish Chemical Society as Chairman of the Electrochemical Section (for eight years), Vice-President (1986–1991), and the Society's President (1992–94), as well as a member of the national Central Board for the Title and Scientific Degrees (for two terms), and a member of the

State Committee for Scientific Research (KBN), a major government granting agency in Poland (for three terms). Zbigniew Galus has served as a member of the editorial board of the *Polish Journal of Chemistry* since 1980, and he became its co-editor in 1994. It is not an overstatement to say that Professor Galus has had a positive influence on everything he has touched. This fact is a direct result of the rare combination of expertise, dedication and integrity.

Paweł Kulesza and Jacek Lipkowsk

Mixed Adsorption Layers Formed at the Electrode–Solution Interface

by J. Nieszporek, D. Gugala, D. Sieńko, J. Jankowska and J. Saba

*Faculty of Chemistry, Maria Curie-Skłodowska University,
Pl. M. Curie-Skłodowskiej 3, 20-031 Lublin, Poland*

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The current knowledge and most recent advances in the study of mixed adsorption layers on the mercury electrode have been reviewed. Wide spectrum of two-component adsorbate systems containing neutral organic molecules as well as organic and inorganic ions have been presented. The effect of co-adsorption on the kinetics of electrode processes (inhibition in particular) has been discussed.

Hydrogen Atom and Hydrogen Ion Interactions with the [100] Surface of Transition Metals (Pd, Ni, Ag, Cu)

by **W.M. Bartczak**^{1,2}, **S. Romanowski**² and **J. Stawowska**¹

¹*Institute of Radiation Chemistry, Technical University, 93-590 Łódź, Wróblewskiego 15, Poland*

²*Department of Theoretical Chemistry, University of Łódź, Łódź, Poland*

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Quantum calculations of interaction of the atomic hydrogen with metal (Pd, Ni, Ag, Cu) clusters with the structure of the fcc [100] surface have been performed. The calculations have been based on the gradient-corrected methods of the Density Functional Theory. For a given position (X,Y) of the hydrogen atom over the metal plane the distance Z from the plane was optimized in order to obtain the highest binding energy which was defined as the difference between the total energy of the H-Me cluster and the energy of the separate H atom and metal cluster. The results of the calculations allowed us to construct the Potential Energy Surfaces for a series of systems. It appears that the H atom binding energy along the valley perpendicular to the metal-metal bond varies only slightly. This suggests easy diffusion of hydrogen along this path. The potential barrier for the hydrogen diffusion over palladium surface is of the order of 0.17 eV. In the case of Ni, Ag and Cu we observe potential barriers with a maximum above the metal-metal bond, with the barrier height 0.68 eV, 0.62 eV and 0.79 eV, respectively. Separate calculations have been performed for the positively charged clusters. For the case of the charged clusters the potential barriers are lower than the value for the neutral clusters. The barriers are 0.27 eV for Ni, 0.35 eV for Ag and 0.58 eV for Cu. For Pd the barrier for the positively charged cluster is 0.5 eV, higher than the value for the neutral case, but for the negatively charged cluster the barrier is practically 0. The results of calculations for all the cases considered suggest the possibility of easy, sometimes activationless, diffusion of hydrogen atoms over the metal surface.

Electrosorption of Carbon Dioxide on Rh Binary Alloys with Pt and Pd

by **H. Siwek**^{1,2}, **M. Łukaszewski**¹ and **A. Czerwiński**^{1,2}

¹*Warsaw University, Department of Chemistry, Pasteura 1, 02-093 Warsaw, Poland*

²*Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland*

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Pt-Rh and Pd-Rh alloys were prepared by electrochemical codeposition. Surface compositions of the alloys were determined from the potential of surface oxides reduction peak. Carbon dioxide was electrosorbed at constant potential in the range where underpotentially deposited hydrogen exists on the electrode surface. The presence of adsorbed CO₂ causes remarkable diminution of hydrogen adsorption signals on the voltammograms recorded after CO₂ adsorption for both Pt-Rh and Pd-Rh alloys. In the case of hydrogen-absorbing Pd-Rh electrodes adsorbed CO₂ does not influence significantly hydrogen insertion into the alloy bulk. Oxidative removal of CO₂ adsorbed on Pt-Rh and Pd-Rh results in a characteristic voltammetric peak, whose potential and shape depend on alloy surface composition. Eps (electron per site) values calculated for the oxidation of CO₂ adsorbed at a fixed potential (0.015 V) and alloy surface composition, being higher for alloys containing more Rh, with a maximum for pure Rh. It suggests that the structure and composition of CO₂ adsorption product vary with electrode surface properties and experimental conditions.

The Comparison of Electrochemical and Radiochemical Methods in Adsorption Study of Thiourea on the Polycrystalline Silver Electrode in Neutral Solution

by A. Łukomska and J. Sobkowski

*Warsaw University, Department of Chemistry, Żwirki i Wigury 101, 02-089 Warsaw, Poland
e-mail: jotes@chem.uw.edu.pl*

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Radiometry and impedance spectroscopy have been compared in the study of thiourea (TU) adsorption on polycrystalline silver electrode. Differential capacity of silver electrode in 0.01 M NaClO₄ solution containing TU of concentrations from 10⁻⁶ to 5×10⁻⁴ M has been measured. The isotherms of TU adsorption, θ vs c determined from the capacitance and radiometric measurements have been compared and the Gibbs energy of adsorption was calculated. The experimental data were described by the Langmuir isotherm. The radiometric method allowed us to determine the surface concentration of TU. It was found that TU adsorption takes place in the entire range of the applied potential. The process of adsorption is reversible with respect to the electrode potential and the bulk concentration of TU, though the desorption process is not completed and small amounts of TU remain on the surface of Ag electrode.

The Adsorption and the Influence of Modified β -Cyclodextrins on the Kinetics of Several Electrode Reactions

by D. Trzciński, W. Kośnik, J. Stroka and A. Temeriusz

University of Warsaw, Department of Chemistry, Pasteura 1, 02093 Warsaw, Poland

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The adsorption of modified β -cyclodextrins (β -CD) on the mercury electrode was investigated in NaClO_4 solutions using differential capacity measurements. The investigated cyclodextrins revealed stronger affinity towards mercury electrodes than native β -CD. Their behaviour was typical for a monolayer and consistent with that predicted by the Frumkin isotherm. The electrode kinetics of $\text{Cu}^{2+}/\text{Cu}(\text{Hg})$ and $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$ couples was significantly inhibited in the presence of modified β -CD in the solutions while much faster in surfactant free solutions the electrode process of $\text{Tl}^+/\text{Tl}(\text{Hg})$ system remained reversible also in the presence of CD's.

New Methods to Study Thin Organic Films at Electrode Surfaces

by **I. Zawisza**^{1,2}, **X. Cai**¹, **V. Zamlynniy**^{1,3}, **I. Burgess**¹, **J. Majewski**⁴,
G. Szymanski¹ and **J. Lipkowski**¹

¹*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, N1G 2W1 Canada*

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

³*Chemistry Department, Acadia University, Wolfville, Nova Scotia, B4P 2R6 Canada*

⁴*MLNSCE, LANSCE-12, Los Alamos National Laboratory, Los Alamos, NM 87545, USA*

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Chronocoulometry, scanning tunneling microscopy (STM), neutron reflectometry (NR) and *in situ* polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) have been employed to study the properties of a monolayer of *n*-octadecanol at a Au(111) electrode surface. Chronocoulometry has been used to determine the charge density at the electrode surface covered by the film of *n*-octadecanol. The surface pressure of this film was calculated from the charge density data. The film pressure data were used to describe the film properties at the gold solution interface. It has been found that at film pressures larger than 12 mN m⁻¹ the monolayer is in a compressed state and at lower film pressures in a decompressed state. STM imaging, NR and PM-IRRAS have been employed to determine the nature of the two states. We have demonstrated that the properties of a monolayer of *n*-octadecanol at the metal-solution interface display many similarities to the properties of an equivalent film at the air-solution interface.

Two-Layer Structures of Ultra-Thin Metal Hexacyanoferrate Films: Charge Trapping and Possibility of Application to Corrosion Protection

by **K. Miecznikowski¹, M. Chojak¹, W. Steplowska¹, O. Makowski¹, P.J. Kulesza¹, L. Adamczyk², M.A. Malik², M. Galkowski² and H. Bala²**

¹*Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland*

²*Division of Chemistry, Department of Materials and Process Engineering and Applied Physics, Czestochowa University of Technology, Armii Krajowej 19, PL-42-200 Czestochowa, Poland*

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The possibility of fabrication of ultra-thin films of metal hexacyanoferrates, Prussian Blue, PB, and nickel hexacyanoferrate, NiHCNFe, by multiple sequential attachment of metal cations (self-assembled on 4-aminobenzoic acid monolayer) and hexacyanoferrate anions, has been demonstrated. These films can form a bilayer arrangement on glassy carbon when PB and NiHCNFe are deposited as inner and outer films, respectively. To avoid mixing of the NiHCNFe and PB redox sites, we introduce a polymer interlayer from poly(4-vinylpyridine) and Nafion. Since the outer NiHCNFe film is physically separated from the electrode surface, and it undergoes redox reactions at potentials characteristic of the inner PB film, an effect of the reversible charge state trapping (bistable switching) is observed. A stable bilayer structure can also be deposited on stainless steel. The whole concept may be of importance to corrosion protection since charge accumulated in the oxidized bilayer film tends to stabilize corrosion potential within passive range.

Recent Developments in Digital Simulation of Electroanalytical Experiments

by L.K. Bieniasz¹ and D. Britz²

¹*Institute of Physical Chemistry of the Polish Academy of Sciences, Department of the Electrochemical
Oxidation of Gaseous Fuels, ul. Zagrody 13, 30-318 Cracow, Poland*

E-mail: nbbienia@cyf-kr.edu.pl

http://www.cyf-kr.edu.pl/~nbbienia

²*Department of Chemistry, Aarhus University, 8000 Århus C, Denmark*

E-mail: britz@chem.au.dk

http://www.chem.au.dk/~db

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This review covers developments in digital simulations of electroanalytical experiments, since 1996. Over the period of time considered, a number of new techniques has been applied. Among them are: the method of lines approach using the differential algebraic equations formulation, extrapolation and Rosenbrock time integrators, multipoint and high-order compact spatial discretisations, finite-element-like methods, adaptive techniques and sensitivity analysis. More simulation software is now also available.

On the Role of Specific Characteristics of the Streaming Mercury Electrode in the Generation of the Nonlinear Electrochemical Dynamical Phenomena

by **M. Orlik and R. Jurczakowski**

*Laboratory of Electroanalytical Chemistry, Department of Chemistry, University of Warsaw,
ul. Pasteura 1, PL-02-093 Warsaw, Poland*

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The streaming mercury electrode was recently found by us a very powerful electrode type for the observation of sustained oscillations and multistability accompanying the electrode processes with the region of the negative differential resistance (NDR) in their I - E characteristics. Following our earlier experimental and theoretical studies of the electroreduction of the pseudohalogenide complexes of nickel(II) at the streaming mercury electrode, we discuss the conditions for the onset of oscillations and multistability in these processes, taking into account the dependence of the double layer capacitance on the electrode potential. The improved stability criteria, involving both the differential C_d and integral K capacitances are derived and compared with our earlier simplified theory. Based on the experimental characteristics of the Ni(II)-SCN⁻ electroreduction it is quantitatively shown, how the two factors specific to the streaming electrodes: the permanent flow of the capacitive current and – in particular – the relatively small thickness of the diffusion layer determine the characteristics of the bistable and oscillatory behaviour.

The Influence of the Experimental Setup Upon the Modelling of the Impedance Spectra in Molten Salts

by **A. Kiswa, J. Kaźmierczak and B. Meisner**

*Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland
E-mail: kiswa@wchuwr.chem.uni.wroc.pl*

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To settle the frequently raised problem of the influence of cell geometry on the value of the evaluated by the electrochemical impedance spectroscopy (EIS) double layer capacitance, in this paper two types of cells have been tested in two and three electrodes experiments in molten salts. In the first type cell, the working silver electrodes were immersed directly in the molten NaCl – KCl eutectic mixture at 700°C, while in the second type cell, the working silver electrodes were placed inside quartz tubes connected to the bulk melt by a small hole. The only effect of the quartz tube was the desired increase of the electrolyte resistance from 0.7 Ω to 5.5 Ω , which is important in lowering the ac measuring current of the Solartron 1260 Phase Gain Analyser. The evaluated values of the double layer capacitance were to experimental uncertainty the same in both cells. It can be thus concluded, that the frequently raised in aqueous electrolytes problem of the influence of the cell geometry upon the values of the evaluated double layer capacitance, in molten salts does not lead to any significant errors. This is presumable due to the fact that the conductivity of molten salts is usually two order higher than aqueous electrolytes, and the corresponding ohmic drops are much smaller.

On Benefits of the Zero-Pole Representation of Electrochemical Impedance Spectroscopy Data Close to Discontinuity Point

by A. Sadkowski

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

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Unusual electrochemical impedance spectroscopy (eis) data obtained for dissolution and passivation of a copper rotating disc electrode in copper sulphate solution and analogous to data reported recently by other authors was represented as a rational function of frequency in terms of zeros and poles. The conditions of stability under potential control (pc) and galvanostatic control (gc) were formulated based on values of zeros and poles and were illustrated with calculated responses to potential and current steps. The loss of stability under pc due to resistance added in series was interpreted as change of the sign of the impedance zero.

Validity of Impedance Spectra Obtained by Dynamic Electrochemical Impedance Spectroscopy Verified by Kramers-Kronig Transformation

by K. Darowicki and J. Kawula

Gdańsk University of Technology, Faculty of Chemistry, Department of Electrochemistry, Corrosion and Materials Engineering, G. Narutowicza Str. 11/12, Gdańsk 80-952, Poland

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The paper presents the verification of the validity of impedance spectra obtained by recently developed experimental technique – Dynamic Electrochemical Impedance Spectroscopy (DEIS). The technique assumes, that the investigated system is pseudo-stationary if the measurement time is suitably short. The time necessary to calculate single spectrum depends on the window length used during Short Time Fourier Transform (STFT) application. The verification of the validity of impedance spectra was performed using Kramers-Kronig transform. The verification confirmed, that the obtained spectra are valid in respect to KK transform.

The Analysis of Stationary Electrochemical Noise

by K. Darowicki and A. Zieliński

*Laboratory of Electrochemistry, Corrosion and Materials Engineering, Faculty of Chemistry,
Technical University of Gdańsk, Narutowicza Str. 11/12, 80-952 Gdańsk, Poland*

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Electrochemical noise is electrochemical technique of growing interest. In the case of random signals obtained by discussed method the power spectral density is one of the fundamental characteristic of process. However its correct estimation imposes stationarity condition on signal under analysis. In the paper the authors present technique for quantitative assessment of degree of non-stationarity for electrochemical noise data by means of the Wigner-Ville transform, which enables calculation of local power spectra.

Time-Frequency Characteristics of Chemical Oscillations. Experimental and Model Studies

by K. Darowicki and W. Felisiak

*Department of Electrochemistry, Corrosion & Materials Engineering, Chemical Faculty,
Gdańsk University of Technology, 80–952 Gdańsk, Narutowicza 11/12, Poland*

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Chemical oscillations exhibit nonlinear, and nonstationary features and their complete characterization cannot be accomplished *via* classical Fourier transform. That is why there is a need for another analysis framework in joint time-frequency domain. In this paper the authors propose a proper methodology of spectral analysis of Belousov-Zhabotinsky (BZ) reaction. The short time Fourier transformation (STFT) has been applied to the analysis of potential registers of BZ reaction in a batch reactor. The method allowed finding the frequency and energy distribution of chemical oscillations in the function of time. The similarities and the differences between the spectrograms generated for the experimental data and simulated time series, based on the modified Oregonator model, are briefly discussed.

Review of PEO Based Composite Polymer Electrolytes

by Z. Florjańczyk, M. Marcinek, W. Wiczorek and N. Langwald

Warsaw University of Technology, Faculty of Chemistry, ul. Noakowskiego 3, 00-664 Warsaw, Poland

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The present paper describes a short review of solid polymer electrolytes composed of high or low molecular weight poly(ethylene oxide), lithium salts and various types of nano and micro sized additives. The mechanism of ionic conductivity in the system is discussed in relation to the Lewis acid-base interaction between the components and the strategies of developing practical materials for lithium batteries are proposed.

Copper Metal Matrix Composite Cu-TiO₂ Electrodeposited in Aqueous Suspensions of the Nanometric Size Particles of Anatase and Rutile

by **V. Medelienė¹**, **R. Juškėnas¹**, **M. Kurtinaitienė¹** and **M. Jaskuła²**

¹*Institute of Chemistry, A. Goštauto 9, 01108 Vilnius, Lithuania*

²*Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland*

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The electrolytic codeposition of nanometric size TiO₂ particles with copper from an aqueous electrolyte has been investigated. Two crystalline modifications of TiO₂ – anatase and rutile were used to prepare a nanodispersed suspension. Qualitative dispersion-hardened Cu-TiO₂ composite coatings were obtained with the reproducible results only from a freshly prepared concentrated electrolyte-suspension. It has been revealed that nanodispersed materials can be obtained electrochemically with an anatase sort of titania. Rutile powder is not as suitable as anatase for this purpose.

Modification of Boron-Doped Diamond Thin Film Surface by Covalent Attachment of Redox Active Molecules

by **P. Krysiński**

*Laboratory of Electrochemistry, Faculty of Chemistry, University of Warsaw,
02-093 Warsaw, Pasteura 1, Poland;
phone: (+4822) 8220211; fax: (+4822) 8225996; e-mail: pakrys@chem.uw.edu.pl*

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This paper reports on the formation of adipoyl chloride adlayer covalently bound through an ester-like bond to the surface of boron-doped diamond electrode. The exposed functional groups of this monolayer can participate in subsequent surface reaction with aminomethylpyrene electroactive fluorophore molecules *via* the carbodiimide chemistry. Since pyrene derivatives are frequently used as polarity-sensitive optical probes, the ability to covalently bind such probes to variety of surface will broaden the field of relaxation dynamics studies of these molecules.

Electrochemical Synthesis and Properties of Micro- and Nanocrystallites of Cobalt

by **A. Wiśniewski, P. Paklepa and P.K. Wrona**

Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

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The electrochemical synthesis of cobalt particles has been performed by electroreduction of Co(II) ions on the mercury electrode at potentials about -1.4 V vs. SCE. The electroreduction of Co(II) observed in cyclic voltammetry (CV), was a totally irreversible process due to the formation of an unstable cobalt amalgam, which decomposed into metallic cobalt. It has also been observed that metallic cobalt, practically insoluble in mercury, tends to aggregate, forming nanocrystallites and clusters that finally separate from mercury in the form of a black powder. The black cobalt powder, obtained this way, has been characterized using scanning electron microscope (SEM) imaging, X-ray analysis and specific surface measurements (nitrogen adsorption according to BET isotherm). The results of these experiments indicate that the cobalt powder obtained from the amalgam consists of partially oxidized crystallites of dimensions less than 20 nm. These nanocrystallites form aggregates of dimensions up to several or more μm . Due to their specific surface exceeding $30\text{ m}^2/\text{g}$, such crystallites can be used for the preparation of metallic catalysts. A hypothesis, concerning the nucleation and further aggregation of Co from a homogeneous cobalt amalgam, leading to the formation of nanocrystallites, is discussed according to the burst-nucleation theory.

Electrochemical Intercalation of ZnCl₂-CrO₃-GIC (Graphite Intercalation Compound) with Sulphuric Acid

by J.M. Skowroński and J. Urbaniak

*Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry,
ul. Piotrowo 3, 60-965 Poznan, Poland
E-mail address: jan.skowronski@put.poznan.pl*

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The intercalation processes of CrO₃ and H₂SO₄ into ZnCl₂-GIC have been confirmed by X-ray diffraction analysis and voltammetric technique. The proposed mechanism of the intercalation of ZnCl₂-GIC with CrO₃ assumes the formation of co-intercalation domains within the interlayer spacings of the graphite structure. Upon the successive intercalation of the graphite compound with H₂SO₄, the peaks characteristic of ZnCl₂ and CrO₃ have been observed in the voltammogram. This is an evidence of the formation of quaternary ZnCl₂-CrO₃-H₂SO₄-GIC.

Development of New Supercapacitor Electrodes Based on Carbon Nanotubes

by **E. Frąckowiak¹**, **K. Jurewicz¹** and **F. Béguin²**

¹*Poznań University of Technology, Institute of Chemistry and Technical Electrochemistry,
60-965 Poznań, Piotrowo 3, Poland*

²*CRMD, CNRS-University, 45071 Orléans, rue de la Férellerie, France*

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Carbon nanotubes (CNTs) are essentially a mesoporous material with very limited microporosity, hence, they supply only moderate capacitance values. After KOH activation their capacitance values increase significantly from 15 F/g to *ca.* 100 F/g. CNTs are especially adapted as component of supercapacitor electrodes due to their exceptional conducting and mechanical properties. They play a perfect role of backbone for materials with pseudocapacitance properties. In this work a profitable role of nanotubes in nanocomposites with polypyrrole and polyaniline is demonstrated. High capacitance values from 200 to 360 F/g were obtained for such composites with a good cycling behavior, however, strongly affected by the operating voltage range of supercapacitor.

Applications of Reticulated Vitreous Carbon (RVC[®]) in the Electrochemical Power Sources

by **Z. Rogulski^{1,2}, W. Lewdorowicz^{1,2}, W. Tokarz^{1,2} and A. Czerwiński^{1,2}**

¹*Warsaw University, Department of Chemistry, Pasteura 1, 02-093 Warsaw, Poland*

²*Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland*

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Reticulated Vitreous Carbon (RVC[®]) is an open pore foam material composed solely of vitreous carbon *i.e.* glass-like carbon, but this material combines some properties of electron-conductive glass with some of those of normal industrial carbons. Over 200 papers have been published on different important electrochemical application of the RVC[®]. The use of the RVC[®] electrodes modified with metals has been proposed for the electrooxidation of impurities, optically transparent electrodes in thin layer constructions, removal and/or recovery of metal contaminations. This paper is a summary of recent literature on application of RVC[®] in electrochemical cells including our latest work. The use of RVC[®] in the construction of accumulators and batteries is discussed in detail showing the perspectives for wide application of this material in electrochemical power sources.

Polymer Electrolyte Based on Ionic Liquid (EMIm)₃PO₄ as an Electrolyte for Electrochemical Capacitors

by **A. Lewandowski and A. Świdarska**

*Faculty of Chemical Technology, Poznań University of Technology,
ul. Piotrowo 3, PL-60 965 Poznań, Poland*

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A series of polymer electrolytes, based on ionic liquid (EMIm)₃PO₄, and the polymers PAN, PVdF, PVdF-HFP, PVA and PEO were prepared as thin-foils, using the casting technique. The composite electrolytes showed conductivity at a level of *ca.* 10 mS/cm, apart from the system PEO-(EMIm)₃PO₄. The electrochemical stability window of the electrolytes based on PAN, PVdF and PVdF-HFP, as determined at the glassy carbon, was at a level of *ca.* 4V. The solid electrolytes polymer-(EMIm)₃PO₄ were applied in a series of double-layer capacitors. The specific capacity expressed *versus* the active carbon mass was at a very high level of 230 F/g (for an activated carbon powder with a specific surface area of *ca.* 2600 m²/g). Good specific conductivity, a broad electrochemical stability window and very high specific capacity suggest that the polymer-(EMIm)₃PO₄ composites are good candidates for application in double layer capacitors.

Modification of Catalytic Activity of Cu-Ti Amorphous Alloy Ribbons by Cathodic Hydrogen Charging

by **M. Pisarek**^{1,2}, **M. Janik-Czachor**¹, **P. Kedzierzawski**¹,
Á. Molnár³, **B. Rác**³ and **A. Szummer**²

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

²*Faculty of Materials Science and Engineering, Technical University of Warsaw, Warsaw, Poland*

³*Department of Organic Chemistry, University of Szeged, Szeged, Hungary*

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Since hydrogen is known to be one of the most efficient embrittling atomic species, cathodic hydrogen charging was used in an attempt to modify the structure, composition and morphology of Cu-Ti amorphous alloy ribbons. Various methods of analysis such as X-ray electron microanalysis, SEM, XRD and electrochemistry, with varying lateral resolution and different information depths, as well as catalytic tests, were used to follow the changes within the ribbons and at the surface, and their interrelations with catalytic activity. The activity in a test reaction (dehydrogenation of 2-propanol) was enhanced up to a conversion level of 66%, which is much higher than that obtained with all other pre-treatments previously applied.

Electrochemical Formation and Properties of (Ir+Pb) Oxide

by A. Piekarska¹, H. Elżanowska¹ and V.I. Birss²

¹*Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

²*Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4*

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The incorporation of Pb redox sites into nanoparticulate Ir oxide films has been realized by the initial electrodeposition of Pb metal on Au substrate, followed by Ir metal coating. The amount of Pb was varied according to the conditions of the deposition process, i.e. time, potential and solution used. Nanoparticulate metallic Ir films were obtained via sol-gel (SG) route and the oxidation of the surface was performed electrochemically in sulfuric acid solutions. The amount of Pb incorporated into the oxide film significantly changed the electrochemical response of the mixed oxide. With a relatively large amount of Pb deposit, consisting of under potential deposition (upd) Pb monolayer and Pb clusters, metallic Ir coating is more difficult than on Au and, consequently, only a small amount of Ir oxide is formed by potential cycling of the Au/(Pb+Ir) metallic electrode. The redox kinetics of Ir(III)/Ir(IV) sites, calculated from chronocoulometric data as a diffusional constant $D^{1/2}C$, is diminished. In contrast, with a relatively small amount of Pb present only as clusters on the Au/Pb electrode after potential cycling in sulfuric acid solution, the diffusional kinetics of Ir(III)/Ir(IV) sites is enhanced ($7 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1/2}$ vs. $4 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1/2}$) as compared to Ir oxide. Also, a small negative shift of the prepeak region of the (Ir+Pb) oxide suggests the presence of additional redox process due to incorporation of Pb sites into the oxide structure. When such mixed (Ir+Pb) oxide containing a small amount of Pb is transferred into 1 M KOH solution, the redox processes of Ir and Pb are then more clearly separated and new redox peaks appear negative of Ir oxide peaks at -0.2 V , and also at $+0.3 \text{ V}$ and $+0.9 \text{ V}$, proving the presence of Pb in the oxide. These redox potentials are comparable to the potentials of $\text{Pb}_2(\text{Pb}_x\text{Ir}_{2-x})\text{O}_{7-y}$ compound obtained thermally and to the redox potentials of Pb electrode in alkaline solutions. The structure of the Pb and Ir deposits and the mixed (Ir+Pb) oxide films was probed using STM imaging. The Pb monolayer (upd) and uniformly distributed Pb clusters ca. 100–150 nm in size were observed on the Au support. The size of metallic Ir nanoparticles is estimated as close to 3–4 nm, increasing to 10–15 nm and 20–30 nm after oxidation of IrO_x and mixed (Ir+Pb) oxide, respectively.

Electronic Aspect of Intercalation in Layered, Spinel and Olivine Type Cathode Materials

by J. Molenda

*Faculty of Materials Science and Ceramics, AGH University of Science and Technology,
Al. A. Mickiewicza 30, 30-059 Cracow, Poland
e-mail: molenda@uci.agh.edu.pl*

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The ability and efficiency of lithium intercalation into transition metal compounds has been found to depend strongly on their electronic structure. This work is a brief review of physicochemical properties of intercalated transition metal compounds with layered, spinel or olivine type structure in order to correlate their microscopic electronic properties *i.e.* the nature of electronic states with the efficiency of lithium intercalation process which is directed by the chemical diffusion coefficient of lithium. The data concerning cell voltages and character of discharge curves for various materials are correlated with the nature of chemical bonding and electronic structure. The nature of the metallic type conductivity of doped phospho-olivine is discussed and some fundamental arguments against the bulk nature of the observed high electronic conductivity are presented.

Impact of an Electrolyte Used for Electrodeposition of Polypyrrole on Ion Transfer and Bulk Resistances of the Polymer Electrode

by M. Grzeszczuk

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

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Different electropolymerization counterions induce differences in the performance characteristics of the polypyrrole electrode. The primary counterion polypyrrole electrode, prepared in aqueous solution of sodium hexafluoroaluminate, was compared to the secondary counterion polypyrrole electrode, prepared in a presence of the sodium chloride solution. In general, the EIS and CV characteristics of the two system are similar due to the most marked contribution of the electrolyte to the electrical characteristics of the polymer electrode through ion transfer and ion transport resistances. The impact of electropolymerization counterion on the interfacial resistance was found to be more significant than on the bulk resistance. The effective polymer charge transport diffusion coefficients were found in the range of 10^{-7} – 10^{-9} cm^2s^{-1} and the polymer redox capacitances were found in the range 50–100 Fcm^{-3} .

Electrochemical Formation of Two-component Films from 2'-Ferrocenylpyrrolidino[3',4';1,2][C₆₀]fullerene and Transition Metal Complexes

by M.E. Płońska¹, A. Makar¹, K. Winkler¹ and A.L. Balch^{2**}

¹*Institute of Chemistry, University of Białystok, Hurtowa 1, 15-399 Białystok, Poland*

²*Department of Chemistry, University of California, Davis, CA 95616, USA*

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Redox active films have been generated electrochemically by reduction of the chemically modified fullerene, 2'-ferrocenyl-pyrrolidino[3',4';1,2][C₆₀]fullerene–FcC₆₀, and [Pt(μ -Cl)Cl(C₂H₄)₂] or Ir(CO)₂Cl(*p*-toluidine). The film is believed to consist of polymeric network formed *via* covalent bonds between the metal atoms and the fullerene moieties. Ferrocene is covalently linked to the polymeric chains through the pyrrolidine rings. The FcC₆₀/Pt film is electrochemically active in both positive and negative potential ranges. At positive potentials, oxidation of the appended ferrocene is observed. In the negative potential range, electron transfer processes involving the fullerene take place. FcC₆₀/Pt films exhibit higher permeability to anions than to cations. Only an outermost layer of this film is reduced. During the oxidation of the film significant structural changes occur. Film formation is also accompanied by platinum deposition. The presence of a metallic phase in the film influences its morphology, structure and electrochemical properties. An FcC₆₀/Ir film has been formed during reduction of solutions containing both FcC₆₀ and Ir(CO)₂Cl(*p*-toluidine). The yield of this film is low with only very thin layer deposited on the electrode surface. No electrochemical activity of the electrode modified with FcC₆₀/Ir was detected in acetonitrile containing only supporting electrolyte.

Ceramic Carbon Electrode Modified with Redox Probe and Salt Solution in Hydrophobic Polar Solvent

by **G. Shul and M. Opallo**

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

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Ceramic carbon electrode modified with redox probe and salt solution in hydrophobic polar solvent was prepared and studied. The electrode consisting of graphite powder, homogeneously dispersed in hydrophobic silicate matrix, was prepared from the mixture of methyltrimethoxysilane based sol and graphite powder by sol-gel method. Then it was immersed in *t*-butylferrocene and tetrabutylammonium perchlorate solution in nitrobenzene. The electrode properties were investigated by cyclic voltammetry and chronoamperometry in KNO_3 solutions of different concentration. Linear polarization of the electrode towards positive potentials results in peak shaped symmetric voltammogram originating from electrooxidation of *t*-butylferrocene. The peak current is few times larger than that obtained when organic phase does not contain salt. It is also proportional to the concentration of the redox probe in organic phase and salt in aqueous phase, whereas the midpeak potential is almost not affected by these factors. The reasons of these effects are discussed.

Composite Ni-P + TiO₂ Electrocoatings for Hydrogen Evolution Reaction in Alkaline Solutions

by **B. Łosiewicz¹**, **A. Budniok¹**, **A. Lasia²** and **E. Łągiewka¹**

¹*Institute of Materials Science, Silesian University, 40-007 Katowice, Bankowa 12, Poland*

²*Département de Chimie, Université de Sherbrooke, Sherbrooke, Québec, J1K 2R1 Canada*

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Hydrogen evolution reaction (HER) has been studied in alkaline media using three types of electrodes: (i) electrocoated with Ni-P + TiO₂, (ii) electrocoated with Ni-P + TiO₂ and heated at 400°C, (iii) electrocoated with Ni-P + TiO₂ and heated at 500°C. The heating was carried out in argon atmosphere. Topographical and structural changes of Ni-P + TiO₂ coatings before and after heating were investigated applying geometric surface structure (GSS) and X-ray diffraction (XRD) methods. GSS results were presented graphically in 2 and 3 dimensions. Steady-state polarization and *ac* impedance spectroscopy were used to determine electrode activities. HER proceeded *via* Volmer-Heyrovský mechanism. The effectiveness of HER depended on the intrinsic activity. HER was enhanced when heating was applied, due to the increased amount of non-stoichiometric Ti oxides (facilitating H reduction/adsorption), comparing to the unheated Ni-P + TiO₂ electrode. The most efficient HER proceeded under the following conditions: 5 M KOH, 25°C, Ni-P + TiO₂ electrode heated to 500°C.

Studies on Spontaneous Discharge of Oxidized Polypyrrole and Poly(N-methylpyrrole)

by J. Dumańska and K. Maksymiuk

Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warszawa, Poland

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Spontaneous processes of charging/discharging of conducting polymers affect analytical characteristics of potentiometric sensors using conducting polymer films as ion sensitive membranes (detection limit, selectivity, sensitivity to redox interferences). These effects also contribute to undesirable loss of charge accumulated in the polymer phase used in charge storing devices. For polypyrrole and its derivatives the charging process is mainly related to oxidation by oxygen or other oxidants present in solution. On the other hand, the nature of the discharge process of oxidized polymer is still not quite clear. This work is oriented towards revealing the nature of the discharge reaction of polypyrrole and poly(N-methylpyrrole). The significance of spontaneous processes, especially for analytical characteristic of potentiometric sensors based on conducting polymers, is highlighted. Therefore, the effect of electrolyte concentration, solution acidity, influence of oxygen, conditioning time and medium was studied. The results of potentiometric and coulometric studies support the thesis that the discharge process is related to the polymer deprotonation; its rate is affected by pre-polarization of the electrode and conditioning of the polymer film.

Interfering Effect of Surfactants on Electrochemistry of Poly(pyrrole) Conducting Polymer Films

by U. Nadrzycka and A. Michalska

Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland

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The effect of anionic, non-ionic and cationic surfactants in solution on electrochemical responses of poly(pyrrole) films were studied. It was found that surfactants present in solution in mmol/dm^3 concentrations practically do not affect voltammetric behavior of cation-exchanging poly(pyrrole) films doped with hexacyanoferrate ions. In contrary, for anion-exchanging poly(pyrrole) films doped with chlorides, PPyCl, charge transfer process observed under conditions of voltammetric experiment was significantly, irreversibly, inhibited by surfactants in solution in $\mu\text{mol/dm}^3$ concentration; regardless the charge of surfactant molecule. As shown by AC voltammetric experiments the choice of frequency (time) scale can be used to amplify or suppress the conducting polymer sensitivity of the current response of polymer for surfactants. These effects are important from the analytical point of view. For high frequencies or under potentiometric conditions surfactants do not interfere with ions concentration determination. On the other hand, for low frequencies surfactants interactions with PPyCl membrane give rise to analytically useful signal. The linear dependencies of current on logarithm of surfactant concentration were obtained within the concentration range at least from 10^{-7} to 10^{-4} mol/dm^3 .

Electrooxidation of *o*-Aminobenzylalcohol – Identification of Oligo-benzylether Structures and Polyaniline Type Polymer by IR and UV/VIS Spectra

by B. Boczek and B. Palys

*Laboratory of Electrochemistry, Department of Chemistry, University of Warsaw,
Pasteura 1, 02-093 Warsaw, Poland*

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The electrooxidation of *o*-aminobenzylalcohol was studied in aqueous acidic solutions. Two distinct electroactive and electrochromic products were identified by cyclic voltammetry, *in situ* UV/VIS and infrared spectra. In initial electrodeposition cycles the oligomers containing benzylether units are formed. Further oxidation–reduction cycles lead to the polyaniline-type polymer. Effects of the kind of acid present in the polymerization bath and of the acid concentration were also studied.

Electrooxidation of Poly (p-Aminoazobenzene) Films – Kinetic Studies

by A. Frydrychewicz and K. Jackowska

*Laboratory of Electrochemistry, Department of Chemistry, Warsaw University,
Pasteura 1, 02-093 Warsaw, Poland*

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The electrooxidation of poly (p-aminoazobenzene) [poly (p-AAB)] was studied in the presence of H^+ and of $Fe(CN)_6^{4-}$ ions by the means of cyclic voltammetry, chronoamperometry and rotating disc electrode. The diffusion coefficients and heterogeneous rate constants were determined from the analysis of Cottrell and Levich-Koutecky plots. It has been found, that the oxidation of poly (p-AAB) in acidic solution is kinetically controlled and independent of the transport of H^+ ions to the polymer surface. The results obtained in the presence of $Fe(CN)_6^{4-}$ have shown that poly (p-AAB) films are permeable to the ions from electrolyte solution.

Synthesis, Electrochemical and Spectroelectrochemical Properties of Viologen Derivative of PEDOT

by **A. Czardybon¹, J. Żak² and M. Łapkowski^{1,2}**

¹*Institute of Coal Chemistry of Polish Academy of Sciences, 44-121 Gliwice, Poland*

²*Faculty of Chemistry, Silesian University of Technology, 44-101 Gliwice, Poland*

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Poly(3,4-ethylenedioxythiophene) (PEDOT) is a highly conductive, low band gap (1.6 eV) polymer. In the oxidized state, thin films of PEDOT are stable and nearly transparent. We present here a derivative of EDOT, a new compound, 1-methyl-1'-(6-(2,3-dihydrothieno[3,4-b][1,4]-dioxine-2-yl-methoxy)-hexyl)-4,4'-bipyridylium bis(hexafluorophosphorane). During electro-polymerization it forms a polymer combining good electrochemical and electrical properties of PEDOT with redox and electrochromic properties of viologen. The monomer was also copolymerized with EDOT. The stability of these polymers was examined using cyclic voltammetry (CV). The CV curves of the thin films of PEDOTM-C₆-V²⁺2PF₆⁻ and the copolymer obtained in the solution of the pure electrolyte have proved the existence of the characteristic, reversible redox system at -0.50 V that is assigned to the viologen radical cation.

Conducting Polymer Films as Model Biological Membranes. Electrochemical and Ion-Exchange Properties of PPy and PEDOT Films Doped with Heparin

by **B. Paczosa**¹, **T. Błaż**¹, **J. Migdalski**¹ and **A. Lewenstam**^{1,2}

¹*Faculty of Material Science and Ceramics, AGH-University of Science and Technology,
al. Mickiewicza 30, PL-30059 Cracow, Poland*

²*Center for Process Analytical Chemistry and Sensor Technology (ProSens), c/o Process Chemistry
Center of Excellence, Åbo Akademi University, FIN-20500 Turku-Åbo, Finland*

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The interaction of calcium, magnesium potassium and sodium cations with heparin (Hep), a highly negatively charged glycosaminoglycan, was studied by using conducting polymer (CP) films. The CP-Hep films were obtained by electrochemical deposition of poly(pyrrole) (PPy) or poly(3,4-ethylenedioxythiophene) (PEDOT). In order to induce magnesium or calcium sensitivity, all films were conditioned in alkaline solution containing magnesium or calcium ions, respectively. After conditioning, the potentiometric response towards calcium or magnesium ions with a close-to-Nernstian slope was observed. The calcium or magnesium sensitive CP-heparin films do not respond to Na or K ions, but the response towards Mg or Ca ions was almost identical. A distinct difference in dynamic open-circuit response to calcium or magnesium ions was observed and its relevance to biological membrane processes is stressed. CP-heparin films can be used for testing an ion exchange as well as transport processes that occur in biological membranes.

Parallel Electrode Processes in Absence of Supporting Electrolyte. Further Strong Enhancement or Depression of Transport of Ionic Species

by **A. Nowicka¹**, **W. Hyk¹**, **Z. Stojek¹** and **M. Ciszowska²**

¹*Department of Chemistry, Warsaw University, ul. Pasteura 1, 02-093 Warsaw, Poland*

E-mail: wojhyk@chem.uw.edu.pl; stojek@chem.uw.edu.pl

²*Department of Chemistry, Brooklyn College, CUNY, Brooklyn, NY 11210-2889, USA*

E-mail: MalgCisz@brooklyn.cuny.edu

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Several ferrocene derivatives, including 1,1'-ferrocenedimethanol, ferrocene, sodium ferrocenesulfonate, sodium ferroceneacetate and ferrocenylmethyltrimethylammonium hexafluorophosphate, were used to examine possible situations in voltammetry, if two of them are present together in the cell under the conditions of absence of supporting electrolyte.

The pairs of ferrocene derivatives were selected for the examination in such a way that one substrate was ionic and the other one neutral. Also, the diffusion coefficients of the species in the solution were sufficiently similar to avoid the effect of nonadditive voltammetric currents. If the ion formed from the neutral substrate and the second ionic substrate are the key ions in the process of preserving the electroneutrality in the diffusion layer at the electrode surface, a significant enhancement or depression of the transport of the ionic substrate takes place. The corresponding wave heights are either much higher (different signs of the ion charges) or lower (identical signs), compared to a situation, where the ionic substrate is present alone in a solution with no supporting electrolyte. The sequence of voltammetric waves of the two substrates determines, which wave is actually affected. The situations demonstrated in the paper may be useful in analytical strategies, aiming at enhancing or depressing a particular voltammetric signal.

Does Electro-Oxidation of 1-Ethyl-naphthalene Proceed Similarly as that of 2-Ethyl-naphthalene?

by **R.E. Sioda¹**, **B. Frankowska¹**, **A. Łobuzińska¹** and **T.Z. Fahidy²**

¹*Institute of Chemistry, University of Podlasie, ul. 3 Maja 54, 08-110 Siedlce, Poland
E-mail: romsioda@ap.siedlce.pl*

²*Department of Chemical Engineering, University of Waterloo,
200 University Ave. W., Waterloo, Ont., Canada N2L 3G1
E-mail: tfahidy@engmail.uwaterloo.ca*

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Electro-oxidation of 1- and 2-ethyl-naphthalenes is conducted. Products determined by GC-MS show that ethyl group is attacked in 1-ethyl-naphthalene, while two isomeric ethyl-1,4-naphthoquinones are obtained from 2-ethyl-naphthalene.

Anodic Oxidation of Trolox in Aqueous Solutions

by J. Małyżko and M. Mechanik

Institute of Chemistry, Akademia Świętokrzyska, PL-25020 Kielce, Poland

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Electrochemical oxidation of trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) was investigated on glassy carbon (GC) electrodes in buffered aqueous solutions in the pH range of 1.0–8.8. The results were interpreted in terms of the formation of phenoxyl radicals, and their subsequent dimerization (radical-radical coupling, *i.e.* DIM1). Dimerization rate constants were estimated from peak heights. pK_a value of the carboxyl group was determined by potentiometric acid/base titration.

Cognitive Aspects of the Cap-Pair Effect

by K. Sykut, G. Dalmata, B. Marczewska and J. Saba

*Department of Analytical Chemistry and Instrumental Analysis, Faculty of Chemistry,
Maria Curie-Skłodowska University, 20-031 Lublin, Pl. M. Curie-Skłodowskiej 3, Poland*

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The paper discusses the cap-pair rule discovered by the authors. The cap-pair rule is associated with acceleration of electrode processes by organic substances. The mechanism and the kinetics of electrode processes in aqueous solutions and aqueous-organic solvents are discussed. A new concept of the “piloting ion” to study mixed adsorption layers based on the cap-pair rule is presented.

A Voltammetric Study of the Reduction of Triptindanones in *N,N*-Dimethylformamide

by **J.S. Jaworski¹** and **D. Kuck²**

¹*Faculty of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland*

²*Fakultät für Chemie, Universität Bielefeld, Postfach 100131, D-33501 Bielefeld, Germany*

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The mechanism of electroreduction of 9-triptindanone (**1**), 9,10-triptindanedione (**2**), and 9,10,11-triptindanetrione (**3**) was studied by use of the cyclic voltammetric method. All carbonyl groups were reduced giving one, two, and three one-electron cathodic peaks for **1**, **2**, and **3**, respectively and the corresponding oxidation peaks. The first electron transfer is reversible and the radical anions formed are stable. Additional small peaks for **2** and **3** were discussed in terms of an adsorption of reactants and intermediates and their reactions with the participation of supporting electrolyte cations as well as the residual water.

Cyclic Voltammetric Study of the Complexation of Pb²⁺ Ions by Dibenzopyridino-18-crown-6 in Some Nitriles

by **G. Chojnacka-Kalinowska¹** and **M.K. Kalinowski²**

¹*Institute of Precision Mechanics, 3 Duchnicka str., 01-796 Warszawa, Poland*

²*Faculty of Chemistry, Warsaw University, 1 Pasteura str., 02-093 Warszawa, Poland
(e-mail: mkalin@chem.uw.edu.pl)*

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A cyclic voltammetric study of the interaction of Pb²⁺ ions with dibenzopyridino-18-crown-6 in acetonitrile, propionitrile, butyronitrile, benzyl cyanide and benzonitrile has been carried out at various temperatures. Stability constants of the resulting 1:1 complexes were found to decrease with increasing DN, the solvent donor number. The enthalpy and entropy of complexation were calculated from the temperature dependence of the stability constants; the complexes were enthalpy stabilized, but entropy destabilized in all the solvents under study. The relationships ΔH° vs. DN and ΔS° vs. DN were found.

The Influence of Solvent on the Reaction Between Iron (II), (III) and *tert*-Butyl Hydroperoxide – Electrochemical Catalytic Processes of Reductants

by T. Paczeński and A. Sobkowiak

Faculty of Chemistry, Rzeszów University of Technology, P. O. Box 85, 35-959 Rzeszów, Poland

E-mail: asobkow@prz.rzeszow.pl

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It has been found that *tert*-butyl hydroperoxide is analogous to hydrogen peroxide with respect to their reactivity towards iron(II) and iron(III). In water iron(II) is oxidized by *tert*-butyl hydroperoxide, whereas in acetonitrile iron(III) is reduced by *tert*-butyl hydroperoxide. The last reaction when performed by cyclic-voltammetry is an example of electrochemical catalytic processes of reductants.

The Application of Magnesium Ion Selective Electrode in Clinical Analysis

**by A. Malon¹, Ch. Brockmann², J. Fijalkowska-Morawska³,
P. Rob⁴ and M. Maj-Zurawska¹**

¹*Warsaw University, Faculty of Chemistry, Pasteura 1, 02093 Warsaw, Poland*

²*Medical University Luebeck, Department of Anesthesiology, 23538 Luebeck, Germany*

³*Medical Academy, Department of Nephrology, 90153 Lodz, Poland*

⁴*Medical University Luebeck, Department I of Internal Medicine, 23538 Luebeck, Germany*

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The role of magnesium is primarily that of a cofactor in intracellular biochemical reactions, therefore, the concentration of intracellular ionized magnesium is much more physiologically relevant. The determination of the ionized magnesium (iMg_e) in erythrocytes by ion-selective electrode for routine clinical measurements was first time investigated. Intracellular and extracellular magnesium concentration in critically ill postoperative patients and in dialyzed patients was compared with healthy individuals. Of the investigated parameters, iMg_e seems to be the best magnesium parameter to observe hypo- or hypermagnesemia for both groups of patients. The correlation that was found between extracellular and intracellular magnesium concentrations can be also used to evaluate the magnesium status.

Voltammetric Determination of Cr(VI) in the Presence of Cr(III) with Application of CDTA as a Masking Agent

by **M. Grabarczyk, Ł. Kaczmarek and M. Korolczuk**

Faculty of Chemistry, Maria Curie-Skłodowska University, 20-031 Lublin, Poland

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A selective and sensitive method for determination of traces of Cr(VI) in the presence of a large excess of Cr(III) by differential pulse adsorptive stripping voltammetry is presented. For minimization of Cr(III) interference cyclohexanediaminetetraacetic acid (CDTA) was used as a masking agent. The determinations were performed in a flow system. The calibration graph is linear from 5×10^{-10} to 2×10^{-8} mol l⁻¹ for accumulation time 60 s. The relative standard deviation for 1×10^{-8} mol l⁻¹ Cr(VI) is 5.8 % (n = 5). The detection limit for an accumulation time of 60 s is 2×10^{-10} mol l⁻¹. The influence of common foreign ions is also presented. The validation of the method was made by comparing the analytical results for water and soil samples with those obtained by reference methods and by a recovery test for river water.

Multi-scan Voltammetric Determination of Carbohydrates at Noble Metal Microelectrodes Following Flow Injection and After Capillary Electrophoresis Separation

by A. Basa, T. Krogulec and A.S. Baranski

Institute of Chemistry, University of Białystok, 1 Hurtowa St., 15-399 Białystok, Poland

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Two multi-scan techniques: cyclic voltammetry (CV) and fast Fourier transform square-wave voltammetry (FFT SWV) with Pt and Au microelectrodes were tested for the determination of five carbohydrates (lactose, sucrose, glucose, fructose and ribose) under FIA conditions. The best analytical results were obtained for the FFT SWV with a Pt microelectrode; in this case the detection limits were below $2 \times 10^{-7} \text{ mol} \cdot \text{dm}^{-3}$ for all studied analytes. In addition, both methods were applied for end-capillary detection in capillary electrophoresis (CE) and tested during an analysis of a mixture of eight sugars. The advantages of scanning methods over constant potential (amperometric) detection methods are also discussed.

Design of Ferrocene Organothiol Monolayer as Intermediate Phase for Miniaturized Electrochemical Sensors with Gold Contact

by **S. Sęk¹**, **R. Bilewicz¹**, **E. Grygółowicz-Pawlak²**, **I. Grudzień²**,
Z. Brzózka² and **E. Malinowska^{2**}**

¹*Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

²*Department of Chemistry, Warsaw University of Technology, 00-664 Warsaw, Poland*

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New design of back side contact (BSC) chips for miniaturized electrochemical sensors with Au contact modified by monolayers of purposely synthesized organothiol molecules is described. Voltammetric studies of the monolayers indicate reversible behavior of the compounds and efficient coverage of the gold electrode. Properties of 5 compounds are compared. The electroactive benzenethiol based self-assembled monolayer is selected as a convenient intermediate layer in solid contact potentiometric sensors since it forms a hydrophobic barrier between the electrode and the solution and at the same time provides efficient electronic wiring to the electrode. Stable electrode performance is obtained and the potentiometric response remains as fast as using bare gold contact which should be favorable for the application of the described intermediate layers in ion-selective electrodes.

Influence of the Transport Conditions on Determination of Trace Arsenic by Cathodic Stripping Voltammetry

by **R. Piech¹**, **W.W. Kubiak¹** and **J. Gołaś²**

¹*Faculty of Materials Science and Ceramics,*

²*Faculty of Mining Surveying and Environmental Engineering, AGH University of Science and Technology, 30-059 Krakow, al. Mickiewicza 30, Poland*

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The cathodic stripping voltammetry has been used to study arsenic(III) and its determination in presence of copper. Dependence of stripping peak on convective transport during the deposition step for the system seems to be unique and its character indicates that stirring rate is an important factor and thus it should be carefully optimized. The optimal stirring rate depends on cell and stirring bar geometry, electrode size, copper concentration and deposition time. The existing in literature ambiguity on selenium influence on arsenic peak current is discussed and explained by taking into consideration the observed dependences. Detection limit for As(III) as low as 0.4 nM (0.03 ppb) at 50 s deposition time could be obtained when optimal stirring conditions were applied.

Sol-Gel Immobilization of Aldehyde Dehydrogenase and NAD⁺ on Screen-Printed Electrodes for Designing of Amperometric Acetaldehyde Biosensor

by **Th. Noguier¹, D. Szydłowska², J.-L. Marty¹ and M. Trojanowicz²**

¹*Université de Perpignan, Centre de Phytopharmacie, UMR CNRS 5054,
52, Avenue de Villeneuve, 66860 Perpignan Cedex, France*

²*University of Warsaw, Department of Chemistry, Pasteura 1, 02-093 Warsaw, Poland*

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The stability of response of amperometric biosensors based on entrapment of aldehyde dehydrogenase (AIDH) and nicotinamide adenine dinucleotide (NAD⁺) in a sol-gel matrix on the surface of screen-printed electrodes modified with the mediator Meldola Blue-Reinecke salt was studied. The operational stability of biosensors was tested using acetaldehyde as substrate by applying a potential of -150 mV vs. pseudo Ag/AgCl screen-printed electrodes. The type and ratio of silicium alkoxides precursors, the amounts of AIDH and NAD⁺, as well as the influence of drying and storage temperature on the stability of electrodes were examined. Among the tested biosensors, the most stable devices were those incorporating a sol-gel layer containing both AIDH and NAD⁺, which was covered by an additional sol-gel layer in order to avoid the co-enzyme leaching.

Application of Isotachophoresis for Determination of Anionic Forms of Phosphonic Acids

by H. Górecki, B. Szczygiel and I. Dreła

*Institute of Inorganic Technology and Mineral Fertilizers, Department of Chemistry,
Wrocław University of Technology, Wyb. St. Wyspiańskiego 27, 50-370 Wrocław, Poland*

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Using a capillary electrophoresis analyser, the concentrations of anionic forms of 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) and N-trismethylenephosphonic acid (NTMP) were determined by the isotachophoresis method. The measurements were performed at pH = 4.2, 6.0 and 8.0. In each case the proper leading/terminating electrolyte system was selected on the basis of literature and authors' own research. The results of isotachophoretic analyses were found to be in good agreement with the results derived from dissociation constants determined by potentiometric method. Considerable difficulties were encountered in interpretation of the results obtained for pH = 8.0 since individual steps in the isotachopherograms were fuzzy and distorted probably due to incomplete separation of the analysed sample into zones. Knowledge of the kind and concentration of ligand forms of chelating compounds, to which PBTC and NTMP belong, can be useful for reclamation of soils polluted with heavy metals.

Anodic Stripping Voltammetry in the Presence of Fumed Silica and Nonionic Surfactants

by **W.W. Kubiak, A. Kamiński, E. Niewiara and B. Baś**

*Faculty of Materials Science and Ceramics, AGH University of Science and Technology,
al. Mickiewicza 30, 30-059 Kraków, Poland*

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In this paper we describe the stripping voltammetric method for the determination of metals in the presence of surfactants at the ppm level. The method employs fumed silica for selective adsorption of surfactants directly in the voltammetric cell. In the present work the suppressing effect of the surfactant is studied. The latter depends mainly on the kind of metal and on the parameters of the deposition stage. The fumed silica usually allows for the full restoration of the suppressed signal. In addition, it is possible to enhance the depolarizer signal in solution with silica suspension if high stirring rates are used during the deposition step. The method is validated by analyzing certified reference material and then tested with the natural sample.

Molecular Geometry as a Source of Chemical Information. Part I: How H-Bonding Modifies Molecular Structure in the Vicinity of Hydrogen Donating Group. The Case of Phenol Derivatives Interacting with Nitrogen and Oxygen Bases

by H. Szatyłowicz¹ and T.M. Krygowski²

¹*Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland
E-mail: halina@chemix.ch.pw.edu.pl*

²*Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland*

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Analysis of geometrical patterns of 635 variously substituted phenols in H-bonding complexes with bases revealed that C₁O, C₁C₂, C₁C₆ bond lengths as well as ipso bond angle change regularly with variation of the acidity (p*K*_a) of phenols. The Bent-Walsh rule is fulfilled and the approximate linear dependence between the above mentioned geometry parameters works. The perturbation in the OH group, due to H-bonding, is transmitted even on further fragments of the ring. DFT modelling at the B3LYP/6-311+G** level of theory for the simplest cases illustrate nicely the conclusion derived for variously substituted systems.

Contribution of Electrochemistry to the Knowledge on Structure and Properties of Amalgams

by **C. Gumiński**

*Laboratory of Chemical Electroanalysis, Department of Chemistry,
University of Warsaw, Pasteura 1, 02-093 Warszawa, Poland
E-mail: cegie@chem.uw.edu.pl*

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The most contemporary shapes of the binary phase diagrams of mercury with all elements are displayed in an integral form. Such presentation allows to follow changes of the phase diagram boundaries in the groups and periods of the periodic table of elements. Selection of the critically assessed solubilities of elements is given in a tabular form. Formation of intermetallic compounds, when two metals are introduced into mercury, is briefly characterized. Our knowledge on these fields of interest was considerably extended by the use of various electrochemical techniques. Diffusion coefficients of metals in mercury are mainly determined by electrochemical methods. An analysis of the diffusion data contributes with important informations about structure of simple amalgams; these conclusions are confirmed by other physico-chemical measurements. A linear dependence is observed between logarithms of the standard rate constants of discharging of aquo-ions on mercury electrode and the metal solubilities in mercury.

Measurements of Interfacial Area in Helicoidal Reactor

by S. Wroński and T. Ryszczuk

*Faculty of Chemical and Process Engineering, Warsaw University of Technology,
ul. Waryńskiego 1, 00-645 Warszawa, Poland
Fax +48 22 825 14 40, tel. +48226606295, E-mail: wronski@ichip.pw.edu.pl*

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Interfacial area was measured in a helicoidal reactor for the two-phase gas-liquid flow, assuming plug flow. Measurements were accomplished using the method of oxygen chemical absorption in alkaline solutions of $\text{Na}_2\text{S}_2\text{O}_4$. Large values of the interfacial area were found. A correlation between changes in the interfacial area and changes in the flow structure within the reactor was observed.

Molecular Interactions in Binary Mixture of Nitrobenzene/Decahydronaphthalene Studied by Dielectric Methods

by M. Dutkiewicz¹ and E. Dutkiewicz²

¹*Faculty of Physics, A. Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland*

²*Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*
E-mail: edutkiew@amu.edu.pl

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Dielectric methods: relative permittivity (ϵ) measurements and the nonlinear dielectric effect (NDE) have been applied to study molecular interactions in a system of nitrobenzene/decahydronaphthalene. The electric permittivity (ϵ), density (d) and NDE parameter ($\Delta\epsilon/E^2$) have been determined as a function of temperature (T) and concentration (x – mole fraction). The results obtained indicate the "precritical behaviour" of the system under investigation for a given temperature and composition. A pronounced maximum of the NDE parameter for $\cong 0.4$ mole fraction of nitrobenzene at lower temperatures has been observed.

**New Application of
1,1,3,3,3-Pentafluoropropene-diethylamine Adduct
(PFPDEA) as Fluorinating Agent. Synthesis of
3,3,3-Trifluoropropionates of Vicinal Fluorohydrins**

by **J. Walkowiak¹**, **G. Haufe²** and **H. Koroniak¹**

¹*Adam Mickiewicz University, Faculty of Chemistry, Grunwaldzka 6, 60-780 Poznań, Poland*

²*Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster,
Corrensstraße 40, D-48149, Germany*

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Reaction of various ω -fluoro-(ω -1)-hydroxy and ω -hydroxy-(ω -1)-fluoro fatty acid methyl esters with adduct of 1,1,3,3,3-pentafluoropropene-diethylamine (PFPDEA) has been studied. As a products mixture of corresponding vicinal difluorides and vicinal fluoro-3,3,3-trifluoropropionates was obtained.

The Synthesis, Structure and Complexing Properties of New Triazacoronands

by **A. Nikonowicz¹, P. Grzegorzewski¹, M. Palys¹ and J. Jurczak^{1,2}**

¹*Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

²*Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland*

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Five new macrocyclic compounds of the triazacoronand type have been synthesized, starting from dimethyl iminoacetate and appropriate α,ω -diamines, in methanol as a solvent. Their complexing properties were investigated using the voltammetric method.

Simulations of Corrosion Processes with Spontaneous Separation of Cathodic and Anodic Reaction Zones

by **C. Vautrin-UI¹, A. Chaussé¹, J. Stafiej² and J.P. Badiali³**

¹*Laboratoire Analyse et Environnement, UMR 8587, Université d'Evry Val d'Essonne,
Bd F. Mitterrand, 91025 Evry, France*

²*Institute of Physical Chemistry, Polish Academy of Sciences,
ul. Kasprzaka 44/52, 01-224 Warsaw, Poland*

³*Laboratoire d'Electrochimie et de Chimie Analytique, ENSCP et l'Université P. et M. Curie,
UMR 7575, 4. Place Jussieu, 75005 Paris, France*

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We present a simple cellular automata model for mimicking corrosion processes of corrodable materials covered by an ideal insulating and protective layer. A small defect in this layer brings the corrodable material into the contact with the outer environment and initiates the formation of a cavity. We study the evolution of the cavity in terms of time dependence of its size, morphology and chemical composition as determined by the corrosion-passivation phenomena at the corrosion front and diffusion within the cavity. We mimic the diffusion of reaction products as a random walk and we can control the diffusion rate with respect to that of corrosion. If the diffusion is very fast the cavity can be assimilated to a half-circle filled up by a neutral solution. When the diffusion rate decreases the cavity shape becomes more and more irregular and the solution contains large domains essentially acidic or basic comparable to cavity size. A quantitative analysis of simulations also reveals the existence of an incubation time during which the corrosion is not clearly visible. If the diffusion rate is low, the stochastic processes that we have considered lead to an unpredictable shape for the cavity and to a large dispersion of the incubation times. Then we clearly observe spontaneous formation of the cathodic and anodic reaction zones at the corrosion front. We discuss these results in a simple case.

Potential and Strain Rate Impact on the Electrochemical Properties of 304L Stainless Steel Under Tensile Stresses

by K. Darowicki, J. Orlikowski, A. Arutunow

*Department of Electrochemistry, Corrosion and Materials Engineering,
Gdansk University of Technology, PL - 80-952 Gdansk, 11/12 Narutowicza Str., Poland*

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The majority of this work was to find out if Dynamic Electrochemical Impedance Spectroscopy can be applied for non-stationary electrochemical processes examination, such as the instantaneous changes during the passive layer cracking. Characterization of the passive layer cracking dynamics is very important from the diagnostics point of view. Especially, if investigated materials are protected by passive films exposed to substantial loads. Presented paper proves that the Dynamic Electrochemical Impedance Spectroscopy allows the determination of instantaneous impedance changes during the initiation stage of the SCC process, which is related to the crack of passive layer. Moreover, mentioned procedure makes possible prediction of the passive layer rupture under tensile stresses. Instantaneous impedance spectra for 304L stainless steel specimens in 0.5 M NaCl solution at room temperature were recorded. Measurements were conducted for different potential values and various strain rates according to the double-factor impact – electrochemical and mechanical. Impedance spectra have been depicted in the 3D diagrams illustrating system's impedance evolution over time. Each spectrum refers to 0.6 second of process duration, so reflecting the changes in the investigated system dynamics.

Evaluation of Relative Humidity Effects on Interfacial Impedance at Inter-Coat Interfaces

by **A. Miszczyk¹, K. Darowicki¹ and Th. Schauer²**

¹*Department of Electrochemistry, Corrosion and Materials Engineering, Chemical Faculty, Gdansk University of Technology, 11/12 Narutowicza St., 80-952 Gdansk, Poland*

²*Research Institute for Pigments and Coatings, Allmandring 37, 70569 Stuttgart, Germany*

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Impedance spectroscopy has been applied as potentially non-destructive method for the evaluation of adhesion at the interface between two polymer layers in protective coating system. The aim was to examine the effect of the outdoor humidity on the interfacial impedance. A automotive basecoat/clearcoat system has been investigated. A new electrode sensor has been employed to detect the changes caused by adhesive debonding and accumulation of water at the interface. The electrode comprising two thin stripes of an electroconductive ink was placed between two coating layers. Large changes in the impedance were observed when humidity conditions were altered. The obtained data were indicative for strong sensitivity of the interlayer impedance to the outdoor humidity. Water accumulation in the interlayer and the formation of conductive paths led to the worsening of adhesion and deamination of the coating layers.

Degradation of Organic Coatings Subjected to Alternating Mechanical Stress Impact

by K. Darowicki and M. Szociński

Gdańsk University of Technology, Faculty of Chemistry, Department of Electrochemistry, Corrosion and Materials Engineering, G. Narutowicza Str. 11/12, Gdańsk 80-952, Poland

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The paper presents results of the investigation on cyclic mechanical stress impact on two types of organic coating systems – epoxy and vinyl ones. They have been subjected to a series of bend/release cycles within elastic deformation region of metal substrate. The state of the coatings has been evaluated using electrochemical impedance spectroscopy. Behaviour of as-received coatings has been compared with the response of the samples pre-exposed in the conditions enhancing coating degradation.