

# **9<sup>th</sup> International Frumkin Symposium**



## **Electrochemical Technologies and Materials for XXI Century**

**ABSTRACTS**

**Moscow  
24 – 29 October, 2010**

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**Division of Chemistry and Material Sciences**  
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**9th International Frumkin Symposium**

**“ELECTROCHEMICAL TECHNOLOGIES  
AND MATERIALS FOR 21st CENTURY”**

**ABSTRACTS**

**Moscow 2010**

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EXCHANGE KINETICS AND DIFFUSION OF OXYGEN  
IN LANTHANUM-STRONTIUM COBALTITES

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Lanthanum-strontium cobaltites attract an attention of many researchers due to such oxides can be used as electrode materials in modern electro-chemical devices (solid oxide fuel cells, electrochemical pumps, sensors, reformers, CO<sub>2</sub>-lasers etc.). There are a lot of papers concerned with electrical, transport, catalytic, magnetic and other properties of these materials, but in many cases significant distinguish can be observed between data from different authors. That is probably due to differences in microstructure of the materials, grain-boundary influence etc.

In present work exchange kinetics and diffusion of oxygen are studied using isotope exchange technique with gas phase analysis for oxides La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3-δ</sub>, where  $x = 0.0, 0.3, 0.4$  и  $0.6$  in the temperature range 600–850 °C and oxygen pressure  $(1.33-93.3) \times 10^2$  Pa. Setup description see in [1], Klier and Kucera model [2] is used for experimental data treatment, error isolation procedure is used to estimate accuracy of varied parameters calculation [3].

The oxides have been synthesized with citric-nitrate technique. According to X-Ray powder diffraction analysis (Rigaku-diffractometer D-MAX 2200V, CuK $\alpha$ -radiation on air at room temperature) all the samples have no any reflexes corresponding to impurities. Surface microstructure of the oxides was studied by scanning electron microscopy technique using Jeol (JSM 5900LV) hardware with micro-analyser INCA Energy 200.

Values of interphase exchange rate ( $H$ , at  $\text{sm}^{-2}\text{s}^{-1}$ ) and oxygen diffusion coefficients ( $D$ ,  $\text{sm}^2\text{s}^{-1}$ ) are shown to increase in La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3-δ</sub> with  $x$  – growth, which is probably because of oxygen non-stoichiometry  $\delta$  changes, studied for lanthanum-strontium cobaltites in [4]. Using temperature dependence of  $H$  and  $D$  effective activation energies at constant oxygen pressure  $(6.65 \pm 1.33) \times 10^4$  have been calculated. Effective exchange activation energy decreases with  $x$ -growth and increases for diffusion of oxygen.

Oxygen pressure dependence of  $H$  has power function type,  $H \sim p^n(\text{O}_2)$ . Moreover the index  $n$  increases from  $\frac{1}{2}$  to 1 with  $x$  growth that can be connected with changing of three exchange type contribution to the common oxygen exchange rate in investigated oxides [5]. First exchange type contribution is shown to decrease with  $x$ -growth. The first type goes without any interactions between molecular oxygen of gas phase and oxygen from the solid oxide surface, which can probably be explained by increasing of oxygen vacancies concentration on the solid surface due to growth of acceptor defects [Sr<sup>2+</sup><sub>L</sub>] with  $x$  [4]. Oxygen diffusion coefficient tends to decreasing with oxygen pressure growth, which correlates with oxygen non-stoichiometry changing in investigated oxides.

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**CATALYTIC PROPERTIES OF PLATINUM NANOPARTICLES OBTAINED BY DEPOSITION FROM REVERSE MICELLE SOLUTIONS**

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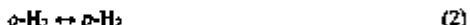
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Nanobjects find ever wider application in different fields of industry and economics. The theory of heterogeneous catalysis describes how the form and size of metal particles and their interaction with the support affect the activity of supported catalysts. One should also consider inseparability and mutual effect of these factors.

The behavior of platinum nanoparticles deposited from inverse micelle solutions was studied [1] regarding reactions of isotopic exchange in molecular hydrogen:



in a wide range of temperatures of 77–250 K and low-temperature ortho-para conversion of protium:



The size and form of micelles formed in reverse micelle solutions (RMSs) are determined using the method of atomic force microscopy (AFM). The adsorption of platinum nanoparticles from RMSs on the support surface was controlled using the method of spectrophotometry.

The adsorptive properties of the particles, their stability in time and values of the metal active surface area are determined on the basis of hydrogen chemisorption at 77 K.

In the course of the work, the dependences of catalytic activity and activation energy for reactions (1) and (2) on the chosen support type, the value of solubilization coefficient  $\omega$  of the initial solutions determining the size of particles and their properties are found.

The obtained high activity values of platinum nanoparticles in homomolecular reactions of hydrogen isotopic exchange show the uniqueness of the properties of nanocomposites and the prospects of their further research.

**Reference**

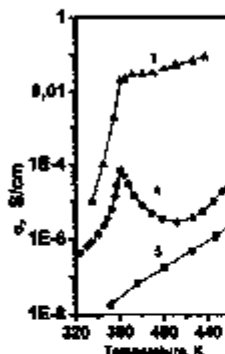
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# SOLID EUTECTIC MIXTURES AND CRYSTALLINE HYDRATES OF ALKALI HYDROXIDES AS NOVEL FAMILY OF PROTONIC CONDUCTORS

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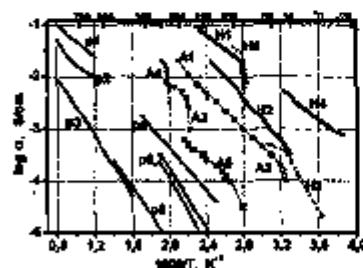
1. Intensive development of composite materials with enhanced ionic conduction has given the impetus to prove this phenomenon on solid hydroxides, but basing on slightly other approach. The self-assembled micro-heterogeneity of the solid eutectic was used instead of the artificial micro-heterogeneity of e.g. "ionics-dielectric" composites. It has been showed that eutectics  $\text{KOH}+\text{KOH}\cdot\text{H}_2\text{O}$ ,  $\text{KOH}+\text{NaOH}$  and  $\text{LiOH}+\text{NaOH}$  are solid superprotonics at 360–370 K, 360–458 K and 400–500 K, respectively. These eutectics have showed substantially higher conductivity than that of individual partners at the same temperature, e.g. as it can see on Fig.1, where curves correspond: 1  $\rightarrow \sigma(\text{KOH}+\text{NaOH})$ , 2  $\rightarrow \sigma(\text{KOH})$ , 3  $\rightarrow \sigma(\text{NaOH})$ .



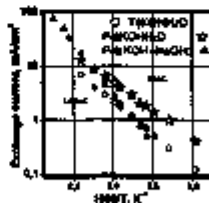
2. Crystalline hydrates  $\text{KOH}\cdot\text{H}_2\text{O}$ ,  $\text{NaOH}\cdot\text{H}_2\text{O}$  and  $\text{KOH}\cdot 2\text{H}_2\text{O}$  have showed also enough high proton conductivity. Our data are presented on Fig.2: H1  $\rightarrow \text{KOH}+\text{NaOH}$ ; H2  $\rightarrow \text{KOH}\cdot\text{H}_2\text{O}$ ; H3  $\rightarrow \text{NaOH}\cdot\text{H}_2\text{O}$ ; H4  $\rightarrow \text{KOH}\cdot 2\text{H}_2\text{O}$ ; H5  $\rightarrow \text{KOH}+\text{KOH}\cdot\text{H}_2\text{O}$  [1–3]. For comparison the conductivity of most popular inorganic proton conductors – perovskite type (p1) and acid salts (A1) – are presented on the base of literature data. Here  $i = 1, 2, 3 \dots$

Perovskites: p1 =  $\text{Y:BaCeO}_3$ ; p2 =  $\text{Nd:BaCeO}_3$ ; p3 =  $\text{Yb:BaCeO}_3$ ; p4 =  $\text{Ba}_2\text{YSnO}_{5.5}$ ; p5 =  $\text{Y:SrZrO}_3$ ; p6 =  $\text{BCN4}$ ; p7 =  $\text{BCN18}$ . Acidic salts: A1 =  $\text{CsHSO}_4$ ; A2 =  $\text{Cs}_2(\text{HSO}_4\cdot\text{HPO}_4)$ ; A3 =  $\text{Rb}_2\text{H}(\text{SeO}_4)_2$ ; A4 =  $\text{CsH}_2\text{PO}_4$ ; A5 =  $\text{K}_2\text{H}_2(\text{SO}_4)_4$ .

3. The electrochemical solid-state cells on the base of these novel electrolytes with a hydrogenated metal (Pd, Ti, TiFe) and graphite as electrodes have been proved as a rechargeable batteries [4]. Metal electrodes have not been under-gone any special treatment before experiments and used as foils (Pd, Ti), wires (Ti) and molten-cast oval nail (TiFe).



It is interesting to the opportunity to work at room temperatures the cell  $\text{TiFe}|\text{KOH}\cdot 2\text{H}_2\text{O}|\text{C}$ .



of this cell is 1.2 V. It has been proved as power source for electronic quartz timer in few months.

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## CATALYTIC PROPERTIES OF PLATINUM NANOPARTICLES OBTAINED BY DEPOSITION FROM INVERSE MICELLE SOLUTIONS

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This work studies the catalytic activity of platinum nanoparticles obtained by radiation chemical reduction of platinum ions in reverse micelle systems (Laboratory of Composite Materials OI SC, the patent of the Russian Federation no. 2322327) and deposited on  $\gamma\text{-Al}_2\text{O}_3$  (Redkinskiy Catalyst Plant) in the reactions of homomolecular isotopic exchange of hydrogen (1) and ortho-para conversion of protium (2):



Both reactions are of great interest for the two most important fields of conventional power engineering: nuclear and hydrogen energetics. Reaction (1) is one of the stages of industrial production of heavy water used in the nuclear industry and is also a model for reactions occurring with participation of hydrogen. Reaction (2) is required in industrial hydrogen liquefaction and rectification for its use as a power source in hydrogen power engineering.

In the course of the work, the dependences are found of catalytic activity and activation energy of reactions (1) and (2) on the value of solubilization coefficient  $\alpha$  of the initial solutions, which is proportional to the size of the applied particles and their concentration in the reverse micelle solution (RMS). Studies of reaction (1) were performed in a wide range of temperatures (77 – 250 K), while reaction (2) was investigated in the low-temperature range.

The size and form of the platinum nanoparticles formed in RMSs are determined using the method of atomic force microscopy (AFM).

The process of adsorption of platinum nanoparticles from RMSs on the surface of the  $\gamma\text{-Al}_2\text{O}_3$  support was controlled using the method of UV-VIS spectrophotometry (Hitachi U-3010 spectrophotometer).

The adsorption properties of the applied nanoparticles, their stability in time, and the value of the metal active surface area are determined on the basis of hydrogen chemisorption at 77 K.

It is found that the activity of the platinum nanosize particles exceeds by more than an order of magnitude the activity of conventional platinum catalysts and approaches the activity of a platinum film. The obtained high activity values of platinum nanoparticles in the reaction of homomolecular isotopic exchange of hydrogen show the unique properties of these systems and the prospects of their further studies.

### **SYNTHESIS OF NICKEL-CARBON NANOHORN COMPOSITE FILMS BY AN ELECTRODEPOSITION TECHNIQUE**

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In this work, electrodeposition of nickel-single walled carbon nanohorns composite is obtained from a sulfamate bath. Microhardness and wear resistance of the composites are investigated. Both properties are highly influenced by the volume fraction of incorporated carbon nanohorns particle.

Electrodeposition of nickel-nanohorn composites is carried out from a sulfamate bath containing up to 2 g/l of dispersed single walled nanohorns with diameter 30 to 50 nm. Deposits with embedded nanohorns, homogeneously dispersed in metal matrix, are obtained. Structure of the deposits and contents of carbon nanohorns particles in these layers were investigated with respect to the possibility of agglomeration of SWNH particles and bath composition (concentration of SWNH in the electrolyte). Microhardness and wear resistance of the composites are investigated. Martens hardness is highly influenced incorporation of particles. Young's modulus and wear resistance of the nickel matrix composites with nanohorns remain unchanged. Morphology of the coatings and the effects of codeposited particles on metal matrix structure are also reported.

## REDOX POTENTIAL MONITORING OF BLOOD SERUM IN PATIENTS AFTER LIVER TRANSPLANTATION

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An interest in medical applications of redox potential measurement in biological media was initially related to prospects of elucidating the pro- and antioxidant equilibrium in the biological media of the organism [1]. However, the development of Nordenström's theory of biologically closed electrical circuits [2] has also brought about the promise of developing diagnostic and prognostic criteria for various pathological states by measuring open-circuit potentials (OCP) of electrodes immersed in the biological media involved. For instance, the OCP of blood serum has been shown to correlate with the toxicity levels in patients with cerebral pathology [3].

The present work is a continuation of investigations of OCP in blood serum, aiming to determine the possibility of utilizing the measured OCP values as a prognostic criterion for timely correction of surgical and therapeutic methods in patients following the transplantation of liver. The importance of this goal is due to the absence of noninvasive methods for predicting an impending rejection of the transplanted organ by the patient.

In the course of monitoring the OCP in patients following the transplantation of liver, in two of 21 patients under observation, abrupt changes in the OCP of platinum electrode were observed. In Patient K., a potential shift from -30 mV to -70 mV was observed, 22 days after the surgery, and Patient S. had an OCP change from -54 mV to -92 mV. In both cases, this correlated with clinical data indicating early-stage liver rejection.

Thus, monitoring the post-surgical OCP of blood serum in a group of patients with liver transplants has revealed the possibility of using OCP of blood serum as a diagnostic test to detect the rejection of the transplanted liver.

An attempt was also made to ascertain the possibility of replacing platinum for a material, which is less expensive and more stable in the test media. Electrodes made of mixed indium and tin oxides were investigated. The OCP measurements with these electrodes in aqueous solutions at various pH values showed that the OCP values after measurement and washing of the electrodes quickly returned to the initial values. For instance, the electrode OCP in an ascorbic acid solution (50 mg/l in 0.15 M NaCl) was +59 mV, returning to +203 mV after washing with 1.0 M Na<sub>2</sub>SO<sub>4</sub>, which was quite close to the initial value in the same solution (+216 mV).

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# **SURFACE MICROSTRUCTURE ANALYSIS OF OXIDES BASED ON LANTHANUM COBALTITE USING SCANNING ELECTRON MICROSCOPY DATA**

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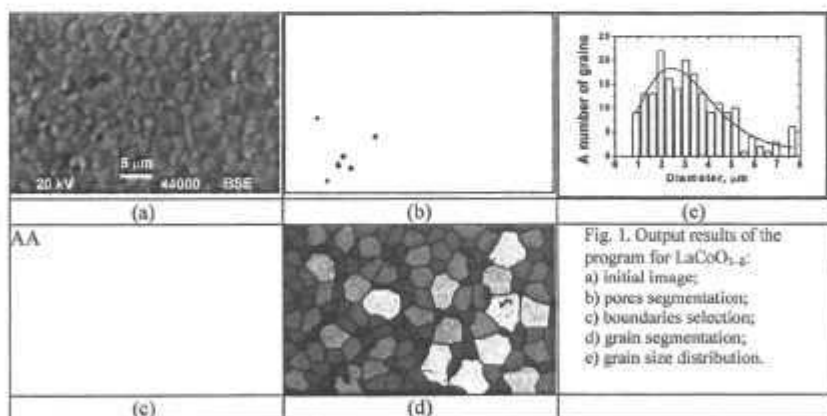
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Scanning electron microscopy (SEM) is widely used for surface microstructure analysis. It is necessary to develop image analysis methods.

Electron microscope images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, chemical composition and other properties such as electrical conductivity.

Grain size distribution of the main phase and impurities, fraction of the secondary phase, open porosity of the material, pore size distribution are the main microstructure parameters to be estimated.

In the present work algorithms for image microstructure analysis have been developed and debugged on the image examples of  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  oxides, which attracts an attention of scientists as prospective functional materials for modern electrochemical devices. Output result of the image analysis in case of  $\text{LaCoO}_{3-\delta}$ -oxide surface is represented in Fig. 1.



Images have been done using scanning electron microscope Jeol (JSM 5900LV) with microanalyzer INCA Energy 200.

*The work was supported by Russian Foundation for Basic Research (project # 08-03-01028-a) and young innovation grant of Ural Division of Russian Academy of Sciences.*

# KINETICS OF THE HYDROGEN EVOLUTION ON GOLD ELECTRODE. A NEW CASE OF THE BARRIERLESS DISCHARGE

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Among all the metals poorly adsorbing hydrogen gold is the most electropositive one; this allows to study the hydrogen evolution reaction on this electrode up to very low overpotentials, where the barrierless discharge can be expected. The literature data do not contradict this expectation but they cannot be used to draw an unambiguous conclusion.

In our experiments, we used gold electrodes electrodeposited on gold or platinum plates. All the reactants were chemical pure, water bidistilled. The test solution was purified by pre-electrolysis; to increase its effectiveness, the ratio of the solution volume to cathode's area was made rather small, about 0.5 ml per 1 cm<sup>2</sup>, and the solution was agitated intensively by an argon stream. The solution in the working cell was deaerated with argon. The measurements were performed potentiostatically; potential was shifted stepwise by 20 mV from negative to more positive potentials, and than in reverse direction. No hysteresis was observed. At each potential the electrode was kept for 5 min, then argon was bubbled during 2-3 min causing no change of current in an unstirred solution. Removing the dissolved hydrogen by argon stream, we were able to perform the measurements at low polarizations avoiding the interference of the anodic back-reaction.

The polarization curves consist of two linear segments with Tafel slopes about 0.06 V and 0.12 V. This shape of the polarization curve was reproduced in 22 independent experiments, the slopes varied in limits of 53-69 mV and 105-141 mV, the average values are 63 mV and 123 mV. For the different electrodes, the similar in shape polarization curves differed by several tens of millivolt; some changes were observed also after keeping the electrodes during few days. We needed the accuracy of order of few millivolts. Therefore, we measured polarization curves in different solutions on the same electrode during one day, and we controlled stability of its surface by capacitance measurements (CVA, 10 V s<sup>-1</sup>).

Polarization curve with two Tafel slopes of 0.06 V and 0.12 V is typical of the slow discharge mechanism with discharge at low overpotentials being barrierless ( $\alpha = 1$ ), and a usual (ordinary) discharge at higher overpotentials ( $\alpha = 1/2$ ). To test the reality of this mechanism, it was necessary to study the overpotential dependence on the solution composition. For solutions of 1 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M H<sub>2</sub>SO<sub>4</sub> + 0.9 M NaClO<sub>4</sub>, at the slope  $b = 0.12$  V, the overpotential in the second solution is by ~0.03 V higher than in the first one, at  $b = 0.06$  V only small (~10 mV) difference was observed. The effect of the  $\psi_1$ -potential was studied in two ways - by increase of the total ionic strength (0.1 M H<sub>2</sub>SO<sub>4</sub> pure and with addition of 0.9 M NaClO<sub>4</sub>) and by tetrabutylammonium addition to 1 M H<sub>2</sub>SO<sub>4</sub>. In all cases, the shift of  $\psi_1$ -potential increased overpotential at high Tafel slope as predicted for the ordinary discharge. At the same time; at  $b = 0.06$  V no change of overpotential was observed in limits of. 1-2 mV. Hence, all the dependencies studied correspond strictly to the mechanism of the barrierless discharge followed by an ordinary discharge. We have analyzed the alternative mechanisms proposed in the literature, and have shown that they do not agree with the experimental data.

*This work was supported by Russian Foundation for Basic Research (project # 09-03-00085-a).*

# STANDARD RATE CONSTANTS OF CHARGE TRANSFER FOR THE REDOX COUPLE Cr(III)/Cr(II) IN CHLORIDE MELTS: EXPERIMENT AND CALCULATION

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Standard rate constants of charge transfer for the redox couple Cr(III)/Cr(II) were determined by cyclic voltammetry on the glassy-carbon electrode in molten salt systems NaCl-KCl (equimolar mixture)-CrCl<sub>3</sub>, KCl-CrCl<sub>3</sub> and CsCl-CrCl<sub>3</sub> using the Nicholson's equation:

$$\psi_p = \frac{k_s (D_m / D_{ox})^{1/2}}{\sqrt{(\pi D_m n F v) / RT}} \quad (1)$$

Equation (1) is valid for quasi-reversible process if it is not complicated by the formation of insoluble product, so for each system the interval of polarization rate was found where the using of equation (1) is correct.

Standard rate constant of charge transfer ( $k_s$ ) were determined in the temperature range 973–1173 K and they increase with increasing temperature. It was found that in molten salt systems NaCl-KCl, KCl, CsCl the standard rate constants of charge transfer decrease monotonically. The "apparent" activation energies of charge transfer were determined and it was shown that the transfer of electron between Cr(III) and Cr(II) complexes proceeds quasi-reversibly mostly under diffusion control.

At absence of complications the relation of the standard rate constants of charge transfer should correspond to the relation of the  $E_{act}$  activation energy in series of outersphere cations Na-K-Cs. The  $E_{act}$  values have been calculated by quantum-chemical methods. Preliminary compositions of the most stable particles  $nM^+ \cdot Cr(3)Cl_6^{3-}$  were determined, where M – outersphere cations (M – Na, K, Cs;  $n = 1-6$ ). The maximum of stability was retrieved at  $n = 5$  for M – Na, K and  $n = 4$  for M – Cs. The  $E_{act}$  calculations were carried out by Marcus formula:

$$E_{act} = (E_r + \Delta G_r)^2 / 4E_r \approx E_r / 4, \quad (2)$$

where  $E_r$  is the value of reorganization energy calculated by quantum-chemical methods. For these most stable particles the  $E_{act}$  values increase in series Na < K < Cs, that corresponds to a ratio of experimental standard rate constants of charge transfer.

However, estimations of the relation of charge transfer rates, based on the account of standard recharge potentials for Cs particles with  $n = 4$  and 5, have shown, that electron transfer should proceed via the  $5Cs^+ \cdot Cr(3)Cl_6^{3-}$  particle. In this case the relation of activation energies still corresponds to experiment. Besides that the  $E_{act}$  values become more close to each other, improving accordance of these values to the experimental results on the standard rate constants of charge transfer.

The study was supported by Russian Foundation for Basic Research (project # 08-03-00397-a).

**ELECTROCHEMICAL AND ESR STUDY OF C-H BOND ACTIVATION,  
MECHANISM OF OXIDATION OF ORGANIC COMPOUNDS  
IN THE PRESENCE OF RADICAL CATION OF PYRAZINE-DI- N-OXIDE  
AND ITS SUBSTITUTED DERIVATIVES AS MEDIATORS**

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We found earlier [1-3] that electrochemically generated radical cations of aromatic di-N-oxides are the carriers of active oxygen capable of activating the C-H bond of substrates. Using the methods of CVA, ESR-electrolysis and quantum chemical simulation, we studied the mechanism of oxidation of organic substances (alcohols, ethers and cyclohexane) in the presence of electrochemically generated radical cations of phenazine-di-N-oxide (PheDNO  $E_0 = +1.28$  V), pyrazine-di-N-oxide (PyrDNO  $E_0 = +1.59$  V) and its derivatives ( $E_0$  is between +1.42 and +1.53 V). Our ESR electrolysis studies of the PheDNO oxidation in methanol and its deuterated derivatives,  $\text{CH}_3\text{OD}$  and  $\text{CD}_3\text{OD}$  made it possible to observe the ESR spectra of radical intermediates with the following g-factors: 2.0023 in  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  and 2.0023 and 2.0036 in  $\text{CD}_3\text{OD}$ . It was assumed that radical intermediates represent complexes of the PheDNO radical cation with methanol and its deuterated derivatives. The detection of one and the same intermediate in  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  pointed to the involvement of the alcohol  $\text{CH}_3$  group in its formation. To explain the obtained results, a new mechanism of the overall two-electron electrocatalytic oxidation of the substrate ( $\text{E}_1\text{C}_1\text{E}_2\text{C}_2$ ) that involved the formation of a complex with the aromatic di-N-oxide radical cation in  $\text{C}_1$  stage was put forward.

In the present work we study the mechanism of the oxidation of methane and *t*-BuOH (substrates are characterized by high energy of the break of C-H bond, 422.79 kJ/mol in *t*-BuOH and 435.43 kJ/mol in methane) in the presence of mediators, electrochemically generated radical cations of PyrDNO, 2,5-di-Me- and 2,3,5,6-tetra-Me- pyrazine-di-N-oxides by the methods of CVA, ESR electrolysis and quantum chemical simulation. The study was carried out at QC and Pt electrodes in 0.1 M  $\text{LiClO}_4$  solutions in acetonitrile and at Au electrode in *t*-BuOH used as a solvent and a substrate simultaneously.

ESR spectra of radical cations of aromatic di-N-oxides at 25°C in *t*-BuOH and in the absence and in the presence of methane at -45°C in acetonitrile are recorded. The effect of methane and *t*-BuOH on the shape of CVA curves and the intensity of ESR signals of radical cations of pyrazine-di-N-oxides was studied. The changes in the shape CVA curves and the intensity of ESR signals of di-N-oxides radical cations in the presence of methane and *t*-BuOH point to the activation of the C-H bond followed by its oxidation. A quantum chemical simulation of the reaction of the unsubstituted PyrDNO radical cation at the C-H bond of methane and *t*-BuOH was carried out. Based on the obtained results, it was assumed that in the presence of electrochemically generated radical cations of PyrDNO and its substituted derivatives, methane and *t*-BuOH were oxidized by the mechanism of overall two-electron oxidation of an organic substance within its complex with the PyrDNO radical cation.

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KINETICS OF CATHODIC REACTIONS IN THE ELECTRODEPOSITION  
OF COBALT-MOLYBDENUM ALLOY

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Cathodic reactions kinetics in ammonia-citrate solutions for electrodeposition of Co-Mo alloys was investigated by the method of steady-state polarization curves. The electroreduction of molybdenum-containing species at the surface of solid electrodes at potentials more negative than  $-0.85$  V (the electrode potentials are related to the standard hydrogen electrode,) proceeds to metallic molybdenum. It was confirmed by XPS analysis. The sodium molybdate concentration in the solutions under study affects the partial polarization curves of cobalt and molybdenum electrodeposition. An increase in  $c(\text{Na}_2\text{MoO}_4)$  causes decrease of partial current density of cobalt electrodeposition ( $i_{\text{Co}}$ ). The  $\text{Na}_2\text{MoO}_4$  concentration influence on partial current density of molybdenum electrodeposition ( $i_{\text{Mo}}$ ) is more complicated. The effects observed can be explained by changes in the part of electrode surface occupied by adsorbed molybdenum-containing species caused by varying of  $\text{Na}_2\text{MoO}_4$  concentration in the solution.

The effect of hydrodynamic conditions on  $i_{\text{Co}}$  and  $i_{\text{Mo}}$  was studied by method of rotating disk electrode (RDE). To suppress hydrogen evolution reaction, which impedes the measurements, the surface of RDE preliminary amalgamated. The electroreduction of molybdenum species in these conditions also proceeds to  $\text{Mo}(0)$ . This conclusion was made from coulometric measurements. The dependences of  $i_{\text{Co}}$  and  $i_{\text{Mo}}$  on square root of angular velocity of RDE are rather complicated. The data obtained can be explained by Co and Mo incomplete reduction products adsorption at the cathode. These adsorption phenomena can not be ignored even at relatively small concentrations of sodium molybdate in the solution.



## THE PARAMETERS OF HYDROGEN EVOLUTION REACTION ON Cu, Au, Pd AND Cu,Au- AND Cu,Pd-ALLOYS

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The cathodic hydrogen evolution reaction (HER) on Ag, Au and Ag,Au-alloys in aqua sulfuric-acid solution proceeds by Volmer-Tafel path [1]. For all examined alloys the stage of  $H_3O^+$  discharge realizes in a barrier-free regime at low overpotentials and turns to usual regime when the overpotential grows. The aim of this work is to reveal the kinetic scheme of cathodic hydrogen evolution on Cu, Au, Pd and their homogeneous Cu, Au- and Cu, Pd-alloys in a wide range of alloy compositions.

The experiments were carried out in 0.5 M  $H_2SO_4$  and 0.05 M  $H_2SO_4$  + 0.45 M  $Na_2SO_4$  bubbled with argon by a method of cyclic voltammetry ( $d\eta/dt = 0.5 \text{ mV s}^{-1}$ ) and by a method of potential transient after the polarization switching off.

It was found that in 0.5 M  $H_2SO_4$  at  $\eta$  from 0 to  $-0.45 \text{ V}$  the potentiodynamic curves of direct and reverse scan coincides for all electrodes under review within the error. Two linear plots appear on voltammograms in semi-logarithmic coordinates. The slope of the first plot ( $b_c$ ) on  $\eta$ ,  $\lg i$ -curves (at low overpotentials) is between 0.059 and 0.071 V for all examined electrodes. Only for Pd and Cu, Pd-alloys with  $X_{Au} \leq 30 \text{ at. \%}$   $b_c$  is equal to 0.030 V. The slope of the second linear plot (in a range of high  $\eta$ ) does not depend on alloy composition in a whole. Its value is 0.100–0.150 V and increases to 0.170 for Pd and Cu, Pd-alloys with high Pd concentration.

At transition to 0.05 M  $H_2SO_4$  the overpotential of HER grows in the range of high  $\eta$ . The values of  $b_c$  remain the same or slightly increase. The latter means that  $H_3O^+$  discharge proceeds in usual regime in that range of overpotentials. The values of overpotential in 1 linear plot does not depend on solution composition for examined metals and alloys which approves the barrier-free discharge. In the whole range of  $\eta$  the HER proceeds by the Folmer-Tafel route.

The influence of Cu, Au- and Cu, Pd-alloys composition was revealed on the overpotential and change-current of the cathodic  $H_3O^+$  reduction. With increase of the concentration of the noble metal in the alloy the overpotential diminishes but the relevant change current grows. This effect is especially noticeable for Pd-containing alloys. Even a little concentration of Au and Pd result in a sharp enhancement of the rate of hydrogen evolution on alloys. However the little amount of Cu in the crystal lattice of Au and Pd weakly influences the kinetic parameters of cathodic hydrogen evolution. The values of pseudo-capacity of atomic hydrogen adsorption and degree of surface coverage correlate with the Folmer-Tafel route.

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## ELECTRON TRANSFER REACTIONS ACROSS A CONDUCTING NANOWIRE/ELECTROLYTE SOLUTION INTERFACE

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Some properties of a charged metal nanowire/electrolyte solution interface as an electrochemical system was broadly addressed for the first time by Leiva et al. [1]. Lemay et al. [2] employed a quantum mechanical theory of electron transfer (ET), in order to describe the influence of specific structure of the density of electronic states of carbon nanotubes on the ET rate. The electrical double layer (EDL) effects on the electroreduction of anions at conducting nanowires (nanotubes) were investigated theoretically in [3]; a quantum-chemical model was developed recently to describe the catalytic hydrogen oxidation on metal nanowires [4]. In spite of these efforts, the modelling of charge transfer across the interface between a charged nanowire (nanotube) and an electrolyte solution is still in its infancy. That is why we extend the approach based on a combination of modern quantum mechanical theories of charge transfer and the EDL models with quantum-chemical calculations [3] to other electrochemical systems.

In this work we explore the reduction of a peroxodisulphate anion at charged conducting cylinders of nano-size in contact with an electrolyte solution. Bond breaking electron transfer is considered in adiabatic limit; current-voltage curves were computed for a plain metal electrode as well, which is chosen as a reference system. It is argued that the EDL effects play a crucial role and entail a significant rise of current density at the nanowires, as compared with a plain metal electrode. The well-known polarization "pit" on the current-voltage dependencies was observed to disappear starting from a certain value of the radius of a nanocylinder.

As a next step we extend our approach to outer-sphere ET processes at low overvoltages considering complex cations  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+/2+}$  and  $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$  as model redox-pairs. Since in this case the EDL does not affect significantly the reaction kinetics, main emphasis was put on estimations of electronic transmission coefficient ( $\kappa_e$ ). In order to investigate the effect of electrode material on the ET rate, we have addressed Cu, Ag, Au and Pt electrodes, which were modeled as slabs and monatomic wires. The electronic structure of metals was described by using periodic DFT calculations. The decreasing of  $\kappa_e$  values for the outer-sphere ET (inhibition effect) was predicted when going from the plane electrodes to the metal nanowires. A possible comparison of the computational results with experimental data is discussed as well.

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# EXPERIMENTAL AND CALCULATION INVESTIGATIONS OF THE SECOND COORDINATION SPHERE INFLUENCE ON THE STANDARD RATE CONSTANTS OF CHARGE TRANSFER FOR THE Nb(V)/Nb(IV) REDOX COUPLE IN CHLORIDE-FLUORIDE MELTS

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The diffusion coefficients ( $D$ ) of Nb(V) and Nb(IV) complexes in chloride-fluoride melts NaCl-KCl (equimolar mixture)-K<sub>2</sub>NbF<sub>7</sub>, KCl-K<sub>2</sub>NbF<sub>7</sub> and CsCl-K<sub>2</sub>NbF<sub>7</sub> were determined by methods of linear sweep voltammetry, chronopotentiometry and chronoamperometry.

The smaller values of  $D$  were obtained when the cation in the second coordination sphere changes from Na to Cs. Logarithms of Nb(V) and Nb(IV) diffusion coefficients linearly depend on reciprocal value of alkali metal radius. Such changes are due to the decrease of the counter-polarizing effect of cations from Na to Cs, resulting in a decrease of metal-ligand bond length. Diffusion coefficients decrease when niobium oxidation state increases while the activation energies for diffusion increase.

The effect of the second coordination sphere on the standard rate constants of charge transfer for the Nb(V)/Nb(IV) redox couple in chloride-fluoride melts was studied. The next row:  $k_s$  (KCl) <  $k_s$  (CsCl) <  $k_s$  (NaCl-KCl) as a function of the composition second coordination sphere was obtained by cyclic voltammetry method.

Under equal conditions the ratio of the standard rate constants of charge transfer is determined by a ratio of the  $E_{act}$  activation energy. For estimation of this ratio the *ab initio* calculations have been carry out in the systems  $nM^{+} \cdot NbF_7^{2-}$  and  $nM^{+} \cdot NbF_7^{2-}$  ( $M = Na, K, Cs$ ;  $n = 1-6$ ). Preliminary the  $E_{act}$  energies of outersphere shell formation for  $nM^{+} \cdot NbF_7^{2-}$  particles were calculated under the formula (for  $nM^{+} \cdot NbF_7^{2-}$  by analogy):

$$E_{act} = E(nM^{+} \cdot NbF_7^{2-}) - E(NbF_7^{2-}) - nE(M^{+}),$$

where structures of particles are specified in brackets. The maximal stability the Nb(V) particles have at  $n = 4$  and the Nb(IV) particles - at  $n = 5$ . In conditions of electrochemical experiment charge transfer is carried out close by equilibrium when the value of Gibbs energy of electron transfer reaction ( $\Delta G_r$ ) is approximately equal to zero. In result general Marcus formula becomes simpler:

$$E_{act} = (E_r + \Delta G_r)^2 / 4E_r \approx E_r/4.$$

The value of reorganization energy  $E_r$  was calculated in this case as a difference full energies an initial  $nM^{+} \cdot NbF_7^{2-}$  particle in equilibrium geometry of a final  $nM^{+} \cdot Nb(IV)F_7^{2-}$  particle and in its own equilibrium geometry. It was found for the most stable  $nM^{+} \cdot NbF_7^{2-}$  particles ( $n = 4$ ) the  $E_{act}$  values increase in series Na < Cs < K, that corresponds to a ratio of experimental standard rate constants of charge transfer.

The study was supported by Russian Foundation for Basic Research (project # 08-03-00397-a).

# EXCHANGE KINETICS AND DIFFUSION OF OXYGEN IN OXIDES $\text{LaMnO}_{3+x}$ AND $\text{LaCoO}_{3-x}$

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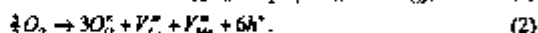
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Processes of oxygen exchange play an important role in work of electrochemical devices, in which materials based on  $\text{LaMnO}_{3+x}$  и  $\text{LaCoO}_{3-x}$  can be used as electrode materials, membranes (solid oxide fuel cells, electrolyzers, electrochemical gas sensors, reformers, etc.).

In this work exchange kinetics and diffusion of oxygen are studied using isotope exchange method with gas phase analysis. The detailed description of experimental setup and technique see in [1]. Klier and Kucera model [2] is used for experimental data treatment.

Oxides  $\text{LaMnO}_{3+x}$  и  $\text{LaCoO}_{3-x}$  have been prepared using ceramic and citric-nitrate techniques consequently. According to X-Ray powder diffraction analysis (Rigaku-diffractometer D-MAX 2200V,  $\text{CuK}\alpha$ -radiation on air at room temperature) the samples have no any reflexes corresponding to impurities.

The difference of defect structure between  $\text{LaMnO}_{3+x}$  and  $\text{LaCoO}_{3-x}$  is caused an interest to study exchange kinetics and diffusion of oxygen at the temperature range 600–850°C and oxygen pressure  $(1.33\text{--}93.3)\times 10^2$  Pa. Under the experimental conditions defect structure of these oxides is described with different models. For cobaltite [3] oxygen nonstoichiometry as a function of temperature and oxygen pressure is described with the model of free or localized electron carriers in B-sublattice (1). In case of  $\text{LaMnO}_{3+x}$  [4] defect structure is described with the model of Shonki defects formation in La- and Mn-sublattices, according to (2), which can explain the reason of the oxygen "excess" existence in comparison with stoichiometric composition ( $\text{LaMnO}_{3+x}$ ) in investigated temperature and oxygen pressure range.



In the present work values of interphase exchange rate and diffusion coefficient of oxygen for  $\text{LaMnO}_{3+x}$  is shown to be considerably lower than in case of  $\text{LaCoO}_{3-x}$ , which has oxygen content close to 3 but less than 3 in investigated range of temperatures and oxygen pressures [3] in comparison with lanthanum manganite, which has "excess" of oxygen [4].

Values of effective activation energy of exchange and diffusion of oxygen have been calculated. Oxygen pressure dependence of interphase exchange rate has power function type. Contributions of three exchange types have been estimated (the detailed description see in [3]). The first exchange type is found to predominate in case of  $\text{LaMnO}_{3+x}$ . The type goes without participation of oxygen from solid oxide surface, whereas in  $\text{LaCoO}_{3-x}$  the both second and third exchange types have significant contribution with increase of temperature.

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## SYNTHESIS OF NANOPARTICLES IN REVERSE MICELLE SYSTEMS

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The purpose of this work was to obtain and identify nanoparticles.

Platinum nanoparticles were obtained using a radiochemical method in reverse micelle systems. The source of ionization radiation was a  $\gamma$ -<sup>60</sup>Co setup. These systems represent micelles formed on the basis of surfactants (sodium bis(2-ethylhexyl)sulfosuccinate, AOT) in isooctane containing a solubilized aqueous platinum salt solution. The advantage of this method as compared to other methods is the possibility of varying the size of stable nanoparticles providing a minimum size distribution. This possibility is implemented by selecting the value of the molar ratio of water and AOT. Their variation allows changing the size of micelles and, correspondingly, the size of the obtained nanoparticles. The high particle stability is due to the fact that the shell of AOT molecules protects them from aggregation.

Different methods of analysis were used to confirm formation of the nanoparticles, their characterization and control: UV-VIS spectrophotometry, atomic-force microscopy (AFM), and also adsorption and catalytic studies.

One of the most important tasks is development of the procedure of applying a micelle solution on the surface of mica support for AFM studies of nanoparticles. The difficulties appearing here result mainly from adsorption of micelles with nanoparticles on the surface. Due to the low adsorption value, the micelles can hardly be retained on mica in the course of its surface rinsing, which renders the performed studies nearly impossible.

Optical absorption spectra of the studied nanoparticles in reverse micelle solutions were studied in advance using the method of optical spectrophotometry. Their adsorption properties were investigated on different supports: carbons,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (trefoil), SiO<sub>2</sub>.

This work presents the results of studying micelles and nanoparticles using an atomic force microscope. The obtained results evidence that this method of synthesis allows obtaining nanoparticles with the minimum size of 0.6 nm (with the mean diameter of 1.1 nm) to 10 nm. Nanoparticles are stable for many months and feature high catalytic activity. Thus, the method of synthesis of nanoparticles can be considered promising and requires further studies.

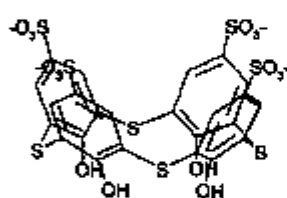
# RED-OX-SWITCHABLE SYSTEMS BASED ON CALIX[4]ARENES, IONS AND TRANSITION METAL COMPLEXES

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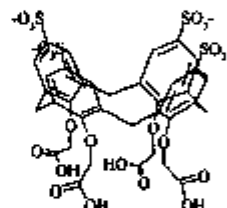
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In recent decades, supramolecular systems containing redox-active blocks have attracted considerable attention of researchers from the viewpoint of constructing molecular devices and machines, systems with switchable properties such as colour and luminescence. Action of such a systems is based on reversible redox-switchable binding of components of supramolecular system in which electron transfer gives rise to reversible molecular motion.

It has been exemplified by means of cyclic voltammetry that ions  $[M(bipy)_3]^{3+/2+}$  ( $M = Co, Fe, Ru, Cr$ ) bind to *p*-sulfonatothiacalix[4]arene (TCAS) and carboxylic calix[4]arene (CCAS) in aqueous solutions at various pH values through the sulfonate groups of the upper rim. The oxidized forms bind stronger than reduced ones which is understandable taking into consideration electrostatic character of interaction.



TCAS



CCAS

It has been shown that electrochemical reduction of  $Fe(III)$  coordinated via lower phenolate rim in the system  $TCAS + Fe^{3+}$  in aqueous and water-DMSO solutions triggers fast dissociation of the complex. Subsequent oxidation brings back the initial state of the complex. This system is an example of redox-switchable binding.

Single-electron reduction in the system  $TCAS + Fe^{3+} + bipy$  (pH 2.5) results in metallocentre transition from the lower rim ( $Fe(III)$ ) to the upper one ( $[Fe(bipy)_3]^{2+}$ ). Backward transition is impossible due to mediator oxidation of TCAS. In the system  $CCAS + Fe^{3+} + bipy$  (pH 1.7), reversible redox-switchable binding of complex ion  $[Fe(bipy)_3]^{2+}$  through the upper rim occurs upon single-electron transfer, whereas in the system  $[Co(bipy)_3]^{3+} + CCAS + Fe^{3+}$  two-electron reduction results in reversible swapping of  $[Co(bipy)_3]^{3+}$  with  $[Fe(bipy)_3]^{2+}$  through the tetrasulfonated rim of CCAS. In all of the investigated systems redox-switchable binding is accompanied with synchronized colour switching.

This work was supported by Russian Foundation for Basic Research (projects # 07-03-91560 and 10-03-00207).

**MASS TRANSFER UNDER NATURAL CONVECTION OF SOLUTION  
IN THE ELECTROLYTIC CELL WITH HORIZONTAL ELECTRODES****Origina V.M.<sup>1</sup>, Reznikova L.A.<sup>2</sup>, Davydov A.D.<sup>2</sup>**<sup>1</sup>*Tula State University, Tula, Russia*<sup>2</sup>*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry,  
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The work is devoted to the numerical simulation of mass transfer under natural convection of electrolyte solution containing three types of ions in the axisymmetric electrochemical cell with horizontal disk electrodes, on which the redox electrochemical reaction proceeds. The results are compared with the experimental data obtained earlier [1].

The mathematic model of the process involved the Navier-Stokes equations in the Boussinesq approximation, the equations of ionic transfer of electrolyte components, which is caused by diffusion, convection, and migration, and the electroneutrality condition. The kinetics of redox electrochemical reaction was taken into consideration by using the Butler-Volmer equation. Due to the axial symmetry of the cell, it was assumed that the distributions of all dependent variables (concentrations of ions, electric potential, hydrodynamic velocity, and pressure) are axisymmetric.

The numerical solution of the system of differential equations reduced to the dimensionless form was performed by the method of finite elements with a nonuniform grid. As a result, the time dependences of (1) the current at a constant imposed voltage and (2) the voltage at a given current were determined.

Using the numerical simulation, for the triiodide reduction in KI and I<sub>2</sub> aqueous solution, the dependences of the distributions of ion concentrations, electric potential, solution density, local and average mass-transfer rates on the concentrations of electroactive ion and supporting electrolyte, the interelectrode distance, and imposed voltage (current) were studied. It was found that the calculated results agree well with the experimental data obtained earlier [1]. In particular, the numerical solution also shows that the current passing through the cell monotonically decreases even upon reaching the linear distribution of concentrations in the stagnant solution. The simulated results enabled us to explain this effect by the natural convection of solution in the peripheral part of the cell; as a result, an average concentration of electroactive ion in the interelectrode space decreases.

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# GASEOUS 3D-NUCLEATION IN KINETICS OF HYDROGEN EVOLUTION REACTION

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In the course of cathodic reduction of  $H_3O^+$  the bubbles of hydrogen arise at electrode surface. The aim of this work is to reveal the effect of gaseous 3D-nucleation in kinetics of hydrogen evolution reaction on Cu, Ag, Au, Ni, Pd and Pt by method of potentiostatic chronoammetry. The experiments were carried out at 298 K in argon deaerated solutions of (0.5–X) M  $H_2SO_4$  + X M  $Na_2SO_4$  prepared with bidistillate. To realize the quasi-equilibrium hydrogen electrode on transition metals we applied the cathodic pre-polarization by special method for each electrode and saturated the solution with purified hydrogen.

In overpotential range  $\eta$  from  $-0.05$  to  $-0.7$  V the chronoammograms of  $H_3O^+$  cathodic reduction are obtained. As overpotential increases to certain  $\eta_{max}$  so the current maximum arises on  $i,t$ -curves. With growth of  $\eta$  the maximal amplitude of current increases and the peak shifts to less moments of time. The value of  $\eta_{max}$  depends on the metal nature and solution compound (table)

X, M	$\eta_{max}$ , V					
	Cu	Ag	Au	Ni	Pd	Pt
0.00	-0.15	-0.15	-0.25	-0.09	-0.10	-0.11
0.05	-0.15	-0.15	-0.25	-0.09	-0.10	-0.11
0.10	-0.17	-0.17	-0.30	-0.09	-0.10	-0.11
0.15	-0.21	-0.23	-0.35	-0.09	-0.10	-0.13
0.20	-0.23	-0.27	-0.40	-0.09	-0.10	-0.15
0.25	-0.27	-0.33	-0.45	-0.10	-0.11	-0.17
0.30	-0.29	-0.35	-0.50	-0.11	-0.12	-0.19
0.35	-0.35	-0.39	-0.55	-0.11	-0.12	-0.21
0.40	-0.39	-0.43	-0.60	-0.11	-0.12	-0.25
0.45	-0.45	-0.50	-0.65	-0.11	-0.14	-0.29

It was shown, that the appearance of maximum on chronoammograms at  $\eta > \eta_{max}$  is connected presumably with nucleation of hydrogen at the electrode surface, but not with the change of surface coverage by atomic hydrogen. The analyses of  $i,t$ -curves (by the method described in [1]) was performed with different models of 3D-nucleation. It was found that latent nucleation centers are activated instantly, and the process proceeds in a initial-diffusion regime ( $j \sim t^{1/2}$ ), which is caused by surface diffusion of atomic hydrogen. Inclusion to the solution of surface-active organic substances increases  $\eta_{max}$  but does not affect the regularities of nucleation. So the scheme of HER process on transition metals must be added with stages of formation and growth of phase  $H_2$ .

This work is supported by Russian Foundation for Basic Research (project # 08-03-00194) and FCFR "Scientific and scientific-pedagogical personnel of innovating Russia" (state contract P2572)

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## THIN LAYER ELECTROLYTIC METAL SULFIDE-GRAPHITE COMPOSITES IN THE MODEL OF LITHIUM SECONDARY BATTERY

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Me-sulfides (Me – Fe, Mo, Ni, Co), produced in thin layers on the aluminum cathode from the solutions, containing Me-sulfate and thiosulfate-ions, are suitable for the positive electrodes of low temperature lithium accumulators [1, 2]. The possibility to use electrolytic Co, Ni-sulfides deposited on a stainless steel in the negative electrodes of lithium-ion batteries is also shown [3]. The two-Volt lithium-ion system is offered with the electrolytic iron sulfide and LiCoO<sub>2</sub> as negative and positive electrodes, correspondingly [4]. The discharge capacity of such model system achieves 350–400 mAh/g Fe-sulfides.

In the last case use of Me-sulfide material is limited by the tendency to decline its discharge capacity at cycling as the result of deposit adhesion relaxation to a substrate. Technology of Me-sulfide/graphite composite synthesis as a thin layer compact precipitations is elaborated for the increased stability of the exchange capacity of Me-sulfide composition at the more effective its use in the negative electrodes of lithium-ion system. Addition of the dispersion phase of graphite and lauryl sulfate in the electrolyte for Me-sulfide synthesis by the method [5] solves the problem. The varieties of the natural Chinese graphite and the modified natural graphite of the Superior Graphite production, synthetic graphite, as well as EUZ M trade-mark graphites were used with a different size of particles for the codeposition with Me-sulfide.

The positive effect of the synthesized composite is achieved due to a certain increase of electrode material conductivity that is provided by graphite dispersion phase, and by the even of its distribution within the deposit volume ranging from 1 up to 20 %, as well as the increase of deposit adhesion up to a metal substrate.

We have studied electrolytic iron sulfide-graphite composites as a promised electrode material for lithium secondary batteries. Iron sulfide-graphite composites with the mass of 1–20 mg/cm<sup>2</sup> produced on a stainless steel by the cathode reduction of the solutions comprising FeSO<sub>4</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and graphite in the models of lithium chemical power sources with (EC, DMC, LiClO<sub>4</sub>) electrolytes can be electrochemically transformed with the efficiency of 500 mAh/g during more than 80 cycles within the 2.8–0.01 voltage range. Graphite admixture in the composite structure promotes increasing the discharge rate of electrode process. Structure and morphology of the synthesized composites were examined.

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## PREPARATION OF THIN LAYERS OF THE PALLADIUM ON VANADIUM AND NIOBIUM FOR HYDROGEN PURIFICATION

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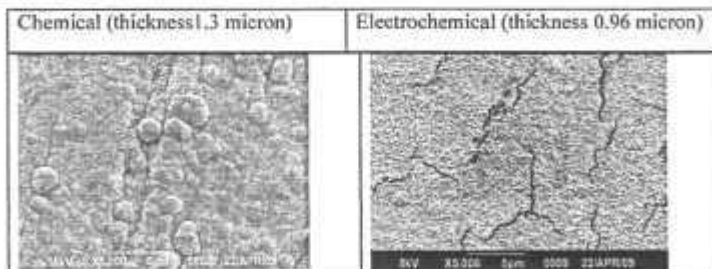
It is known that thin palladium membranes with high selectivity and permeability to hydrogen are widely used for extraction high purity from gas mixture [1]. However, an application of these membranes is limited by their high cost. At the same time, in metals of vanadium subgroup of (V, Nb, Ta) solubility and permeability of hydrogen is high enough. Therefore, the purpose of the present work was to receive thin strong and continuous coverings of a palladium on vanadium and niobium by electrochemical deposition and chemical sedimentation. Since the surface of these metals is strongly oxidised, the role of surface preparation is very important. Vanadium and niobium electrodes are degreased, then pickled in a mixture of fluoric, nitric and dairy acids.

For electrochemical plating of palladium monoethanolamine and glycine-chloride electrolytes were used.

Thickness of covering was measured by gravimetry, determining the weight of the plated metal. Calculations were made according to formula  $d = m/Sx$ , where  $d$  – is a thickness of a covering,  $S$  – the electrode area,  $x$  – weight of a covering with the thickness of 1 micron of surface per unit of surface (for a palladium it is 1.2 mg/cm<sup>2</sup>).

Samples of niobium and vanadium with a palladium deposition of a various thickness have been received and the area of an active surface of palladium was calculated by cyclic voltammetry. According to the size of areas under adsorption and desorption peaks of hydrogen, received at different scan rates the quantity of electricity  $Q$  ( $\mu$ C) spent on formation of a monolayer of hydrogen on a palladium surface. The area of the active surface of palladium was calculated with formula  $S = Q/420$ .

The samples prepared on niobium and vanadium have been examined by means of scanning electron microscopy. It appeared that electrochemical depositions contain microcracks, while chemical ones were absolutely continuous. Therefore, for preparation of pore-free continuous depositions of a palladium on vanadium and niobium for hydrogen purification the chemical method of sedimentation has been recommended.



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## HIGH PERFORMANCE SUPERCAPACITORS WITH NONAQUEOUS ELECTROLYTES

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Electrochemical capacitor (supercapacitor) is a secondary power source, which occupies an intermediate position having specific power and energy in range between batteries and aluminum oxide-electrolytic capacitors [1]. Accumulation of energy in supercapacitors is the result of charging the electric double layer, which capacitance depends on the surface area of the electrodes. Therefore, the use of electrode materials (such as activated carbon, carbon aerogels, carbon nanotubes) with high specific surface area (up to 3000 m<sup>2</sup>/g) allows to create cells with an electric capacity of up to several thousands farad.

The report presents the results of studies of composite electrode materials for supercapacitors based on activated carbons of different nature, carbon multi-walled ("Taunil") and single-walled nanotubes. Dependence of specific capacitance and equivalent series resistance of the supercapacitor on the ratio of micro-/mesopores in active carbons is presented. Established specific capacitance and electrical resistance of the composite electrode material based on nanostructured carbon material, an electrically conductive filler and polymeric binder, deposited on a metallic current lead.

The original techniques for synthesis of high-purity components of traditional non-aqueous electrolyte (tetraethylammonium tetrafluoroborat, metiltrietilammoniya tetrafluoroborat) and fundamentally new - ionic liquid (1-methyl-3-etilimidazoliya tetrafluoroborat, N, N-diethyl-N-(2-butoksietil)-N-metilammoniya triflate, N-(2-Metoksetil)-N-metil-pyrrolidine tetrafluoroborat, N-(2-etoksietil)-N-metilpiperidine tetrafluoroborat) are worked out. Using non-aqueous electrolytes based on ionic liquids has increased the specific capacitance of nanostructured carbon material up to 85 F/g and reduced equivalent series resistance of the supercapacitor by 30 %. Investigation of electrochemical stability of nonaqueous electrolytes based on ionic liquids showed their stability in range of  $\pm 3$  V. On the basis of composite nanostructured carbon material and non-aqueous electrolyte containing ionic liquid developed roll designed 5-100F supercapacitor with equivalent series resistance 10-100 mOhm and leakage 20-300  $\mu$ A. The higher solubility of ionic liquids provides the supercapacitors work at -45 °C with an increase of equivalent series resistance in 1.7 times and reducing capacity by 10 %.

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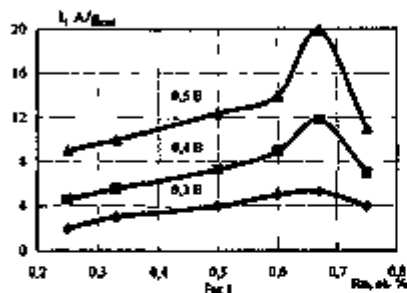
## DEVELOPMENT OF NON-PLATINUM ANODE CATALYSTS FOR ALKALINE DIRECT ALCOHOL FUEL CELLS

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Alkaline direct alcohol fuel cells are developed as reserve energy supply and power sources for mobile applications (portable electric vehicles, mobile telephone and laptop). The advantage of using alkaline media in fuel cell is the potential use of non-Pt catalysts in the electrodes. Requirements of low cost, high activity, acceptable stability are imposed on catalysts.

The catalysts should provide high fuel utilization.



A series of RuNi/C catalysts was synthesized at 400–450 °C by reduction in hydrogen atmosphere of respective salts adsorbed on carbon support [1, 2].

Specific surface area of catalysts was determined by CO stripping voltammetry. Chemical composition and crystallographic structure of catalysts was studied by XRD method. X-ray photoelectron spectroscopy (XPS) was used to identify composition of the outer layer. Cyclic voltammetry and chronopotentiometric measurements were

applied to evaluate stability of the catalysts. Model experiments were carried out in 2 M KOH + 1 M alcohol at 40 °C using rotating disk electrode. Activity of RuNi/C catalysts in ethanol, propanol-2, ethylene glycol and glycerol electrochemical oxidation was determined by cyclic voltammetry. According to these studies, the oxidation rates of these alcohols at RuNi/C catalysts could be arranged in the following sequence: propanol-2 > ethanol > ethylene glycol > glycerol. The respective values of the open circuit potential are 0.56, 0.105, 0.190 and 0.225 V versus HRE.

Membrane electrode assemblies comprising RuNi/C catalyst in anode and CoNi/C catalyst in cathode were tested using 3 M KOH+2 M EtOH feed to reveal the performance and long-time durability of catalysts.

The RuNi/C catalysts were optimized by adjustment of duration and temperature of the treatment, Ru:Ni atomic ratio and type of carbon support. The catalyst 20 wt. % RuNi (2:1 at.)/Ketjenblack EC-600 JD was proved to be the most active and stable in the ethanol electrooxidation process.

The dependence of ethanol oxidation current on composition of the (Ru-Ni) catalyst is shown in fig.1. The EtOH oxidation current value, normalized per unit mass of the catalyst, is plotted on the Y-axis. Current readings were measured at fixed potentials 0.3 V, 0.4 V, and 0.5 V (HRE).

The work was supported by the Federal Agency on Science and Innovations (Rosnauka), State contract № 02 740.11.0264 on 07.2009

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## THE ELECTRODEPOSITION OF $\text{CuInSe}_2$ , $\text{CuInGaSe}_2$ THIN FILMS FOR SOLAR CELLS

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The development of a low-cost thin film solar cell device has attracted research interest during past decades. Most successful cells are based on absorber thin film semiconductor material  $\text{CuInSe}_2$ ,  $\text{CuInGaSe}_2$ . The electrodeposition is more simple and reliable method, which allow to decrease cost of cell production compared with other methods.

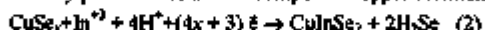
The electrochemical reactions for electrodeposition of three or four components in one study defines the stoichiometry of deposited compound. Therefore it is need to investigate the electrochemical reactions on electrode for separate ions  $\text{Cu(II)}$ ,  $\text{Se(IV)}$ ,  $\text{In(III)}$ ,  $\text{Ga(III)}$  and for it's simultaneous reduction with possible chemical reactions near electrode surface.

In report the results of investigation of  $\text{CuInSe}_2$  and  $\text{CuInGa}_{1-x}\text{Se}_2$  electrodeposition are presented for different electrolytes (sulfur, sulfamic, sulfosalicylic acids, Na citrate, K biphthalat) on different electrodes. The stationary disk electrodes have been used (glass-carbon, molybdenum, copper) for investigation of reduction process by cyclic voltamperometry method. The method of X-ray phase analysis, method of electronic probe and method of atomic force microscopy have been used for confirmation of structure and composition of deposits.

It was showed that first stage was the electrodeposition of copper followed by formation of copper film on surface of all studied electrodes. After this the simultaneous reduction of copper and selenium ions has been observed with formation of intermediate double compound on equation:



$\text{In(III)}$  ions is able to reduction only for high negative potentials, for instance  $-950\text{mV}$  ( $\text{Ag/AgCl}$ ) in  $0.1\text{M}$  sodium citrate.  $\text{Ga(III)}$  ions don't reduction to region of hydrogen evolution in acid electrolytes. However the formation of  $\text{CuInSe}_2$  deposits at potentials  $-300\text{ mV}$  has been founded. It was confirmed that the reduction of indium ions was realized by UPD mechanism on electrode surface, covered by precursor of double compound copper-selenium.



The chemical reactions of selenide ions and indium ions also have importance for formation of triple compound on electrode surface. Therefore the stoichiometric composition of deposit connects with ratio of ions concentration in electrolyte.

The electrodeposition of four component compound is carried out in conditions of concurrent reduction of ions of indium and gallium presents in electrolyte.

The composite of compound electrodeposited at constant potential dependences from concentration of ions. For high concentration of gallium ions the full connection of selenide-ions was reach for formation of compound  $\text{CuIn}_{0.9}\text{Ga}_{0.1}\text{Se}_2$ . The size of particle was  $50\text{--}100\text{nm}$ .

**ELECTROCATALYTIC LAYERS FOR SOLID-POLYMER FUEL CELLS****Dobrovolsky Yu.A.***Institute of Problems of Chemical Physics,  
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The work on the research and development of low temperature fuel cells is actively expanding nowadays. The success in implementation of fuel cells can be reached only after eliminating shortcomings, such as high cost, short life-span, and high requirements for purity of used fuel. These drawbacks can be eliminated partially by using new types of catalysts.

It is known from the research that one of the ways to eliminate these drawbacks is to use more stable supporting material instead of carbon that is used as a catalyst support in the modern catalysts.

Results of experimental work on replacement of carbon black as a support by carbon nanotubes, semiconducting highly doped oxides ( $\text{SnO}_2$ ,  $\text{WO}_3$ ,  $\text{TiO}_2$ ) and proton conductors on the basis of tungsten bronzes and heteropolycompounds have been discussed in this report.

It was shown that stability and catalytic activity of platinum clusters depend to a considerable degree on surface treating of nanostructured carbon.

Method that allows obtaining catalytic active layer from platinized nanofibers directly on the surface of gas diffusion layers was suggested.

Accelerating effect of oxide supports on electrocatalytic properties of platinum in oxidation reactions of hydrogen and alcohols was studied. Possible mechanism of this effect was discussed.

Influence of electronic and protonic conductivity of platinized supports (electronic and proton conductors) on the efficiency of electrocatalytic layers functioning was studied.

## ELECTROCHEMICAL PROPERTIES OF Ni-Pd ELECTROPLATINGS AT EVOLUTION OF HYDROGEN AND OXYGEN IN ACID AND ALKALINE ENVIRONMENTS

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There are actually important based on the technical-economical analysis questions of creation of highly effective bipolar electrodes, electrode-diaphragm blocks with zero-gap for alkaline electrolyzes, and from there are questions of replacement of expensive oxygen Pt-Ir electrode and the cathode with the platinum electrocatalyst for membrane electrolyzes.

The work purpose was plating and investigation of electrocatalytical and hydrogen sorption properties of galvanic Ni-Pd coverings on various substrates. The Ni-Pd coverings were obtained from ammonium-chloride and ammonium-sulfuric-chloride electrolytes.

The charging curves were obtained for these coverings on various substrates. The initial section of charging curves corresponding to  $\beta$ -phase of palladium hydride was practically linear. The dim peak desorption of hydrogen was observed at potential to be more positive 0.2 V and the area of peak was much more for porous substrates than that area to be for smooth nickel. The smooth of peaks, most possibly, was caused by the alloy formation of nickel with palladium and the saturation of Ni-Pd covering by hydrogen together with possible formation of new phases. The horizontal platform of charging curves for the Ni-Pd covering on smooth and porous nickel was observed at range of potentials from 0.8 to 1.35 V as well as the platform for palladium electrodes that corresponded to so-called  $\beta$ - $\alpha$  transition, i.e. transformation of the rich hydrogen phase ( $\beta$ -phase) in phase impoverished by hydrogen ( $\alpha$ -phase). However, the horizontal section in charging curve for the Ni-Pd alloy covering on smooth and porous nickel was displaced in the area of positive potentials on 0.7 V, and the horizontal section for this alloy on the porous titan was transposed more than on 1 V in comparison with the horizontal section in charging curve for palladium covering. Maximal limiting currents were reached at rate of potential to be more 0.05 V/s.

It was established, that the Ni-Pd coverings plated on porous titanic substrates and thermoprocessed in air at temperature 500 °C possessed raised electrocatalytical activity in evolution of hydrogen, oxygen, direct anode conversion of ethanol in alkaline media, corrosion resistance in nitrate, fluoride, chloride media at temperature 80 °C. Using the XRD method, scanning electronic microscopy with chemical energydisperse analysis, chemical etching it was established, that uniform volume distribution of Ni-Pd covering in porous structure of titanic substrate had been result of thermodiffusion processes.

The palladium and nickel has close electronic structure and the different sizes of atoms. Taking into account that energy of activation to increase at accretion of lattice sizes, it is possible to expect increase of exchange current with magnifying of the maintenance of nickel in alloy.

Thus, the analogy in behavior of adsorbed and dissolved in Ni-Pd covering hydrogen as well as the hydrogen in palladium coverings and the hydrogen adsorbed on platinum surface was observed that testified to similarity high electrocatalytical properties of these materials in evolution reaction of hydrogen.

## DEPENDENCE OF ENERGY AND POWER PERFORMANCES OF LITHIUM-IONIC BATTERY ON MACROSTRUCTURE PARAMETERS OF ELECTRODE MATERIALS AND ELECTRODES

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The requirements to electrode materials and electrodes for batteries of energetic and power types are significantly distinguished. Energy density as the most important parameter of energetic type lithium-ionic battery (LIB) operating at low and moderate charging and discharging rate ( $I < I_{C_{50\%}}$ ) depends in the biggest degree on specific capacity of electrode materials, potential difference of positive and negative electrodes and contribution of these materials to battery weight and volume. At the same time, electrode materials and electrodes for energetic type LIB have to make sure first of all the high specific power of battery, i.e. have high rate possibilities to a considerable extent depending on electronic and ionic conductance. Ohmic and diffusion parameters of electrodes are defined by the composition of electrode layer (type and relation of active material, binding agent and electroconductive additive), macrostructure parameters of electrode materials and electrodes of them (particle size and form, thickness, electrode layer density).

In this contribution, the influence of macrostructure parameters of both electrodes and their active materials on energetic and power parameters of battery was studied by experiment. As active material of negative electrode, carbon materials based on natural graphite with particles of scaly and spherical shape were used and cathodic materials are  $\text{LiCoO}_2$ ,  $\text{LiNi}_{1/3}\text{Co}_{2/3}\text{O}_2$  and  $\text{LiFePO}_4$ .

Electrodes from above-mentioned materials of various macrostructure were tested in half-cells with lithium counter electrode and in prismatic batteries with 1 M  $\text{LiPF}_6$  solutions in equivolume mixture of ethylene carbonate, dimethyl carbonate and ethylmethyl carbonate as electrolyte. The procedures on assembling of half-cells and batteries were fulfilled in glove box in the atmosphere of dry argon. The measurements of their electric parameters were performed by galvanostatic method with using automated test setup. Macrostructure of electrode materials and electrodes were studied by SEM method.

It was shown the advantage carbon material with spherical particles in terms of rate parameters in comparison with material with scaly particles. Spherical particles permit to form electrode layer equiavailable for electrolyte at optimal density. The influence of particle form and electrode layer density is enhanced when increase of electrode layer thickness.

On the basis of obtained experimental data, the main parameters of LIB under study, namely, Ragone diagram for batteries with electrodes of various composition, thickness and density were calculated. Diagram analysis permits to optimize the parameters of electrodes for different conditions of battery operation.



# NONSTATIONARITIES AND FLUCTUATIONS OF HYDROGEN FUEL CELL ELECTRICAL REGIME AND ITS DIAGNOSTIC FEATURES

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Proton Exchange Membrane Fuel Cell (PEMFC) is modern high-performance electrochemical source of electric energy. Stability and efficiency of PEMFC operation depend on a large set of parameters such as pressure, moisture of supplied gases, fuel cell (FC) temperature, electrical operating conditions, etc., as well as substantially depends on the current status of membrane-electrode assembly and gas-transport channels. All these factors have also a significant influence on efficiency of energy conversion and consistency of operation. Therefore, nowadays in modern hydrogen energetics based on fuel cell technology one of the main problems is development of reliable, non-destructive, on-stream methods for fuel cell diagnostics. In frame of this project the information capabilities of electrical noise was offered to use like basis for the appropriate diagnostic systems. The fact that noise measurement does not implied electrochemical system disturbance by any external probing signal is the important features of noise diagnostic methods.

The method of fuel cell electrical noise diagnostic was proposed for identification of relations between noise characteristics and membrane-electrode assembly current status alterations. Essence of the method is as follows. During long time period FC electrical noise measurement is carried out without perturbation of FC operational regime. Periodically noise measurements are interrupted and frequency characteristics of FC impedance are measured. FC impedance characteristics are used for identification of parameters of four FC electrical model elements: double layer capacity  $C$ , Warburg elements  $Z_w$ , membrane resistance  $R_m$  and electrochemical reaction resistance  $r_e$ . On the basis of frequency identification electrical model elements parameters trend and electrical noise statistical parameters (spectrum, wavelet, correlation, probability distribution function) trend are observed. Comparison of these two trends allows to search out diagnostic properties of electrical noise. While arrangement of the corresponding regression dependences will allow to express quantitative diagnostic interdependence.

Hydrogen PEMFC fluctuations characteristics was estimated by experimental studies results. Analysis of experimental data showed that fluctuations behavior is appreciably determined by fuel cell operation parameters.

Relations between fuel cell electrical fluctuations and parameters which characterized FC technical state was shown in this work. Obtained results allow to predicate that electrical noise has diagnostic capabilities which is necessary for development of fuel cell technical diagnostics system.

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**DEVELOPMENT OF FUEL CELLS AND ELECTROLYZERS WITH PEM IN RUSSIAN RESEARCH CENTER "KURCHATOV INSTITUTE"****V.N. Fateev***RRC "Kurchatov Institute", Moscow, Russia*

Fuel cells and electrolyzers are the key components of hydrogen energy for long term perspective. PEM systems are considered to be one of the most perspective for solution of large series of tasks (creation of hydrogen infrastructure, transport, backup power and so on). Large attention is paid to these systems in the frame of Federal Agency on Science and Innovations (Rosnauka) projects. It is necessary to underline that the level of developments is very high and business organizations are participating in their further development and commercialization.

In the frame of Federal Target Scientific Technical Program RRC "Kurchatov Institute" in cooperation with CNISET, MPEI, and others was developing a pilot plant with PEM fuel cell with power 10 kW. It was developed original materials and technology that solves the basic problem of creating a domestic PEM fuel cells. In particular, developed new nanostructured electrocatalysts with reduced consumption of platinum, modified membrane with high thermal stability and other key materials, developed a new plasmachemical fuel converter for hydrogen production from gas and liquid hydrocarbons. In the course of the work was created significant scientific and technical and technological basis needed to create prototypes of plants with PEM fuel cells allowing to enter the serial production of such power plants and commercial use.

Goals of the project are:

- creation and experimental-industrial use of PEM power plants with power 3–100 kW for stationary application;
- creation of experimental-industrial unit for production and tests of experimental-industrial PEM fuel cell power plants (10 units per year).

Together with development of fuel cells projects on high efficient PEM electrolyzers for hydrogen energy (creation of hydrogen infrastructure) are carried out. Such electrolyzers produce hydrogen of high purity (99.99 %) at pressure up to 130 bars without additional compression. The project is carried by RRC "Kurchatov Institute" together with Plant "Red Star", MPEI and etc.

The project has enabled the creation of technologies for the main components of new generation of electrolyzers: nanostructural not platinum electrocatalysts and mixed oxide electrocatalysts with reduced platinum metals loading and increased life time, membrane with low gas permeability, bipolar plates and current collectors with protective coatings. The pilot installation of 10 nm<sup>3</sup> of hydrogen per hour and has successfully passed the preliminary tests.

**ANODE NANOSTRUCTURE CATALYSTS ON THE BASIS OF ORGANO-METALLIC CLUSTERS FOR LOW-TEMPERATURE FUEL CELLS****Grinberg V.A.<sup>1</sup>, Mayorova N.A.<sup>1</sup>, Pasyanski A.A.<sup>2</sup>**

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Development of fuel cells, operating on the basis of alcohols direct oxidation without external reforming and borohydrides direct oxidation, looks especially attractive because of significant simplification of their design which is one of crucial factors in the production of effective power sources for portable devices. Both ethanol and sodium borohydride have high specific energy density – 8.1 kWh/kg at 1.14 V and 9.3 kWh/kg at 1.64 V. Besides, ethanol is very perspective and interesting as a renewable fuel which can be produced in abundance from biomass.

In the present work we suggest a new approach to the synthesis of electrocatalysts on the basis of individual heterometallic clusters of prescribed composition, which were subjected to thermal destruction at highly dispersed carbonaceous carriers at temperatures 250–500 °C. The distinguishing feature of these catalysts is their good reproducibility with respect to composition, as well as uniformity of the catalyst distribution over carrier, which results in stability and reproducibility of the catalyst's characteristics [1, 2].

Binetallic platinum-tin catalyst (Pt:Sn atomic ratio in surface layer 2:1) and fluor-containing nickel-ruthenium catalyst were synthesized by depositing on highly dispersed carbon black from clusters of the corresponding metals. These catalysts (gross formulae are  $\text{Pt}_2\text{Sn}$  and  $\text{Ni}_{12}\text{RuF}_3$  correspondingly) were characterized by X-ray diffraction and electron-dispersion analyses (EDAX), laser mass-spectrometry (LSM) and transmission electron microscopy (TEM). The mean size of these catalyst's particles was in the range 1–12 nm. According to voltammetry data, specific characteristics of the synthesized catalysts  $\text{Pt}_2\text{Sn}$  (in the reaction of ethanol oxidation) and  $\text{Ni}_{12}\text{RuF}_3$  (in the reaction of sodium borohydride oxidation) are superior to those of the platinum-tin and nickel-ruthenium catalysts described in literature.

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# USE THE ELECTROCHEMICAL NOISE METHOD FOR STUDY AND DIAGNOSTICS OF LITHIUM POWER SOURCES

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It is designed and introduced in laboratory practice suitable and available methods of investigations of nonequilibrium electrochemical noise (potential and voltage fluctuations), which the main reason of the origin are actively-passive transformation of Li electrode surfaces in electrochemical influence [1]. For studies is used as import equipment (Solartron Electrochemical Interface), so designed in A.N. Frumkin Institute original measuring complex. At development of this complex is solved problem to registrations microvolt fluctuations on background high level constant voltage (or potential) in the power source.

Within the framework of work on creation efficient Li-battery with negative electrodes from metallic Li, which could form the competition lithium-ion battery, is carried our studies of the noise characteristics of Li electrodes, polarized in different organic electrolytes. The obstacle industrial realization PS with electrode from metallic Li is instability these electrode in the course of cycling owing to dendrite forming on their surfaces. One of the possible ways of the decision of the specified problem – a selection electrolytes, in which cycling of Li electrode dendrites forming occurs without dendrite forming. The studies of electrochemical noise in miscellaneous electrolytes is installed correlation between level of the noise and intensity of dendrite forming on Li electrode: than below level noise, is more so labored process of dendrite forming and better electrode cycling [2]. This allows to conduct the express-screening optimum electrolyte for considered rechargeable power sources.

The method of electrochemical noise was used also for study dynamics of passivating Li electrode in different electrolytes [3]. It is shown that than quicker falls the power fluctuations of potential of nonpolarized electrode that quicker occurs passivation of electrode surfaces and decreases the declivity to the dendrite forming. This allows it is enough simply and correctly to predict *a priori* possibility of the use the considered electrolyte in lithium power sources.

The serious problem appeared at usages of the primary lithium – thionyl chloride cells is a determination their depth of discharge. At present, the reliable method of such diagnostics is absent. The noise studies of specified power sources (in the course of their uninterrupted discharge at constant load) have shown that fluctuation of the cells voltage, little intensive on considerable part of cycle, sharply increase at the end of the discharge [4]. The got results can serve the base of the development of the real methods of the diagnostics of lithium-thionyl chloride cells. Particularly, valuable information carries the nature of the power spectrum of electrochemical noise, allowing differentiate the cells with different depth of discharge.

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## ELECTROOXIDATION OF METHANOL AT Pt(Mo)-ELECTRODES

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Pt(Mo)-electrodes were obtained by immersion of molybdenum plates into a chloroplatinic acid solution at open-circuit potential. One can recognize the pair of peaks at potentials 0.15 and 0.25 V (The electrode potentials are related to the reversible hydrogen electrode in the same solution.) at Pt(Mo)-electrodes cyclic voltammetric (CVA) curves obtained in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the potential range 0.05–0.5 V. These peaks are typical for platinum electrodes. Presence of Pt clusters at the surface of electrodes obtained was confirmed by scanning electron microscopy. It should be noted that the distribution of Pt clusters at electrode surface is not uniform. The true surface of Pt area for these electrodes is about 5.0 m<sup>2</sup>/g Pt. Pt(Mo)-electrodes exhibited enhanced electrocatalytic activity toward methanol oxidation reaction in the potential range 0.35–0.43 V in comparison with Pt/Pt-electrodes. This phenomenon is attributed to an interaction between methanol adsorption products and molybdenum oxides formed at electrode surface. The conclusion about oxides existence was made from thermodynamic data. Mo oxides, however, could not be identified by XRD analysis. Probably this is due to very small thickness of molybdenum oxides layer. It was proposed that acceleration of methanol electrooxidation by bifunctional mechanism occurs at Pt/MoO<sub>3</sub> boundaries mainly.

Pt(Mo)-electrodes also were obtained from K<sub>2</sub>PtCl<sub>6</sub> solutions in a similar technique. The true surface area of Pt particles in this case is higher (11.5 m<sup>2</sup>/g Pt). The methanol electrooxidation rate normalized to Pt surface is higher in comparison with Pt/Pt but smaller in comparison with electrodes obtained from H<sub>2</sub>PtCl<sub>6</sub> solutions. The latest correlates with assumption about key role of Pt/MoO<sub>3</sub> interfaces in promotion influence of molybdenum oxides.

# NET POLYMERIC MATRIX BASED ON POLYESTERDIACRYLATE FOR SOLID AND GEL ELECTROLYTES: EMPLOYMENT PROSPECTS

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Net polymers based on new Polyesterdiacrylate (PEDA) are a promising polymer matrix for formation of solid (SPE), and gel electrolytes (PGE). It is known diacrylates able to polymerize by the reactionary terminal groups of C=C with form three-dimensional network. Novel PEDA, obtained by condensation of the mixture of 2-hydroxyethylacrylate and diisocyanate anionic polymerization products, contain up to 10 % crown like macrocyclic compounds that is necessary to provide the high ionic conductivity within the polymer matrix and on its interface with the electrodes [1].

The presence polar NHCO-group in the PEDA chain is essential to create the PGE with a high conductivity. This group promotes a stronger retention of polar electrolyte and the stability of PGE. Ability of PEDA to polymerize in the presence of thermal or photo initiator provides an opportunity for cross-linked polymer directly in liquid organic electrolyte and the formation of the gel electrolyte.

PEDA-based PGE [2] with the introduction of up to 85 wt % organic electrolyte have the high ionic conductivity of up to  $4 \times 10^{-3} \text{ Ohm}^{-1} \text{ cm}^{-1}$  at 20 °C. The glass transition temperature,  $T_g$ , vary (-103 – -129 °C) according to the solvent (ethylene carbonate, propylene carbonate, gamma-butyrolactone). The low  $T_g$  provides the storage of electrochemical properties up to -24 °C [3] and opens the principal possibility of improving of the performance of lithium-polymer battery at low temperatures.

PEDA and  $\text{LiClO}_4$ -based SPE have the ionic conductivity of  $1.3 \times 10^{-6} \text{ Ohm}^{-1} \text{ cm}^{-1}$  at 20 °C and  $8.8 \times 10^{-5} \text{ Ohm}^{-1} \text{ cm}^{-1}$  at 100 °C [4], and,  $T_g = -24$  °C. The lithium ions conductivity provided by structural particularity of PEDA chain, namely, by the interchange of ether and ester groups in every link.

Compromise alternative of PGE base on PEDA,  $\text{LiClO}_4$  and ethylene carbonate (EC) was synthesized. EC is retained in the polymer matrix of PEDA at heating to 100 °C when the EC content is 45 wt %. Its conductivity was  $1.9 \times 10^{-4} \text{ Ohm}^{-1} \text{ cm}^{-1}$  at 20 °C,  $T_g = -65$  °C. The fixity of PGE components and high conductivity are a prerequisite to obtain of lithium-polymer battery for electric vehicles. Thus, we can conclude about the uniqueness of the PEDA-based matrix, the modification which allows obtaining of polymer electrolytes with the desired properties.

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**ULTRATHIN CATALYTIC LAYERS SUPPORTED  
AT CARBON NANOTUBES AND POLYMERS****Kharova O.A., Tuseeva E.K., Mikhaylova A.A., Krestinn A.V.<sup>1</sup>***A.N. Frankin Institute of Physical Chemistry and Electrochemistry  
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Thin layers of platinum metals deposited onto carbon supports or non-platinum metals (such as core-shell structures) have attracted attention in recent years due to their peculiar catalytic activity and high degree of precious metal utilization. In this work the *in situ* method of Pt-Ru monolayer deposition at the support of polydiallyldimethylammonium chloride (PDDA) adsorbed at the GC electrode covered with functionalized single wall carbon nanotubes (SWCNTs) was developed. The layer of strong polyelectrolyte PDDA is believed to be adsorbed at SWCNTs due to the  $\pi$ - $\pi$  interaction between PDDA and basal plane of graphene of nanotubes. Pt-Ru nanoparticles were then *in situ* synthesized on the PDDA-SWCNTs layer by chemical reduction of the assemblies between Pt-Ru ions in the solution and positively charged functional groups of PDDA. The prepared catalytic layer showed voltammetric curves characteristic for hydrogen adsorption-ionization on Pt-Ru at the loading  $10\text{--}20\text{ }\mu\text{g cm}^{-2}$  and a specific surface area of  $250\text{ m}^2\text{ g}^{-1}$ . The electrocatalytic activity of this layer in the methanol oxidation reaction was higher, as compared to Pt-Ru deposited onto SWCNTs at the same loading.

Thin films of SWCNTs + polyaniline composites were synthesized at the GC electrodes by electrochemical polymerization from a mixture of 0.25 M solution of  $\text{C}_6\text{H}_5\text{NH}_2$  in 0.5 M  $\text{H}_2\text{SO}_4$  and SWCNTs suspension in isopropanol. The platinum-ruthenium catalysts were then incorporated into composites by keeping the electrode in the solution of the corresponding precursors with subsequent electrodeposition at 0.05 V (RHE).

The composite films have high mechanical durability and conductivity and provide high dispersion of deposited platinum metals. The metal particle size does not increase at the growth of loading from 10 to  $400\text{ }\mu\text{g cm}^{-2}$ . The Pt-Ru specific surface area at a loading of  $160\text{--}200\text{ }\mu\text{g cm}^{-2}$  was about  $200\text{ m}^2\text{ g}^{-1}$  (mean particle size  $\sim 7\text{ nm}$ ) that is much higher, than that of Pt-Ru electrodeposited onto SWCNTs at the same loading. It is possible that three-dimensional structure of the composites prevents the enlargement of catalyst nanoparticles due to their fixation inside the composite's structure.

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## METHODS OF ACTIVATION OF METAL-HYDRIDE ELECTRODES

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The increasing prices on the fossil organic fuel as well as global ecological problems have determined huge interest for the hydrogen as universal power carrier for the stationary and mobile power installations.

Developed by present time hydrogen absorbing alloys consist of the metals that form stable hydrides (rare earth metals, Ti, Zr, Mg and others). They are able to catalyze the atomic hydrogen formation/oxidation process on the alloy (Fe, Co, Ni and others) surface and metals-substitutions which optimize the exploiting characteristics of the alloy.

In the present paper Ti-Ni alloy was picked out as the object to be studied. The availability to intensify the formation/oxidation process of atomic hydrogen on the alloy surface was studied by it's activation with small amount of high dispersed catalysts accelerating these processes. At this stage of our investigation platinum group (Pd, Pt, Rh) metals were used as such catalysts. The activation was realized by the method of chemical reduction of the salt of corresponding metal by hydrogen has sorbated by the alloy.

The availability of the activation effect realization on the dispersed electrode was studied as on the real anode model of the metal hydride accumulator. The electrode was nickel net sublayer with pulverized mixture of the Ti-Ni and Cu (1 : 2) powder layer pressed on it under approximately  $100 \text{ kg cm}^{-2}$ .

The obtained data give possibility to suppose that similar to smooth (non dispersed) electrodes the additional surface activation of the alloy absorbing hydrogen by the catalysts accelerating the process of electrocatalytic formation/oxidation of the atomic hydrogen give possibility in certain conditions to simplify the process of preliminary metal-hydride anode activation and likewise to intensify the process of electrochemical injection and extraction that accelerates charge and discharge processes too.



**BIMETALLIC CATALYSTS FOR DIRECT ETHANOL FUEL CELL SYNTHESIZED ON CARBON NANOTUBES****Korchagina O.V.<sup>1</sup>, Novikov V.T.<sup>1</sup>, Tarasovich M.R.<sup>2</sup>**<sup>1</sup>*D. Mendeleev University of Chemical Technology of Russia, Moscow, Russia*<sup>2</sup>*A.N. Frankin Institute of Physical Chemistry and Electrochemistry,  
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Development of highly active and stable anode catalysts is one of the main tasks for practical accomplishment of low-temperature direct alcohol fuel cells (FC). In this work, PtSn and RuV alloys as catalysts of ethanol electrooxidation synthesized on double-walled carbon nanotubes (CNT) were investigated.

40 % Pt<sub>3</sub>Sn/CNT catalyst synthesized with modified polyol method was investigated in ethanol electrooxidation reaction in acidic media (1 M C<sub>2</sub>H<sub>5</sub>OH+0.5 M H<sub>2</sub>SO<sub>4</sub>). This catalyst activity exceeds significantly the activity of commercial catalysts Pt (40 %) Ru (20 %) HiSPEC 10000 and 40 % Pt (E-TEK). According to XRD data metallic phase of this catalyst is Pt<sub>3</sub>Sn. The average size of particles was approximately 4 nm. According to results of gas-liquid chromatography analysis the mixture of products of ethanol electrooxidation reaction on this catalyst has following composition, namely, 26 mol. % CO<sub>2</sub>, 66 mol. % CH<sub>3</sub>COH, 7 mol. % CH<sub>3</sub>COOH and 1 mol. % CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>. The developed catalyst was tested in membrane electrode assembly of ethanol-oxygen FC. Optimization of catalyst loading and ionomer (Nafion<sup>®</sup>) content in anode active layer is carried out. It was shown that the increase in loading of metal phase (Pt<sub>3</sub>Sn) in anode active layer from 1 to 3.5 mg/cm<sup>2</sup> results in doubling of power density of ethanol-oxygen FC. The maximum power density of ethanol-oxygen FC realized at temperature 75 °C was 51 mW/cm<sup>2</sup>.

The catalyst on the base of the RuV alloy synthesized by reduction of precursors in hydrogen atmosphere was studied in ethanol electrooxidation reaction in alkaline media (1 M C<sub>2</sub>H<sub>5</sub>OH+2 M KOH). Double-walled CNT as support for RuV catalyst were investigated for the first time. The RuV/CNT catalyst containing 30 wt. % RuV (Ru : V = 3 : 1) possessed the highest activity. The activity of RuV/CNT catalyst was higher than that of 30 % Ru/CNT and 20 % Pt (E-TEK) catalysts. Influence of high-temperature vacuum annealing (1700 °C) on CNT properties as support of RuV catalyst was tested. It was shown that this treatment of CNT results in activity increase of the catalyst by 50–60 %.

The performed research revealed the prospectivity of using double-walled carbon nanotubes as support of bimetallic catalysts for ethanol electrooxidation.

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# ELECTROCHEMICAL OXIDATION OF ALIPHATIC ALCOHOLS BY ACTIVE FORMS OF CHEMICALLY BOUND OXYGEN WITH BORON-DOPED DIAMOND ELECTRODE

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Processes of electrooxidation of organic substrates consist, in essence, in the electrochemical generation of high-reactivity intermediates, and on either a cathode or an anode (or, possibly, on both the cathode and the anode simultaneously) and their subsequent chemical reactions with substrates on the anodic surface or, possibly, in an electrolytic solution.

Kinetics and selectivity of the oxidation of butyl and nonyl of alcohols studied. Electrolyses were carried out using undivided cell (volume = 50 mL) with boron-doped diamond anode (BDD) by active chemically bound oxygen. Active chemically bound oxygen ( $\text{HO}_2^+$ ,  $\text{HO}_2^*$ ,  $\text{HO}^\bullet$ ) were generating in situ from  $\text{O}_2$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$  added to the electrolyte. The geometrical anode surface area was 4.16  $\text{cm}^2$ , the cathode (graphite) was 9.5  $\text{cm}^2$ . All electrochemical experiments were carried out at room temperature (23–25 °C) in 0.1 M  $\text{H}_2\text{SO}_4$  solutions. The BDD electrode as anodes is the best choice for the higher generation of  $\text{HO}^\bullet$ -radicals. This radical is a very powerful oxidant ( $E^\circ$ , 2.8 V vs. SHE) which leads to a very effective oxidation process.

Found that at the BDD anode during the oxidation of butyl ( $c = 0.1 \text{ mol l}^{-1}$ ) and nonyl alcohols ( $c = 0.05 \text{ mol l}^{-1}$ ) in aqueous solutions at current densities of 5  $\text{mA cm}^{-2}$  ( $Q = 0.27 \text{ A h}$ ) to produce the corresponding carboxylic acids. The yield on the substance of oil acid – 7.14 %, yield on the current – 60.1 % a. The yield on the substance of pelargonic acid is 98 %, yield on a current – 100 %. The higher density of a current (15–50  $\text{mA cm}^{-2}$ ) and the higher specific charge passed lead to the decrease in an exit of target products. It is explained by the fact that with increasing density of current increases the rate of generation active  $\text{HO}^\bullet$ -radicals. Carboxylic acids (oil and pelargonic) formed after hydroxylation of alcohols, undergoes subsequent non-selective oxidation with the formation of several intermediates. Next, these intermediates decompose to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

Found that paired electrolysis by simultaneously generation on the cathode in situ active forms chemically bound oxygen ( $\text{O}_2^+$ ,  $\text{HO}_2^*$ ) and with BDD anode selectively generating  $\text{HO}^\bullet$ -radicals seems to be selectively to produce competitive carboxylic acids than those direct anodic oxidation or anodic oxidation with  $\text{H}_2\text{O}_2$  added in electrolyte. For example, at the direct oxidation of butanol on BDD anode at a current density of 5  $\text{mA cm}^{-2}$  and specific charge passed of 0.31 A h, is produced yield of oil acid of current is 66.0 %. In paired electrolysis, is  $\text{O}_2^+$ ,  $\text{HO}_2^*$ , produced at the cathode to oxidize the butanol to acid increased to current efficiency 137 %. It is established that at oxidation butanol with increase in specific charge passed from 0.1 to 0.69 A h current efficiency decrease to 54 % for direct anodic oxidation and decrease to 96 % for paired electrolysis. It is connected with increase in the contribution of competitive process of oxidation target product.

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## NANOMATERIALS FOR THE LI-ION BATTERIES

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Parameters of the Li-ion batteries last time were improved. It opens new fields of their application, for example, for the electroautomobiles, the electrobuses, the hybrid automobiles and buses. For a wide application of the Li-ion batteries it is necessary to solve some problems: the charge acceleration, increase of the specific energy and power, a cycle life and an efficiency, the working temperature expansion, especially in the field of low temperatures, and a price reduction. A solution of these problems is sufficiently complicated, because an improvement of some parameters leads to a worsening of others parameters. So it is necessary try to find new and compromise solutions.

One of ways of these tasks solutions is the nanomaterials and nanotechnologies use. The lithium diffusion duration in the nanoparticles is lower, specific surface is higher then in the microparticles. So it permits to accelerate the battery charge and discharge and to increase a battery power. A use of the surface electro-conductive nanolayers increases current density. But with the size particle decreasing the relationship between parts of the surface atoms and the volume atoms increases. It changes structures and properties of the electrode active materials.

More important influence on the electrode behaviour exerts the interparticle layers and the effect of dimensions (a change the electronic and crystalline structures, the vacancies disappearance, a decreasing of an electro-conductivity, a diffusion coefficient, a thermal conductivity and so on). So, it is necessary to find the optimum particle size.

It is possible to receive a considerable improvement of the Li-ion batteries parameters on a way of the new anodic and cathodic nanomaterials application. For the anodic nanomaterials can be use, for example, the modified carbon nanotubes or nanofibres, nanooxides of tin or of transitional metals, compound of silicon, nanocomposites. For the cathodic nanomaterials can be used, for example, the modified nanoolivines, nanospinel, the complex nanooxides of Ni, Co, V, Cr, Al, Mn and. A parameters of the electrodes can be improved also by an optimizing of their composition and structure. An important direction of an improvement of the Li-ion batteries is an application of the polymer electrolytes with nanostructures. In that case it is possible to use the lithium metallic anodes. New technologies of a synthesis of the nanomaterials for the Li-ion batteries ( with an use of the mechano-chemistry, the ultrasound-chemistry, the impulsive technology and other) are developed.

Some new ways of a battery parameters improvement were investigated, other require fundamental investigation. There are in the paper the concrete examples of the nanostructures, the nanomaterials and the nanotechnologies which are used now or will find an application in the Li-ion batteries.

# **SYNTHESIS OF NANOSIZED MATERIALS FOR LITHIUM-ION BATTERIES USING MECHANICAL ACTIVATION. INVESTIGATION OF STRUCTURE AND PROPERTIES**

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Last years, a great interest arose to nanosized electrode materials for lithium-ion batteries, based on the demands to increase their capacity and power characteristics. The advantages of nanomaterials include the increased practical capacity due to better utilization of nanoparticle volume, the improved structural stability due to better adaptability of nanoparticles to volume changes during insertion/extraction of lithium ions, the enhanced high-rate capability due to increased electrode/electrolyte surface contact and accelerated ionic transport, etc. Besides the effect induced by enlarged surface, the effects associated with the changes of the electronic structure are also observed. Numerous defects result in broadening the spectrum of the energetic positions for lithium ions, which influences the electrochemical properties of nanomaterials.

As a rule, nanosized materials are prepared by solution methods (coprecipitation, sol-gel, hydrothermal, etc.). Particle size and crystallinity are controlled by varying the temperature and the duration of subsequent heating. Recently, different functional nanomaterials are widely prepared by a dry, non-waste and energy-efficient method of mechanical activation (MA). Preliminary MA of initial mixtures leads to decrease in temperature and duration of subsequent annealing, thus preventing the coarsening of particles, and to decrease of the amount of intermediate stages, improving the homogeneity of the final product.

In the present study, MA method was applied to synthesize the electrode compounds differing by structure: spinels ( $\text{LiMn}_2\text{O}_4$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ), layered ( $\text{LiNi}_{1-x}\text{Co}_x\text{Mn}_y\text{O}_2$ ) and framework compounds ( $\text{LiFePO}_4$ ,  $\text{LiTi}_2(\text{PO}_4)_3$ ). These materials differ by the value of conductivity from  $10^{-4}$  S/cm for  $\text{LiCoO}_2$  to  $10^{-9}$  S/cm for  $\text{LiFePO}_4$ . According to SEM data, the average particle size was about 50–200 nm. Loose secondary agglomerates with a round form were observed. According to XPS, the particles are characterized by segregation of  $d$ -ions and increased concentration of defects (e.g., oxygen ions with lower electronic density) on their surface, resulting in 1) the rise of surface Li-ion conductivity ( $\text{LiTi}_2(\text{PO}_4)_3$ ), 2) the increase of the ranges of formation of solid solutions during cycling ( $\text{LiMn}_2\text{O}_4$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ), 3) the change of the mechanism of intercalation of lithium ions ( $\text{LiFePO}_4$ ), etc., thus facilitating the capacity and the power properties of as-prepared materials.

It is concluded, that the maximal effect of MA is achieved for materials with low ionic and electronic conductivity. To increase electronic conductivity, nanosized composite materials with a shell formed from high-conductive compound (e.g., carbon) are prepared. For instance, the conductivity of  $\text{LiFePO}_4/\text{C}$  nanocomposites increases by some orders of magnitude. Side reactions of chemically active and large surface of as-prepared materials with electrolyte are suppressed by surface modification with inert compounds (e.g.,  $\text{LiCoO}_2/\text{Al}_2\text{O}_3$ ).

## PROSPECTS FOR CELL LOW SHARE FOR HYDROGEN STORAGE

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In practice, the use of systems for hydrogen storage in the form of hydrides are typically used Pd or Pt. However, their use is limited due to the high cost of these items.

Important role as a deterrent to widespread use of these elements is their high specific weight. This applies in particular to the application of hydrogen batteries in aircraft. As for the light elements, their hydrides have not yet found application as a hydrogen storage for two reasons:

1. The technology of reception is difficult (for example, aluminum hydride  $AlH_3$ ),
2. The energy consumption for its extraction is great ( $t_{decomp} MgH_2 \sim 400^\circ C$ ,  $t_{decomp} CaH_2 \sim 600^\circ C$ ).

The particular interest for the processes of hydrogen absorption are light elements in combination with boron. At the same hydrogen capacity of these compounds increases proportionally to the number of valence bonds. The compounds formed the general form of  $Be(BH_4)_2$  or  $Al(BH_4)_3$  refer to compounds with bridging connections and therefore should have a relatively low temperature of decomposition. Finally, the production of hydrogen from these compounds can be made direct reaction with water.

Experimental confirmation of the possibility of obtaining aluminum hydride electrochemical way has been found in the study of the temperature dependence of internal friction for samples of aluminum subjected to cathodic hydrogenation.

Analysis of the  $Q^{-1} = f(T)$  showed that all samples shows "hydrogen" peak, and its position on the curve and the amplitude depends on the mode of hydrogenation. However, it should dwell on the problems associated with hydride storage of hydrogen in metals with a high degree of passivation. The presence of a potential barrier at the interface in the form of the oxide layer of thick film boemita (for aluminum). Has an inhibiting effect on the desorption of hydrogen from the metal structure. And if the process of dissolution of hydrogen in the structure of barrier-free drive a transition is possible with high probability in electrochemical "charging" in connection with the small size of the particles break out ( $H^+$ ) then, for the desorption of hydrogen molecules, this barrier may have a negative effect.

The authors of attempts to use as alloying components for light metals carbon. The authors observed increased stability of such hydrogen storage materials. In addition they found that increasing the concentration of carbon in the alloy Mg-C-H<sub>2</sub> reduces the temperature of the extraction of hydrogen from the alloy.

From a position of power is preferable as a component alloying for hydride hydrogen storage using boron, because the system  $Al(BH_4)_3$  saturated with hydrogen storage can be carried out by electrochemical method. Ultimately, electrochemical technology of metal hydrides is characterized by a high degree of controllability over technology gas saturation at high pressures and temperatures.

Thus, the use of metal compounds borohydride small periods for storing hydrogen is very promising, but the practical applications of such devices necessary to conduct experimental research on extraction of molecular hydrogen from a reservoir with the least expenditure of energy by reducing the potential barrier, or search for barrier-free crossing.

## NEW ELECTRODE MATERIALS FOR LITHIUM-ION BATTERIES

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All modern lithium-ion batteries (LIBs) are based on traditional electrochemical system. Negative electrodes are made from carbon materials, whereas positive ones are made from lithiated cobalt oxide (overwhelming majority), as well as from lithiated nickel oxides or lithium-manganese spinels. Such strong oxidizers provide rather high voltage of LIB but simultaneously they create serious safety problems. Another origin of the problems is interaction of lithiated carbon with an electrolyte. Specific capacity of the traditional materials of negative and positive electrodes amounts to 350–360 and 120–150 mAh/g, correspondingly.

Some new electrode materials were proposed and studied in Frumkin Institute in cooperation with Lomonosov Moscow State University, Karpov Institute of Physical Chemistry, Ioffe Physico-Technical Institute, and Physico-Technological Institute.

The best materials for negative electrode are based on silicon. Silicon is known to possess the record specific capacity of 4200 mAh/g. It's well known also that lithium insertion in crystal silicon results in huge volume increase and in complete destruction. It was shown that thin films of amorphous Si are capable to reversible cycling, this capability depending on method of the films application. The best results were achieved with laser sputtering and with RF glow discharge. The cycling behavior of such films is improved by doping of Si by Al. Another promising material for negative electrode is composite silicon/carbon. Very convenient method for synthesis of such composites is layer-by-layer magnetron sputtering of Si and graphite onto Cu foil. Actual specific capacity of amorphous silicon and silicon/carbon composites is close to 3500–4000 and 1500–2000 mAh/g, correspondingly.

Rather promising materials for positive electrode are based on vanadium oxides. Usual vanadium oxides are capable to reversible insert small amounts of lithium (up to 150 mAh/g) and attempts to insert more lithium results in irreversible structure changes. At the same time some nanostructured versions of vanadium pentoxide, including composites of  $V_2O_5$  xerogel with conducting polymers, as well as nanobelts of lithium-vanadium bronzes demonstrate reversible capacity up to 500 mAh/g.

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# INVESTIGATION OF ETHANOL ADSORPTION AND ELECTROOXIDATION ON PLATINUM CATALYSTS

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In the present work investigation of ethanol electrooxidation was carried out at three different systems: monoplatinum catalyst 40 wt.% Pt/C, platinum-ruthenium alloy PtRu/C (40 wt.% Pt + 20 wt.% Ru) and PtSn /C (3 : 1 at., 40 wt. % Pt) catalyst, which in accordance with X-ray phase analysis data consists of decorated by Sn oxides PtSn alloy. Carbon carrier in all cases is carbon black XC72. According to the TEM data average particle size is 2–4 nm, specific metal surface area is 50–60 m<sup>2</sup>/g<sub>m</sub>. Investigation of ethanol electrooxidation in acid media (1 M C<sub>2</sub>H<sub>5</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub>, 60 °C) at quasistationary conditions showed the following order for catalysts activity: PtSn > PtRu > Pt [1].

By means of adsorbed hydrogen displacement method occupation (Θ) of PtSn, PtRu and Pt catalysts surface by particles which were formed during ethanol adsorption was measured. Concentration Θ<sub>1</sub>logc and time Θ<sub>1</sub>logt dependencies in middle occupation region correspond to Temkin equation. Comparison of obtained data showed the following order by value of occupation by strongly chemisorbed particles Pt > PtRu > PtSn. Ethanol chemisorptions on Pt starts at lower bulk concentration compared to Pt alloys. Temperature evaluation to 60 °C in case of Pt results in *f* parameter reduction which points at narrower distribution by energies for chemisorbed particles.

Investigation of ethanol electrooxidation products at PtSn, PtRu and Pt in stationary conditions at different potentials was made by means of HPLC and GC analyses. It was shown that acetaldehyde is a main product. At low polarizations reaction with C–C bond cleavage and CO<sub>2</sub> formation is possible. The highest yield corresponds to monoplatinum catalyst. At high polarizations acetic acid yield grows up.

Comparison of adsorbed particles occupation data, quantity of electricity which corresponds to current transients measured during ethanol injection into electrolyte solution and ethanol electrooxidation products analysis data shows that rising of ethanol concentration results in decreasing of CO<sub>2</sub> yield because of catalyst free surface blocking by incomplete oxidation products. Ethanol adsorption at low concentrations is followed by approximately 1 electron transfer per adsorption place. That corresponds to dehydrogenation with 1 hydrogen atom detachment. It seems that in the case of platinum catalyst stronger ethanol adsorption with larger molecule dehydrogenation degree occurs.

Considered anode catalysts and novel tolerant cathode catalysts were tested in direct ethanol-oxygen fuel cell.

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## THE DIRECT OXIDATION OF ALCOHOLS IN A SOLID ALKALINE MEMBRANE FUEL CELL (SAMFC)

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The synthesis of new anion exchange membranes, conducting by the hydroxyl ions, opens the possibility to develop all solid fuel cells similar to PEMFC, but working in alkaline medium [1]

Thus Solid Alkaline Membrane Fuel Cells (SAMFCs) using anionic membranes are promising power sources for small devices working under ambient conditions, such as portable electronic devices. Comparing SAMFC with PEMFC (Proton Exchange Membrane Fuel Cell), the kinetics of the ORR (Oxygen Reduction Reaction) is easier in alkaline medium than in acidic medium, leading to the possibility to activate the electrochemical reactions by non-noble metal electrocatalysts [2]. Furthermore, the crossover of fuels (alcohols, such as methanol, ethanol, ethylene glycol and glycerol) due to the electro-osmotic effect will be limited, as a consequence of the hydroxyl ion conductivity across the membrane. Moreover, the highest activity of electrocatalysts in alkaline medium for alcohol oxidation will allow us to build anodes with low level of platinum, or even without platinum [3]. On the other hand alcohols, such as methanol and ethanol, are very convenient liquid fuels, since they can be easily stored and transported, conversely to gaseous hydrogen.

Besides, other alcohols, such as ethylene glycol (EG) and glycerol (GL), appear to be interesting fuels for SAMFC applications. They are less toxic than methanol, they display a specific energy density close to that of the other alcohols (5.2 and 5.0 kWh/kg for EG and GL, respectively, vs. 6.1 and 8.0 kWh/kg, for MeOH and EtOH, respectively) [4] and each carbon atom carries an alcohol group. As a consequence, their oxidation in alkaline medium to oxalate ( $\text{COO}^- \text{COO}^-$ ) or mesoxalate ( $\text{COO}^- \text{CO} \text{COO}^-$ ) species, as proposed by other authors [5], involves 8 moles of electrons per mole of EG (instead of 10 for complete oxidation to  $\text{CO}_2$ ) and 10 moles of electrons per mole of GL (instead of 14 for complete oxidation to  $\text{CO}_2$ ), which means a faradic efficiency of 80 and 71 %, respectively.

The concept of a Solid Alkaline Membrane Fuel Cell (SAMFC), involving the direct electro-oxidation of alcohols (methanol, ethanol, ethylene-glycol, glycerol, etc.) in alkaline medium, will be first presented in this lecture.

In particular the electrocatalytic oxidation of ethylene-glycol [6] and glycerol [7], inside a SAMFC with a platinum or palladium based anode, will be discussed. Several electrocatalysts ( $\text{Pt/C}$ ,  $\text{Pd/C}$ ,  $\text{PtPd/C}$ ,  $\text{PtBi/C}$ ,  $\text{PtPdBi/C}$ ) dispersed onto a carbon support (Vulcan XC-72) were synthesized by the "water-in-oil" micro-emulsion method [8], which seems to be more appropriate than the colloidal method derived from the Bönninger procedure [9]. After characterization of the catalysts by physicochemical methods (TEM, EDX, XRD, ICP-OES, etc.), their catalytic activity towards the electro-oxidation of EG and GL was investigated by electrochemical methods (voltammetry, RDE, etc.). The adsorbed intermediates and reaction products were analyzed by IR reflectance spectroscopy,  $^{13}\text{C}$  NMR and HPLC. Finally their electrical performance in a SAMFC was evaluated at room temperature.

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# CARBON-SUPPORTED Cu@Pt AND Pt-Cu NANOPARTICLES FOR OXYGEN ELECTROREDUCTION

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Low temperature oxygen-hydrogen fuel cells are associated with cell efficiency losses, because of kinetic limitations of the oxygen reduction reaction. Pt/C is used as electrocatalyst. Carbon-supported platinum alloys with various transition metals (Cu, Ni, Co) are employed to improve activity of the catalyst. Platinum atoms distribution in nanoparticles can play a critical role in catalytic properties of PtM/C. Character of this distribution can change in a broad area – from homogeneous alloys to nanoparticles with core-shell structure.

The aim of this work was to prepare Pt<sub>2</sub>Cu/C catalysts with different metals distribution in nanoparticles and investigate their catalytic activity in oxygen electroreduction reaction. Nanoparticles of the Pt<sub>2</sub>Cu<sub>50</sub> with core-shell structure were prepared by two following methods:

- successive reduction of Cu<sup>2+</sup> and Pt (IV) from solution of precursors;
- successive reduction of PtCl<sub>6</sub><sup>2-</sup> ions over the Cu/C.

Moreover, to modificate Cu particles growth new technique was developed. Small quantity of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O was added to mitigate Cu nucleation.

Particles size was determined by X-ray diffraction, metals content – by X-ray fluorescent analysis. Electrochemical behavior of PtCu/C catalysts in 1 M H<sub>2</sub>SO<sub>4</sub> was studied by cyclic voltammetry on the rotating disc electrode. The electrochemical active surface area was measured by CO stripping voltammetry. The corrosion stability of PtCu/C was investigated too.

Metal's loading on the carbon carrier was 26–32 % wt. Prepared materials had high electrocatalytic activity in ORR and active surface area up to 45–48 m<sup>2</sup>/g. It was shown that Pt<sub>2</sub>Cu/C catalysts with more homogeneous metals distribution in nanoparticles had electrochemical properties and corrosion stability distinguishing from those of PtCu alloys.

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## SIMULTANEOUS ELECTROCHEMICAL AND GAS-COLLECTION STUDIES OF BOROHYDRIDE OXIDATION

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Borohydride has been studied extensively as a fuel for fuel cells. There are two different ways of utilizing borohydride for fuel cells, i.e., to be used a direct fuel or an indirect fuel. In the latter, borohydride plays the role of a hydrogen carrier to produce hydrogen gas to feed the hydrogen-oxygen (air) fuel cells. In this way, a part of the chemical energy stored in borohydride is wasted on the step of hydrogen production from borohydride. Theoretically, it is more energy efficient to use borohydride directly as a fuel. However, this potential advantage of direct borohydride fuel cell (DBFC) over the indirect one can be realized only if the number of electrons involved is 8 and the electrode potential is more negative than the reversible hydrogen electrode (RHE). To reach this goal, there is still a long way to go and a sound understanding of the borohydride oxidation reaction is essential.

Simultaneous electrochemical and gas-collection measurements[1] on a few catalysts (including Pt, Au, Cu, Ni, and Ni-based hydrogen storage alloys) revealed a number of new features of borohydride oxidation. For example, we found that hydrogen evolution can take place at potential more positive than RHE ("underpotential hydrogen evolution") on some catalysts while dihydrogen oxidation can occur at potential more negative than RHE ("underpotential hydrogen oxidation") on some other catalysts. On the basis of these new findings a kinetic model is proposed, featuring a high energy state of adsorbed hydrogen. It is further inferred that the key to make full use of the potential advantage of DBFC is very quick oxidation of the high energy adsorbed hydrogen and a catalyst able to provide active oxygen-containing species might be suitable for this purpose. This postulation seems to have been supported by the performance of a new catalyst Pt/Ti-oxides. With this catalyst, "8-electron oxidation at potentials more negative than RHE" was realized for the first time [2].

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**CARBON NANOTUBES AS A SUPPORT  
FOR PLATINUM CATALYSTS IN DMFC****Mayorova N.A., Tusseeva E.K., Krestinin A.V.<sup>1</sup>, Khazova O.A.***A.N. Frumkin Institute of Physical Chemistry and Electrochemistry,  
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Carbon nanotubes are used as a catalyst support for fuel cell due to their high conductivity and corrosion resistance and the possibility to obtain well dispersed catalyst's deposits. In the work single walled carbon nanotubes (SWCNTs) were synthesized by arc method using the nickel-yttrium catalysts and then were thoroughly purified of amorphous carbon and metal catalysts. After treating nanotubes with a mixture of concentrated  $H_2SO_4$  and  $HNO_3$  oxygen containing functional groups appeared at their surface. In the result of functionalization, the initially hydrophobic SWCNTs become highly hydrophilic which is important for catalyst deposition. The dependence of specific surface area of electrodeposited Pt and Pt-Ru on the structure of the support was studied. At the small deposits of metals ( $5-10 \mu g cm^{-2}$ ) on the functionalized carbon nanotubes (SWCNTs) their specific surface area is very high (up to  $300 m^2 g^{-1}$ ). When the amount of the deposit increased to  $50-200 \mu g cm^{-2}$  the specific surface decreases to  $30-60 m^2 g^{-1}$ . So only at the initial stage of electrodeposition a carbon support structure determines the degree of dispersity of the deposited catalyst, at more prolonged deposition the structure of the deposit depends on parameters of this process.

The electrocatalytic activities of SWCNTs supported Pt and Pt-Ru catalysts were studied in the reactions of oxygen reduction and methanol oxidation. High mass specific currents of the reactions were recorded at the small amount of platinum metal deposit: for oxygen reduction the specific kinetic current reaches to  $400 mA mg^{-1}$  at the potential of  $0.85 V$  (RHE), that is a promising result for developing miniature fuel cells. However, when the loading of platinum metals increased specific currents decreased in accordance with diminishing of the specific surface area of the platinum deposit. The currents at platinum catalysts supported at SWCNTs and at the commercial Vulcan XC-72 referred to a unit of electrochemically active surface area were close, i.e. the intrinsic catalytic activity does not depend on the nature of carbon support. So the high rates of the reactions recorded at low loading were determined by the structure of highly dispersive catalyst layers deposited on SWCNTs.

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# OPERATION MECHANISM INVESTIGATION OF HIGH ENERGY DENSITY SUPERCAPACITOR BASED ON ACTIVATED CARBONS

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In the framework of high specific energy electrochemical capacitors elaboration, the electrodes based on activated carbons (powder ADG and carbon-cloth CH-900 and TSA) with specific surface area 1000–1500 m<sup>2</sup>/g in concentrated solution of sulphuric acid (30%-60% mass fraction) at the wide applied voltage range (from -1 V to +1 V) have been studied

For the purpose of processes charging separation, cycle volt-ampere curves measured at two voltage ranges have been compared. These voltage ranges can be named as a reversible range (from 0.1 V to 0.9 V) and a deep charging range (or -0.8 V до 1 V). The first one corresponds to the charging of electric double layer and fast redox-reaction of surface groups in approximately 10–100 s time. Here total specific charge is about 200 C/g. As for the second one, in the range of negative potential ( $< -0.1$  B) the faraday processes with extremely high pseudo capacity values and charging time from hundreds of seconds to tens of hours are observed (total specific charge is up to 1300 C/g). At these times, not only above mentioned fast processes proceed. Taking into account obtained results, it can be assumed that there are also the processes of chemical hydrogen adsorption on interfacial area carbon/electrolyte and the electrochemical hydrogen intercalation in carbon at deep cathode charging of activated carbons take place. The intercalation process is governed by slowed solid-phase hydrogen diffusion, which may explain very high maximal time of charging until 100 hours as well as the proportionality peak current and square root from the potential scan rate. The values of charge spent on adsorption and intercalation are comparable. The fact of limiting charge growth with increasing of sulphuric acid concentration (from to 30 % to 60 %) has been established and the maximal total charge of 1500 C/g has been obtained. The similar experiments in phosphoric acid have been produced and the maximal total charge of about 1000 C/g has been obtained. Impedance spectroscopy researches of activated carbons electrodes and the active resistance measuring of these electrodes in special cell at direct current have been made. The essential increase (in dozens of times) of electrodes resistance at deep cathode charging process has been found. It may be due to formation of intercalated C<sub>6</sub>H type compound. Possible limit composition is C<sub>6</sub>H, analogous one is C<sub>6</sub>I.

A two-dimensional mathematical model of carbon electrode charge-discharge process has been developed. The model takes into account the following factors: charging of electric double layer, chemical adsorption of hydrogen at an interface carbon/electrolyte, electrochemical hydrogen intercalation into carbon, solid-diffusion, diffusion-migration ion transport in the pores, the characteristics of the electrode porous structure measured by using the method of standard contact porosimetry.

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## CATALYTIC AND CAPACITANCE PROPERTIES OF COMPOSITES FROM CARBON MATERIALS AND POLYANILINE

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The composites of functionalized single wall carbon nanotubes (SWCNTs) and polyaniline (PANI) were studied as a catalyst support for DMFC anodes. The films of SWCNTs + PANI composites at the electrodes were deposited by electrochemical polymerization from the mixture of 0.25 M solution of  $C_6H_5NH_2$  in 0.5 M  $H_2SO_4$  and SWCNTs suspension in isopropanol. The voltammetric and capacity properties of SWCNTs and their composites with polyaniline were investigated. The composite layer is shown to have exceptionally high capacitance (more than  $1000 \text{ F g}^{-1}$ ) that is due to the large surface area of the former and as well due to the proceeding of the reversible faradaic reaction of counter ions intercalation into PANI, proceeding at the narrow boundary layer - polyaniline fibrils / solution in pores. The specific capacitance of the composite layer is 40 % more than the capacitance of pure PANI, the latter can be the result of loosening of the PANI structure upon the nanotubes incorporation.

The platinum-ruthenium catalysts were incorporated into composites by the electrode keeping in the solution of the corresponding salts with subsequent electrodeposition at 0.05 V (RHE). At the prepared electrodes a significantly more pronounced catalytic effect is observed as compared to Pt-Ru electrodeposited on other supports. At the composite supported catalyst (at loading of  $200 \mu\text{g cm}^{-2}$ ) a multi-fold increase of the currents in kinetic region of potentials is observed – 7-fold, 10-fold and even 15–30-fold, as compared to pure polyaniline, SWCNTs and Vulcan XC-72 support correspondingly. It was shown that the methanol oxidation currents referred to the true surface area of Pt-Ru catalyst does not depend on the nature of the supports. So it can be supposed that the main factor that determines the overall catalytic activity is the highly dispersive structure of the catalytic layer incorporated into three-dimensional structure of the composites.

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## STRUCTURAL AND KINETIC CHARACTERIZATION OF GAS DIFFUSION POROUS ELECTRODES IN RECHARGABLE LITHIUM OXYGEN BATTERIES

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Because of their inherent simplicity in concept batteries are at the forefront of the electrical energy storage systems. The amount of energy per mass or volume that a battery can deliver is a function of the cell's voltage and capacity.

Owing to lithium's lightness and its lowest electronegativity amongst the existing metals, lithium based batteries have a high energy density, high specific energy and high operating voltage, and are expected as the potential power sources for many applications. Commercial rechargeable lithium batteries use lithium transition metal oxides, typically  $\text{LiCoO}_2$ , as cathode and graphite as anode. Their specific capacity depends on the capacities of both the cathode and anode materials. Energy storage in these batteries is limited by the cathode and does not exceed  $200 \text{ mA h g}^{-1}$ .

The capacity of a lithium battery system can be enhanced remarkably by using a completely different approach which combines Li as anode directly with oxygen as cathode active material in a Li/Oxygen cell. Oxygen accessed from environment is reduced catalytically on an air electrode surface and the catalytically formed anions react with lithium cations supplied by the anode and delivered by the electrolyte to form  $\text{Li}_2\text{O}_2$  on the air electrode surface during discharge process.

The air electrode in lithium/oxygen batteries is a composite electrode made of a porous carbon, a catalyst and a binder in which several electrochemical and transport processes occur simultaneously. There are many parameters that affect the performance of a lithium oxygen battery, such as: cathode structure, electrolyte composition and how the cell assembling is carried out. The ratios of the materials contained in the cathode, the electrode porosity, the choice of catalyst material are also as important as the structure and morphology of the ingoing compounds. All these parameters should be considered when making a well function cathode. Engineering and chemical advances are also required to prevent the access of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  which could react with either  $\text{Li}_2\text{O}_2$  or lithium metal.

In this study porous catalyzed electrodes with improved kinetics and energy efficiency are designed by preparing polymer based carbon aerogels with controlled porosity at nano scale. The electrochemical performance of the electrodes has been tested in a Li/O<sub>2</sub> cell. Through the galvanostatic charge/discharge measurements, it is found that the cell performance (i.e. discharge capacity and discharge voltage) strongly depends on the porous structure of the carbon used as active material in the electrode and a combined effect of pore volume, pore size and surface area of carbon affects the storage capacity. A Li/O<sub>2</sub> cell using a carbon with a high pore volume ( $3.146 \text{ cm}^3/\text{g}$ ) and a wide pore size ( $17.4 \text{ nm}$ ) showed a specific capacity of  $1682 \text{ mAh/g}$ . This capacity is almost 10 times of the capacity of a commercial lithium ion battery.

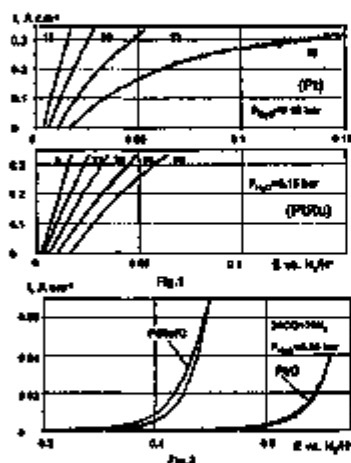
The electrochemical impedance spectroscopy was applied to the investigation of the porous oxygen electrodes. The quantitative analysis of EIS results showed that the shape and value of the resistance in the impedance spectrum of a Li/O<sub>2</sub> cell are strongly affected by the porosity of carbon used in the cathode. Porosity changes due to the build up of discharge products hinder the oxygen and lithium ion transfer into the electrode, resulting in a gradual increase in the cell impedance and charge transfer resistance with cycling.

# CO TOLERANCE AND CO OXIDATION IN FUEL CELL WITH POLYBENZIMIDAZOLE-H<sub>3</sub>PO<sub>4</sub> MEMBRANE

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The use of polybenzimidazole-H<sub>3</sub>PO<sub>4</sub> (PBI-PA) membranes in proton exchange membrane fuel cells (FC) enables to increase the operational temperature of FC up to 180 °C, thus dramatically increasing tolerable level of CO concentration in hydrogen fuel. It is long known that CO tolerance of Pt hydrogen oxidation catalyst can be increased by addition of the second component, e.g. Ru. The effect of Ru addition to Pt is ascribed primarily to the increased rate of electrochemical CO oxidation, which temporarily frees portion of sites on the catalyst surface for hydrogen oxidation. However, oxidation of one adsorbed CO molecule requires one water molecule. In contrast to low temperature FC, the media of FC with PBI-PA membranes is nearly anhydrous. Therefore strong influence of fuel humidification on CO tolerance can be expected.



Influence of fuel humidification on CO tolerance and CO oxidation at Pt/C and PtRu/C hydrogen oxidation catalysts was studied using membrane electrode assemblies with PBI-PA membranes at temperatures ranging from 140 to 180 °C. The platinum group metal loading at the anodes was app. 1.5 mg cm<sup>-2</sup>. Curves of dependence of hydrogen oxidation currents on potential measured at 180 °C at Pt/C and PtRu/C catalysts in presence of CO is shown in fig.1 (CO concentration in H<sub>2</sub>-CO mixtures is indicated as numbers at the curves in volume %). For comparison, when dry mixture (95H<sub>2</sub> + 5CO) was used as fuel hydrogen oxidation overvoltage at 0.3 A cm<sup>-2</sup> reached 50 and 35 mV at Pt/C at PtRu/C catalysts, respectively. The figure reveals significant decrease of hydrogen oxidation overvoltage in presence of CO with fuel humidification and superiority of PtRu/C catalyst. CO oxidation curves measured at Pt/C and PtRu/C

catalysts using humidified (24CO-76N<sub>2</sub>) gas mixture at 180 °C are shown in fig. 2. Comparison of CO oxidation curves measured with these catalysts shows that PtRu/C catalyst is much more active compared to Pt/C catalysts.

The observations help ascribe higher tolerance to CO of PtRu, compared to Pt/C, to increased rate of CO removal from the catalyst surface by electrochemical oxidation.

The mechanism of CO oxidation, which includes strong CO adsorption, slow stage of water activation by one electron reduction, and subsequent reaction of adsorbed species, is supported by measurements of CO oxidation reaction order with respect to water vapor pressure (close to unity) and CO concentration in gas phase (negative values).

The work was supported by the 3P Program of fundamental studies "Chemical Aspects of Power Generation" by Presidium of Russian Academy of Sciences.

# MODELING OF THREE-PHASE BOUNDARY INTERPHASE LAYERS IN THE SYSTEM Li-Sb<sub>2</sub>S<sub>3</sub>

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The Li/Sb<sub>2</sub>S<sub>3</sub> voltamperic study showed similar behaviour of these systems, moreover by the use of the empiric equation

$$\log I = A + B\Delta E^{1/2} \quad (1)$$

Most satisfactory linear approximation is achieved. Earlier we are showed [1, 2], that various composition lithium thioantimonates are products of cathodic process of Li/Sb<sub>2</sub>S<sub>3</sub> system. It is known that analogic dependence takes place in the thermoelectronic and thermoionic emission of a dielectric with electric field applying. Schottky's equation binds emission current ( $i_{\text{th}}$ ) with electric field strength in a dielectric [3]:

$$i_{\text{th}} = AT^2 \exp(-\varphi/kT) \exp(e/kT \sqrt{(e\Delta E)/(4\pi\epsilon_0\epsilon_r d)}), \quad (2)$$

where  $A = 12 \times 10^5 \text{ A/m}^2 \text{ K}^2$  - is the Richardson's constant;  $W = e\varphi$  - is the electron's work function;  $\varphi$  - is the metal-dielectric barrier's height;  $\Delta E = \xi d$  is the voltage drop on dielectric film, it is believed equal to outer;  $d$  - is the dielectric film's thickness, m;  $\xi$  - is the electric field strength;  $k = 1.38054 \times 10^{-23} \text{ J/K}$  - is the Boltzmann's constant;  $e = 1.602 \times 10^{-19} \text{ C}$  - is the electron charge;  $\epsilon_0 = 8.8542 \times 10^{-12} \text{ F/m}$  - is the vacuum dielectric constant;  $\epsilon_r$  - is the relative dielectric constant.

Metal-semiconductor's potential barrier's magnitudes of Li/Sb<sub>2</sub>S<sub>3</sub> system may be determined from the following equation:

$$(\log i_{\text{th}})_0 = \log (AT^2) - 0.43 e\varphi/kT \quad (3)$$

The calculation give magnitudes of Li/Sb<sub>2</sub>S<sub>3</sub> and Li/Sb<sub>2</sub>S<sub>3</sub> system's potential barrier's heights,  $\varphi_1$  and  $\varphi_2$  significances found from the calculations:  $\varphi_1 = 0.53 \text{ V}$  and  $\varphi_2 = 0.691 \text{ V}$  respectively.

Issue from electrophysical parameters of study compound's [4, 5], it is possible to calculate magnitudes of potential barrier's height fro possible systems by difference of electron work functions. For Li/Li<sub>1-x</sub>Sb<sub>x</sub>S<sub>3</sub> systems:  $\varphi = 2.38 - 1.61 = 0.770 \text{ V}$  if  $x = 0.33$ ; but  $\varphi = 2.38 - 1.41 = 0.970 \text{ V}$  if  $x = 0.50$ ; for Li/LiSbS<sub>3</sub>  $\varphi = 2.38 - 1.36 = 1.02 \text{ V}$ , for Li/Sb<sub>2</sub>S<sub>3</sub>  $\varphi = 2.38 - 1.64 = 0.740 \text{ V}$ .

The calculation based on our experimental dates for system Li-Sb<sub>2</sub>S<sub>3</sub> give magnitude of potential barrier height: it is equal 0.753 V. This magnitude is nearly to systems Li/Sb<sub>2</sub>S<sub>3</sub> ( $\varphi = 0.740 \text{ V}$ ), Li/Li<sub>0.33</sub>Sb<sub>0.33</sub>S<sub>3</sub> ( $x = 0.3$ ,  $\varphi = 0.770 \text{ V}$ ).

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# MECHANICAL COMPOSITES ON THE BASIS OF TRANSITIONAL METALS – PERSPECTIVE CATALYSTS FOR CATHODIC PRODUCTION OF HYDROGEN

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An electrolysis of water is one of the most perspective methods of hydrogen production, advantages of which are a high cleanness of the product, simplicity of the technological process, the most valuable by-products (oxygen, heavy water etc.). This method of production of hydrogen is used in countries having the considerable cheap hydro and atomic power resources. Thus, there is a need in development of cheap and effective electro-catalysts for hydrogen production.

There are references in the literature specifying the perspectives of the carbides of transitional metals for electrochemical technology of production of hydrogen (TiC, WC, Fe<sub>3</sub>C, Fe<sub>5</sub>SiC etc.) as the over voltage of releasing of hydrogen on these materials is considerably reduced. However the activity of a number of individual non-equilibrium carbidic phases has not been studied as well as the latter of the composition materials on the basis of the nanosized incorporations of carbides of transitional metals of different morphology in conducting matrices. The most simple method of receiving such materials is mechanosynthesis.

Subsequent dynamic pressing of powders after mechanosynthesis allows getting model materials with density nearly to 100%, which can be used both for anotation of activity of carbides and their incorporations and research of mechanism of hydrogen reaction and co-operation of these materials with the distinguished hydrogen.

Compacting composite materials "α-Fe+ carbides of iron, titan, vanadium and niobium", and also individual carbides (Fe<sub>3</sub>C, Fe<sub>5</sub>SiC) got by the dynamic pressing of the powder-like systems and prepared by the method of mechanosynthesis were studied. Tests of activity were conducted in acidur and alkaline sulfate solutions.

In acid solutions most activity in the process of cathode releasing is possessed by the carbides of iron, on this account that the activity of composites considerably goes up with the increase of propotion of cementite, dispersion of incorporations or forming of a nano sized net typed structure of incorporations of Fe<sub>3</sub>C. It is found out that the most active composites are formed during the mechanosynthesis in liquid organic solutions. Value of br reaction of renewal hydrogen for cementite and most active composites in acid solutions is ~of 60 mV.

The activity of composites and individual carbides of iron in alkaline solutions is considerably lower than in acid ones, and the value of br is ~120 mV. The possible mechanisms of reaction of releasing hydrogen acid and alkaline solutions are also discussed in the article.

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## THE ELECTROCATALISATORS BASED ON THE IRON FAMILY ALLOYS

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The sources of the discharge different carbohydrates are the chemical, chemical-recovery, petrochemical industry and so industries using the organic solvents for painting, varnishing that in the drying process of wood, metal and polymer product escape in the air. The industrial discharges are very variable in their composition. So, the main task of the modern ecology is the problem solving of water pollution with the highly toxic organic compounds. Besides, the actual task is the development of gas treating methods from CO, organic compounds, nitric oxides and the other substances. There is the tendency to increase quantity of catalytic materials on basis of thin-filmed coating.

It has been proved the covering efficiency Co-W in the flameless benzol oxidation reaction. It is observed the maximum concentration CO and CO<sub>2</sub> in the gases in the output reactor by using fallouts optimal point of view the composition catalytic activity – 30 mass. % of the high-melting component. For coating the other composition it is observed the decrease of the single and carbon dioxide concentration in comparison with 30 mass. % tungsten alloy. In this case the degree of carbon oil deep transformation notably CO reduction amounts to 86 %. It has been also found experimentally the increasing catalytic activity of the covering alloy Co-W in comparison with electroplate individual cobalt (fig. 1).

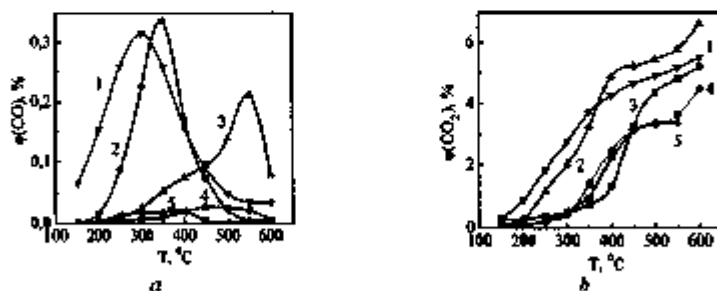


Fig. 1. The dependent temperatures of the volume content CO (a) и CO<sub>2</sub> (b) in the gases in the output reactor in the flameless benzol oxidation reaction on the materials of the different content (mass. %): 1 – Ni-W30; 2 – Co-W30; 3 – Co-W50; 4 – Co-W10; 5 – Co.

The electrodeposited alloys Co-Fe have been tested as electrode materials producing hydrogen by water-neutralizing electrolysis. The data authenticate that the using of the electrodes allows to reduce the bath overstress 10–15 %.

# MATHEMATICAL MODELING OF THE INTERACTION OF HYDROGEN WITH METALS DURING ANODIC TREATMENT

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Strictly speaking, the mechanism of hydrogenation of some metals in their treatment of the anode has an ambiguous explanation of a number of authors. Titan, possessing exceptional but high activity in the interaction with hydrogen, forming hydrides even at room temperature. The authors attempt to establish the relationship amounts of dissolved hydrogen with the chemical composition of titanium alloys has not given a clear dependence on the concentration alloying component. But the fact of hydrogenation of titanium and its alloys during anodic treatment is not confirmed, and the mechanism of hydride formation is still understudied.

Barrier-free transfer of hydrogen at the cathode should be at a certain temperature, whose value depends on the chemical composition of the electrolyte and the current density. According to the dependence  $\lg i = f(10^3/T)$  determined the temperature of barrier-free transition to the hydrogen ions. As a result of our experiment it was found that the gradient of the temperature in the reaction zone is much higher than the calculated values. This in turn provides a basis to suggest the possibility of the mechanism of transfer of  $H^+$  in the structure of the metal when it anodize based on the experimental and model representations of similar processes.

So, in the processing temperature of the electrolyte within the reaction zone will change, its measurement is not always possible, for a stationary process in the presence of simultaneously occurring reactions, we proposed an analytical equation for determining the temperature in the electrode layer through the process parameters.

This equation has the form:

$$\Delta T = \frac{T_{\text{max}}}{a + \frac{1}{i} \times \tau_{\text{max}}}$$

$\Delta T$ —excess surface temperature of the electrode over the middle in the electrolyte

$i$ —the current density of the electrode (A/dm<sup>2</sup>)

$\tau_{\text{max}}$ — exposure time (min)

$a$ — dimensionless coefficient, is a nomogram

The nomogram represents a family of lines  $a = f(\tau_{\text{max}})$  for different values  $i$ .

Based on experimental data on the hydrogenation of titanium at its anodic treatment and results to determine the surface temperature can be physical-chemical basis model of interaction of hydrogen with steel broom titanium. The resulting  $H^+$  ions as a result of leakage at the anode parallel to the oxidation of water to form partially hydrated hydronium ion ( $H_3O^+$ ), partly using the barrier crossing, interact with free metal atoms. Hydrogen ion being chemically active species, easily reacts with a free atom of titanium. When wheelchairs passage of a hydrogen ion should factor in the interaction of the thermal field (thermal diffusion). The vector of this field is opposite to the electric field vector,  $i_e$  increases the probability of barrier-free transition. This is because the ions  $Ti^{2+}$ ,  $Ti^{3+}$ ,  $Ti^{4+}$  and  $H^+$  ions in the electric double layer of hydrated and released at the same time the thermal energy created in the surface temperature gradient, which arises due to thermal diffusion of particles.

The experiment results and analytical calculations for anodize titanium realized temperature in the reaction zone about 100–120 °C.

# INTERRELATION BETWEEN HEAT-SINK ABILITY TO HYDROGEN WITH STRUCTURE ELECTROLYTIC METALS AND ALLOYS

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Ability of hydrogen to co-operate with metals depends on a number of factors. The metal nature concerns them first of all. The most typical hydrogenactive elements are Pd, Pt, elements of 3-4th collateral subgroups 4, 5 and 6 periods.

At research electrolytic metals and alloys it has been established, that interaction of hydrogen with metal is carried out on defects of structure. It is experimentally established, that energy of activation in system hydrogen - electrolytic chrome for the coverings received from chromate of electrolytes depends on electrocrystallization modes (density of a current, maintenance  $\text{CrO}_3$  in electrolyte). On the other hand the number of places of interaction (quantity of defects of structure) in strong degree is defined by the mechanism of formation of metal structure.

From the equation it is visible, that

$$\ln N = \ln N_0^1 - \frac{E_2^2}{\eta_2}$$

quantity of the centers nucleation in direct ratio to an overstrain or density of a current of crystallisation and in inverse proportion to energy nucleation.

The more the centers nucleation it is necessary on surface unit, it is more formed metal hydrides. Influence of structure of the metals received by a method of electrocrystallization on process hydrogenation mismatches classical representations about an estimation of degree of perfection of structure. So, the quantity of the hydrogen dissolved in the sample increases for structures with the small sizes crystalline particle (fine-grained deposits). Whereas, in technology of electroplating such samples are considered more perfect.

Amorphous metals are capable to dissolve considerably great volumes of hydrogen in comparison with metals of crystal structure. However electrochemically it is possible to generate system close on properties to amorphous, using so-called "rigid" modes electrolysis. In this case the sizes of grains of crystalline particle should be minimal. The multilayered metal structure formed in such a way in some approach will be similar "pseudo-amorphous", complete similarity in this case is not observed. Nevertheless presence grain borders in such systems promotes increase hydrogen capacity such systems. For quantity reduction «hydrogen traps» with rigid fixing of gaseous hydrogen it is desirable to bring some channels located in planes perpendicular surface of an electrode-store ("drains" of molecular hydrogen). Such modular electrodes possess capacity on hydrogen, are characterised by perfect degree of adaptability to manufacture and keep all advantages of way hydride hydrogen storages, namely: stability of work of the accumulator, good permeability ability (it is defined by geometry of channels-drains), suppose reusable use.

Thus metal structures on a basis electrolytic metals and their alloys, received by a method of electrochemical formation with application of technology pulsed electrolysis can find application in manufacture of electrodes for hydride hydrogen storages.

# CONCENTRATION DEPENDENCE OF DISTRIBUTION OF CONNECTIONS OF HYDROGEN WITH METALS IN VOLUME OF A FLAT ELECTRODE AT ELECTROCHEMICAL INTERACTION

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Assumed, that the probability of restoring a certain type of ions depends mainly on the current density in some areas of the electrode. However, experimental results of the hydrogen-content determination for separate elementary sites of an electrode are not proved by analytical calculations. As it has been established earlier, interaction of hydrogen with electrolytic metals and alloys is carried out on defects of structure, i.e. the greatest probability of formation of metal-hydrogen communication is carried out in points with the highest power budget. The volume density of such defects is extremely non-uniformly distributed in volume of metal. Complexity of experimental definition of quantity of the dissolved hydrogen it is connected with that fact, that even at exact definition of surface density of current, the volume density of defects in metal structure cannot be connected with it by linear dependence.

For an initial surface of metal with uniform function to nucleation can be written down in the form of expression:

$$N = \sum_{i=1}^n k \times i_{f(x,y)},$$

$N$  – is number of probable formations of Me-H;

$k$  – is number of communications for the given density of a current on certain metal;

$n$  – is number of elementary platforms for all surface of an electrode;

$i_{f(x,y)}$  – is current of a platform depending on its co-ordinate.

There are some reasons to it. The main reason is non-uniformity of distribution of a current and thermal effects arising on a surface. Dynamics of heat-mass exchange becomes complicated also because of the collateral processes arising in blankets on border of metal-electrolyte solution. So as a result of the emerging Sore effect in the electrode area more mobile "light" components are moved to the "hot" region of space, and more "heavy" molecules in "cold" region of space. Thus the equation (1) will be transformed to the kind equation:

$$N = \sum_{i=1}^n k i_{f(x,y,i)} K(i),$$

$i_{f(x,y,i)}$  – is the function considering distribution of a current on layers;

$K(i)$  – is the factor, considering influence of thermal effects in blankets.

The greatest concentration of hydrogen is reached in the most remote from a substrate layers, as the number of defects increases in metal structure with increase in a thickness of a covering. Existing opinion on inverse relationship in kinetics of hydrogen pickup is possible to explain only by impossibility of complete extraction of hydrogen during the experiment. Another acknowledgement of our conclusions is carrying out of parallel tests of definition of hydrogen by a method of vacuum fusion, when all hydrogen, absorbed by the sample, is extracted.

Thus, distinctions in concentration of connection of metals with hydrogen in electrochemical systems type is defined by specific feature of formation of defects in structures of these systems.

**COMPUTER SIMULATION OF LITHIUM-ION BATTERY: CONSTANT CURRENT DISCHARGE, MODEL OF EQUIDIMENSIONAL GRAINS, CALCULATING PERCOLATION CHARACTERISTICS, ACTIVE GRAINS OF HOST, ROLE OF DIFFUSION LIMITATIONS, ESTIMATION OF WORK PARAMETERS OF THE ELECTRODES**

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Computer simulation of processes taking place at negative and positive electrodes of lithium-ion battery at galvanostatic discharge has been performed. The complete research program was accomplished according to general theory of porous electrodes. The program includes (i) investigation of the model of equidimensional grains these grains forming three-dimensional cubic lattice of sites, (ii) investigation of percolation behaviour of active layers, (iii) calculation of effective charge- and mass-transfer coefficients, (iv) development of the complete equation set describing the electrodes' functioning. The model of equidimensional grains describes a negative electrode consisting of two phases – an intercalator and an electrolyte, and a positive electrode consisting of three phases – an intercalator, an electrolyte, and conducting additive.

Some special cases of galvanostatic discharge are considered, specifically, "ideal" electrode; electrode with nanosized grains; electrode with thin active layer. Concept of "active intercalator grain" is introduced. Permissible volume concentration  $g$  of intercalator's grains in an active layer is shown to be limited by  $0 < g < 30\%$  for positive and  $35 < g < 65\%$  for negative electrode.

It is shown that average number  $\bar{N}$  of electrochemically active edges of active grains is less than 6 and is limited by  $1.8 \leq \bar{N} \leq 3.3$  for positive and  $1.9 \leq \bar{N} \leq 3.6$  for negative electrodes.

Optimum working parameters of the electrodes, specifically, volume concentration of intercalator, active layer thickness, whole discharge time, discharge capacity, and electrode polarization. The importance of grains' nanosize and sufficient electrolyte conductance are emphasized.

**SOME STRUCTURE EFFECTS IN THE NANODISPERSED  
Pt/C ELECTROCATALYTIC SYSTEMS**

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One of the main problems of electrocatalysis is determining the relationships between the structure of the electrode and its adsorption and catalytic properties. Adsorption and electrocatalytic reactions at the electrode-electrolyte interface are very sensitive to the structure of the solid phase. For a science-based creation of the catalysts with a view on their practical application requires an understanding of the nature of structural effects. Its role is particularly great in the nano-size systems.

Nanoparticles of supporting catalysts typically have a crystalline structure which different from the structure of solid phase. It can be as a consequence of the size effect as a consequence of the influence of the support that takes the active part during the formation of particles. In this paper we attempt to assess the role of structural effects on the example of one-component Pt/C nanocatalysts which was obtained by different methods. The structural, adsorption and catalytic properties of Pt/C catalysts with different loading of platinum (10 to 40%) and different Pt nanoparticles sizes (from 2 to 10 nm) was investigate. The catalysts were prepared by liquid-phase synthesis (ethylene glycol, oxalic acid or  $\text{NaBH}_4$  in water-ethylene glycol solution were use as reduction agents), by electrochemical dispersion of platinum, as well as the commercial catalyst E-TEK.

The selection of the electrocatalysts should be guided not only by the desire to maximize the use of platinum, which was achieved by creating the smallest possible particle size 1–2 nm. Need to take into account the peculiarities of adsorption in nanoscale systems also. The influence of the negative size effect of  $\text{CO}_{\text{ads}}$ ,  $\text{H}_{\text{ads}}$ ,  $\text{O}_{\text{ads}}$  oxidation in the range of Pt particle size 8–10 nm was much weaker than for small particles. The greater aggregative stability of containing larger particles catalysts is important too. The role of surface defects and their influence to the catalytic properties of nanoparticles now is only being discussed. The paper presents data that may provide evidence of its important role in the complex of factors that led to high activity and stability of the catalyst.

# EFFECT OF THE NATURE AND CONCENTRATION OF DOPANTS ENERGY OF METAL-HYDROGEN "IN ALLOYS"

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Interest in this process is becoming increasingly important in the development of new technologies to create materials for hydrogen batteries.

Such materials must possess a number of properties, namely: good mechanical properties, are resistant to thermal cycling, a sufficiently high corrosion resistance.

In addition the developed material with a fairly simple technology should be able to form a matrix of its branches open-circuited channel type (no closed labyrinths). The last condition is very necessary for the construction of high-mass storage.

Since the formation of chemical bonding of metal-hydrogen is most likely to defect structure, the primary role of the ligand in the alloy is reduced to the creation of the deformation stress in the structure of metal alloy. The deformation of the crystal lattice is usually taken to describe a stress deformation in the complex form:

$$\sigma = \sigma_0 e^{i\omega t}$$

where  $\sigma_0$  — amplitude of the voltage;  $\omega$  — circular frequency of oscillation.

Immediately strain can be determined by the expression:

$$\varepsilon = \varepsilon_0 e^{i(\omega t - \varphi)}$$

where  $\varepsilon_0$  — the amplitude of deformation,

$\varphi$  — the angle at which lag behind the deformation (the angle of loss).

It was experimentally found that for the alloy Ni-B dependence of the amount of dissolved hydrogen in the alloy on the concentration of boron in the structure of the graph  $V_{H_2} = f[C_B]$  has an anomalous failure for the concentration of boron in the alloy

Most likely the increased concentration of boron in the alloy, which forms the phase of implementation, leads to an increase in the number of defects per unit volume. Therefore, the ascending branch of the curve  $V_{H_2} = f[C_B]$  does not contradict logic. As for the falling branch of this dependence, there is observed the localization of the atoms of nickel valence electron of the boron atom with the formation of communication Ni-B. A sharp increase in hydrogen content in the volume of the alloy with increasing concentration of B can be explained by the interaction of hydrogen atoms with boron atoms, this means under these conditions, formation of hydride-type Ni-H and B-H.

We also found that the hydrogen in these cases forms a very unstable connection with these components. It is extracted from the samples already at room temperature.

To confirm the mechanism of formation of compounds expressed by the hydrogen in the alloys doped with boron. Need to conduct further experimental studies of structural-sensitive methods. We can assume that using the method of internal friction can be detected peaks of internal friction on the graphs of dependence  $Q^{-1} = f(T)$ . It can be assumed that their peaks are in the field of cryogenic temperatures and can be imposed on each other. In the range of helium can be detected peak of internal friction, which is characteristic for diffusion occluded model of molecular hydrogen. The results of this experiment allow a fairly accurate fix, in what form and how much hydrogen is contained in the sample.



## ELECTROCHEMICAL BEHAVIOR OF MICRO-GRAPHITE MODIFIED BY MULTILAYER CARBON NANO-TUBES

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The kinetics of hydrogen evolution reaction (HER) was studied on pressed micro-graphite and its composites filled with activated multilayer carbon nano-tubes (MCNT) in acid aqueous and ethylene-glycol solutions with the compound of electrolyte  $x$  M HCl +  $(1-x)$  M LiCl. MCNT with inside diameter 20–60 nm, length up to 1–2  $\mu$ m and specific surface  $144 \text{ m}^2 \text{ g}^{-1}$  were produced by catalytic pyrolysis of propane and butane mixture on a magnesium and nickel catalyst. The initial current-free potentials  $E_{\text{eq}} = 0.4\text{--}0.5 \text{ V}$  of unloaded pressed micro-graphite with cathode-polarization growth shift towards negative values in the section of limit current with HER output into the Tafel section. Under reverse move from  $E = -0.7 \text{ B}$  in situ at  $E_{\text{eq}}$   $i_{\text{lim}}$  ( $i_{\text{lim}}$  being cathode-current density), linear dependence remains up to  $E_{\text{eq}}$ , that is a large hysteresis loop takes place. After ( $\tau$ ) electrode hold at  $E_{\text{eq}}$  and further repeated cycling, the size of the hysteresis loop is determined by time  $\tau$ . At  $\tau \rightarrow 0$ , the loop is absent. The current-free potential of the pressed micro-graphite electrode, which does not contain MCNT, relatively quickly shifts towards the positive side after its preliminary hold for an hour at potential  $-0.7 \text{ B}$ . Two sections are observable on the curves at  $E = \tau$ ,  $dE/dt$  is high in the first one (in the range of small periods) and its extent is practically not related with hydrogen-ion concentration. In the second one,  $dE/dt$  is essentially decreased and attains value which is near or equal to zero. Filter introduction does not alter the quality, which allows for HER kinetic parameters:  $dE/dlg i$ ,  $dE/dlg C_{\text{H}^+}$  and  $dlg/dlg C_{\text{H}^+}$  at  $E = \text{const}$  and  $\eta = \text{const}$ . It may be presumed that under the studied conditions, HER runs, according to the Volmer-Tafel mechanism. Under the cathode polarization of micro-graphite modified by 2 wt. % MCNT in aqueous solutions, the Tafel section corresponding to hydrogen evolution reaction under reverse polarization move (from the cathode area) shifts towards the cathode.  $C_{\text{H}^+}$  growth leads to HER rate increase in accordance with the mechanisms of electrochemical kinetics. The values of  $dE/dlg i$ ,  $dE/dlg C_{\text{H}^+}$  and  $dlg/dlg C_{\text{H}^+}$  at  $E = \text{const}$  are equal to 0.140 B, 0.080 B and 0.1 respectively. 20-Time decrease in MCNT concentration (0.1 mass. %) leads to the following kinetic parameters:  $dE/dlg i = 0.160 \text{ B}$ ;  $dE/dlg C_{\text{H}^+} = 0.06 \text{ B}$  and  $dlg/dlg C_{\text{H}^+} = 0.50 \pm 0.03$  ( $E = \text{const}$ ). Evidently, in the first case, the stage of discharge  $\text{H}^+_{\text{aq}} + e \rightarrow \text{H}_{\text{ads}}$  is slowed down and so is that of recombination  $\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$  in the second one. Thus, the hydrogen coverage of the micro-graphite surface and the studied composites with MCNT on its basis and, therefore, the flow of its diffusion into a solid phase are regulated by the contents of the filler.

Under ethylene-glycol conditions, an extensive hysteresis loop is observable again in the absence and presence of MCNT on the cathode. The value of  $dlg/dlg C_{\text{H}^+}$  is equal to 1 (1.1 at  $E = -0.4 \text{ B}$ ), the values of  $dE/dlg i$  and  $dE/dlg C_{\text{H}^+}$  are equal to 0.180 and 0.095 B respectively. At HER proceeding ( $E = \text{const}$ ) the influence of the solvent nature on  $i_0$  value is observed. So, in the 2 wt. % MCNT presence (0.5 M HCl + 0.5 M LiCl,  $E = -0.45 \text{ V}$ ) the HER rate is equal to  $40 \text{ A/m}^2$  in the aqueous solution and  $8 \text{ A/m}^2$  – in the ethylene glycol one.

## FEATURES OF DECOMPOSITION OF GAMMA-BUTYROLACTONE ON THE LITHIUM ELECTRODE: THE THEORY AND EXPERIMENT

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Rechargeable lithium batteries are rather perspective chemical power sources. But there are a number of the problems caused by passivation of Li/ electrolyte interface. A corrosion of lithium metal and side reactions of decomposition of electrolyte components with gassing are possible at cycling in organic electrolytes. It results in decapsulation of power sources case and even to explosion.

The purpose of this work was experimental and theoretical researches of a decomposition reaction of gamma-butyrolactone (GBL) on lithium electrode surface during a charge. Then the potential of Li-electrode is displaced in negative area.

1M solution  $\text{LiClO}_4$  in GBL at water content 0.008 and 0.2 wt. % was used for studying side reactions of decomposition of electrolyte. The gassing process was studied in a fluid three-electrode cell at constant-temperature conditions (20 °C) at 0.5; 1.0; 1.5 and 2.0  $\text{mA}/\text{cm}^2$  current densities. The metal Li was used as working electrode, chlorine-silver – reference electrode, Pt – counter electrode. The contents and composition of generated gases at decomposition of electrolyte were analyzed by the gas chromatograph "Biochrome" and the mass-spectrometer MI 1201V.

The electrolyte decomposition wasn't observed at low water concentration. The  $\text{H}_2$ , CO and  $\text{CO}_2$  gases in comparable quantities and 5 hydrocarbons gases ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_3\text{H}_6$ ) are generated at current densities  $> 1.0 \text{ mA}/\text{cm}^2$  (overcharge) at water content 0.2 wt. %.

The quantum-chemical modeling interaction GBL with lithium surface was carried out for understanding of the basic features of the gassing mechanism. It was shown, that the energy barriers of reaction will be high in absence of water molecules. It corresponds to the experimental fact, that the gassing wasn't observed at minimally possible water content (up to  $10^{-2}$  wt. %).

The contiguous C-C- and C-O- bonds breakage with the energy gain was observed at modeling reactions of hydrolysis chemisorbed GBL molecules. In results propane and  $\text{CO}_2$  molecule in chemisorbed condition were formed, which have been found out experimentally. Formation of other products which have been found out in mass spectrums, apparently, was connected to passing parallel processes of main products reduction.

Thus, the decomposition reaction of electrolyte based on gamma-butyrolactone at water various content was investigated. The absence of gases products of GBL decomposition reaction at 0.008 wt.% water was experimentally shown. Formations superficial Li-organic compounds from GBL molecules were theoretically shown that was known from the literary data. The electrochemical GBL decay on  $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_6$ ,  $\text{H}_2$ , CO and  $\text{CO}_2$  was experimentally shown at 0.2 wt. %  $\text{H}_2\text{O}$ . The advantage of decomposition reaction superficial Li-organic compounds from GBL molecules with gassing was theoretically shown at the presence of water.

# POSSIBILITY OF USING ACTIVATED CNM IN ELECTROCHEMICAL ENERGY ACCUMULATION DEVICES

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The development of electrochemically reversible hydrogen accumulation processes assumes the use of materials with highly electrocatalytical activity in reaction of hydrogen evolution, hydrogen sorption capacity, providing necessary amount of charge-discharge cycles and corrosion resistance in water alkaline and acid electrolytes. The prior studies [1,2] show, that such materials can be nanocarbon materials, and also composites based on them.

The light-weight fraction of carbon nanomaterials (CNM), synthesized by electroarc method from methane-air mix at atmospheric pressure in presence of catalysts in A. V. Lykov Heat and Mass Transfer Institute of NAS of Belarus, was investigated. The CNM, obtained by ultrasonic division from total mass, were black powder with bulk density up to 0.8 g/sm<sup>3</sup>, consisting of amorphous carbon (not less than 59 %), carbon nanofibres with diameter 20–40 nm, length 1–15 µm and multiwall carbon nanotubes with diameter 20–80 nm and length 1–10 µm. Charge-discharge cycles were discretely carried out in potentiostatic, galvanostatic and potentiodynamic modes in 1 M H<sub>2</sub>SO<sub>4</sub> and 1 M KOH. The parameters of charging were optimized with the purpose of the fullest hydrogen saturation of investigated samples. The electrochemical, capacitor, hydrogen sorption properties of the CNM were considerably increased by electrochemical activation in concentrated electrolyte of sulfuric acid as a result of raising of structure deficiency, inoculation of functional groups, implantation of heteroatoms [1], and by sedimentation of cluster and ad-atoms of catalytically active metals.

The beginning of discharging of activated CNM on constant loading was characterized by the maximal values of specific current up to 1.3 A/g in 1 M KOH and 1 M H<sub>2</sub>SO<sub>4</sub>. The greatest convertibility in repeated charge-discharge cycles was observed at charging current to be 0.4 A/g and it was 93–95 %, but the maximal hydrogen sorption capacity reached 0.63 and 0.75 mas. % of hydrogen in 1 M KOH and 1 M H<sub>2</sub>SO<sub>4</sub>, accordingly. The CNM chemical modification of palladium microquantities in the low concentrated combined palladizing solution allowed increasing more than in 3 times hydrogen sorption capacity of CNM that, most possibly, was caused by surface formation of hell-atoms and clusters of metal palladium. The potential transients of hydrogen-carbon electrode were defined for palladized CNM and the diffusion factors of hydrogen in CNM were calculated. The increase of diffusion factors with raise of current density pointed distribution of process charging in deep structures of CNM.

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**THE INFLUENCE OF DIMEGIN PREADSORPTION AT BENZOTRIAZOLE ADSORPTION ON THE SURFACE OF A PASSIVE IRON ELECTRODE**

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The influence of disodium salt of deuteroporphyrin IX (dimegin) on the anodic behavior of mild steel in a borate buffer solution with pH 7.4, containing 0.01 M NaCl was studied. It was found that already at  $C = 5$  mkM the reduction of passivation current density occurs and potential of pitting increases by 0.23 V. Since the ability of dimegin to inhibit the steel dissolution can be connected with its adsorption on the electrode surface, its adsorption on oxidized iron electrode (at  $E = 0.2$  V) in borate buffer solution with pH 7.4 was studied by ellipsometric method.

The adsorption of dimegin itself is described by the Temkin equation with the value of free adsorption energy  $(-\Delta G_s^0) = 43.3 \pm 2.6$  KJ/mol. It was shown that the dimegin can be not only an inhibitor of anodic dissolution of iron but also modifier of electrode surface for increasing further adsorption of 1,2,3-benzotriazole (BTA) on it.

We carried out modifying of the oxidized iron electrode by dimegin at different surface coverage degrees  $\theta = 0.27-1.0$ , with following washing the cell by background solution without switch off the potential. In all cases the adsorption BTA on pre-modified surface increases in compared with adsorption on oxidized iron electrode. However the dependence of  $(-\Delta G_s^0)$  or the heterogeneity factor (the value  $f$  in Temkin isotherm) on  $\theta$  of dimegin preadsorbed at an oxidized iron is passed through maximum. Some possible reasons of the phenomenon is analyzed.

**SUPERHYDROPHOBIC NANOCOMPOSITE COATINGS FOR  
THE PROTECTION OF LOW-CARBON STEEL AGAINST CORROSION**

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Application of low-carbon steel for the production of construction materials requires the solution of the problem of anticorrosive protection of material surface. One of the methods of corrosion inhibition for porous metallic surfaces consists in the modification of a surface with impart the superhydrophobic properties to the surface. In this work superhydrophobic nanocomposite coatings, containing the layers with various chemical nature and various mechanisms of protection, are proposed.

Three types of coatings, different in composition and wetting behaviour with respect to aqueous media, were obtained and studied. We have analysed the resistance of coatings obtained against corrosion under both the continuous contact with aqueous media and the periodic wetting of surface exposed to 100 % humid atmosphere. The results of our investigations convincingly demonstrate that application of superhydrophobic coatings jointly with either oxidation or phosphatizing provides the sinergetic effect in anticorrosive protection of the composite coating.

## FUNDAMENTALS OF THE CREATION OF MIGRATING CORROSION INHIBITORS

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The strength and durability of reinforced concrete structures often depends on reinforcement corrosion state. Due to the alkalinity of the pore fluid, steel in concrete is passive provided that no chlorides are present. However, penetration of chlorides to the metal from outside, chloride additions during concrete preparation, and decreasing the pore fluid pH due to concrete carbonation create a hazard of reinforcement corrosion.

The problem of corrosion prevention can be solved using corrosion inhibitors. Such inhibitors are generally added during concrete preparation. However, an approach that is intensely developing in recent years is to protect steel reinforcement by migrating corrosion inhibitors (MCIs) that can penetrate the concrete stone and reach the steel reinforcement to slow down its deterioration. MCIs are applied onto the surface of a reinforced concrete article or added to concrete that is used in repair operations. The use of such inhibitors to ensure protection of structures that are already in use and are subject to corrosion shows high prospects. However, products available on the market show low efficiency. As we believe, this is due to weakly-developed scientific bases underlying the creation of migrating inhibitors.

It has been shown in our study that the ability of liquids to penetrate concrete and concrete stone is determined by the wetting of capillary pores. By selecting a surfactant one can vary broadly the permeability of solvents. It has been shown that the methodology of directed creation of MCIs can be reduced to (i) development of inhibitors efficient in the concrete pore fluid, and (ii) selection of surfactants that ensure inhibitor penetration into concrete stone.

A systematic study of the effect of structures of amines and substituted benzoates on the efficiency of steel protection in electrolytes simulating the pore fluid on concrete stone has been carried out. It has been shown that the protective effect of amines under these conditions depends on  $pK_a$  and is mainly determined by electrolyte alkalization. The contribution of adsorption to the protective effect is more significant for ethanolamines whose interaction with the metal is enhanced by the alcohol groups present in the molecule. It has been found that the protective effect of substituted benzoates and nitrite - benzoate formulations under the same conditions can be described by Hansch substituent constants in terms of the "linear free energy relationship" approach. The efficiency of steel protection by inhibitors decreases as hydrophilic or hydrophobic substituents are introduced in the aromatic ring.

Consideration of the above "structure - protection efficiency" regularities combined with rational selection of surfactants allow one to create highly efficient MCIs. Examples are provided to demonstrate the capabilities of this approach to the creation of MCIs.

**INFLUENCE OF TRIAZOL DERIVATIVES ON CORROSION  
OF STAINLESS STEEL IN MINERAL ACID SOLUTIONS****Avdeev Ya.G., Frolova L.V., Kuznetsov Yu.I.***A N Franklin Institute of Physical Chemistry and Electrochemistry,  
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New inhibitors of metal acid corrosion, which are triazol derivatives have been developed. Their investigation showed high effectiveness of low-carbon and high-strength steel protection from corrosion in acid solutions [1, 2], including even such temperatures as  $T = 100-140\text{ }^{\circ}\text{C}$  [3]. In the present work was investigated the effectiveness of stainless steel protection by new inhibitors, at etching of which many of conventional inhibitors, widely used for steel acid etching, show low effectiveness or stimulate corrosion during protection.

It is shown that corrosion of chromium-nickel stainless steel 1X18H9T in 2 M HCl or  $\text{H}_2\text{SO}_4$  proceeds in the area of active metal solution. New inhibitors effectively slow down both electrode reactions of steel 1X18H9T in these acids. They provide high degree of steel protection from corrosion ( $Z > 93\%$ ) and hydrogenation ( $Z > 77\%$ ) in 2 M HCl and  $\text{H}_2\text{SO}_4$  ( $T = 60\text{ }^{\circ}\text{C}$ ) even at low concentrations (5 mM), surpassing in this the famous industrial inhibitor of acid corrosion (catamin AB). Joint application of developed inhibitors with iodide and bromide anions in 2 M  $\text{H}_2\text{SO}_4$  increases retardation of corrosion process and steel hydrogenation substantially.

During etching of steel 12X18H10T in 2 M HCl and  $\text{H}_2\text{SO}_4$  at  $T = 80\text{ }^{\circ}\text{C}$  both triazol derivatives are also noticeably more effective inhibitors of acid corrosion than catamin AB. For their effectiveness in  $\text{H}_2\text{SO}_4$  solutions on this steel one can recommend additions of iodide and bromide anions.

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# CORROSION MECHANISM OF IRON AND LOW CHROMIUM STEELS IN THERMAL WATERS

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One of the major problems connected with the exploitation of geothermal hot water fields is corrosion of the thermal water installation. Thermal water is chemically aggressive system of  $H_2O-CO_2-H_2S$ . Its corrosion aggressiveness depends on the chemical composition of the water (salinity, acidity) and exploitation parameters such as flow rate, temperature and pressure. Choice of proper corrosion resistant materials for pipes, fittings and heat exchangers is essential for correct and economical operation as well of geothermal wells as of surface exploitation systems. The aim of the work is to present the mechanisms of anodic dissolution and corrosion of Fe-Cr alloys and low chromium steels in geothermal water of Geotermia Podhalańska S.A. (low salinity system of  $H_2O-CO_2-H_2S$ ) and Geotermia Stargard S.A. (high salinity system of  $H_2O-CO_2-H_2S$ ). Our investigations of the corrosion behavior of low-chromium steels, performed in field conditions, in operating geothermal heating stations, and in laboratory experiments, revealed that the corrosion rate falls nearly exponentially with chromium content in the steel [1]. The observations are consistent with the results obtained by Ueda [2] and López [3] for carbonic acid environments. Electrochemical investigations of Fe-Cr alloys (1 to 5%Cr) and low alloyed steels show that the corrosion of these materials in  $H_2O-CO_2-H_2S$  system proceeds in the prepassive range (see shadow area on Fig.1) and is controlled by protective properties of insoluble surface layer of corrosion product. SEM and EDX analysis of carbon steel and low chromium steels (1 to 5%Cr), exposed in Geotermia Podhalańska, indicates that the surface product consists mainly of magnetite, mackinavite ( $FeSi_2$ ) and small amounts of siderite  $FeCO_3$ . The layer becomes more compact, homogeneous and fine-crystalline with increase of chromium content in the alloy. It appears that low amounts of Cr stimulate the formation of dense well fitting to the metal surface anodic film. Potentiostatic transient experiments and electrochemical impedance measurements, performed on pure Fe-Cr ferrite alloys, show that the time of formation of surface layer decreases with increase of chromium concentration in the alloy. It seems that the high activity of chromium in the first seconds of anodic etching enhances oversaturation of metal surface in corrosion product, and promotes nucleation of anodic layer. Even negligible chromium content in the ferrite matrix acts as modifier of formation of protective layer of iron surface compounds (magnetite, sulphide). Fig.2 presents the effect of chromium on the growth of the layer.

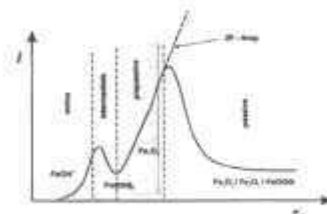


Fig.1. Anodic properties of carbon and low chromium steels in thermal water

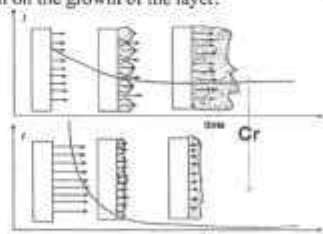


Fig.2. Scheme of the growth of anodic layer on the Fe-Cr alloy surface in the prepassive range

The corrosion rate Fe-Cr alloys depends also on the steel microstructure. Field experiments (LSV, EIS) and laboratory measurements (micro-electrochemical investigations) present that the eutectic phase with fine dispersed carbides (perlite) shows higher corrosion resistance than ferrite or martensite one. High dispersion of cathodic phases (carbides) promotes oversaturation of ferrite matrix in anodic product and nucleation of protective layer.

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## LOCAL CORROSION OF THE OIL REFINING COLUMN EQUIPMENT

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During research of the reasons and kinds of corrosion destructions of petroleum refinery column equipment the aggressiveness of raw materials and the operating conditions are traditionally considered. However the general corrosion stability is determined by integral influence of environment media and conditions at all operation phases and depends on aggressiveness of deposition of sediments and condensates of steam curing as well, those being comparable to aggressiveness of oil and processed technological media. The results of commercial corrosion tests of the St20 carbon steel and the 08X13 steel (main material of the plating layer) in the operating column equipment of primary oil refining units of the Kirishi petroleum refinery testify, that the total speed of steel corrosion in the operating conditions of the refinery units, with rare exception, does not exceed 0.05-0.06 mm/yr that being a good parameter. At such rate of corrosion the depth of corrosion destructions of thick-walled equipment (up to 40 mm) in operating conditions for the units being operating for more than 30 years, should not exceed 1.5-2 mm. However as the result of tests in all columns at operating conditions the pitting corrosion is registered, which depth, in comparison to the total corrosion size, is rather significant, in particular, on the 08X13 steel - the main plating material of the equipment.

The problem of local corrosion damages is aggravated with the fact, that presence of aggressive ions on the surface and in pittings, appearing not only from technological media and deposits, but also being formed during steam curing of the equipment during its repair, thus leading to the further pittings' development and regeneration and to corrosion cracking. During the periods of repair and maintenance inspection cases of corrosion cracking were registered in all columns manufactured of bilayered metals. Metallographic examinations have shown that cracks in welded seams, periscamal zones and plating layers, were characteristic for chloride cracking, being extended both by inter-, and transgranular ways, usually down to the base metal, thus its corrosion in a crack was sharply increased. The cracking, as a rule, began from the pittings. On the average in 4-5 years after detection of the welded seams cracking the development of cracks and ulcers of the total plating layer, down to its complete separation from the base metal and collapse, has been registered. Now for this reason at the petroleum refinery the scheduled replacement of columns with new ones is taking place.

The analysis of the real corrosion problems which have been found out during operation of units, shows the necessity to consider the propensity to local corrosion as the determining factor in comparison with the size of total corrosion when selecting the constructional materials of oil refining equipment. The results obtained show the groundlessness and unsuccessful selection of steel 08X13 as the plating material of the oil refining column equipment. In this connection, search of constructional metals with high pitting resistance for columns and other equipment plating is the extremely important and actual problem.

**CYCLIC THERMAMMETRY OF ELECTROCHEMICAL  
AND CORROSION PROCESSES: IDENTIFYING  
THE ROLE OF TEMPERATURE**

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The much-neglected role of temperature in electrochemical reactions is approached by the technique of cyclic thermammetry. "Thermammetry" is a word coined by the author to describe the measurement (-metry) of current (-am-, from ampère) as a function of temperature (therm-). The role of temperature is usually approached thermostatically, with the electrode potential as the prime electrochemical variable. Cyclic thermammetry is a technique which makes temperature the fundamental control variable, and consists of sweeping the temperature of an electrochemical cell linearly through heating and cooling cycles while the system is held under potentiostatic control. The technique shows the extreme sensitivity of electrochemical reaction rates to temperature. A detailed description of the role of temperature in the passivation of metals is presented. Descriptions of thermal reversibility and thermal irreversibility are described, and some novel reactions are discussed. Cyclic thermammetry reveals processes which are not identified by the results of conventional thermostatic experiments.

**PASSIVATION OF MILD STEEL BY INHIBITORS BASED ON ZINC COMPLEX WITH PHOSPHONIC ACID****Chirkunov A.A., Kuznetsov Yu.I., Filippov L.A., Sorokina O.V.***A.N. Franklin Institute of Physical Chemistry and Electrochemistry  
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Phosphonic acids and their complexes with metal cations are well known as corrosion inhibitors for neutral aqueous solutions. They are widely used for water treatment in circulating systems. The mechanism of their action is linked mainly with formation on metal surface of thin films consisting of barely soluble hydroxides and polynuclear complexes [1]. This mechanism allows one to assume that the phosphonate inhibitors can be used for creation of passivating layers on steel which are able to prevent the atmospheric corrosion.

A zinc complex of 1-hydroxyethane-1,1-bisphosphonic acid (HEDPZn) is known as effective inhibitor in neutral aqueous solutions. It has been shown that the films formed on steel surface in the solutions of HEDPZn allow to prevent an atmospheric corrosion for a time. Efficiency of such films is essentially affected by preliminary treatment of the surface, temperature and pH of a solution. The most stable layers are formed at 60 °C and neutral pH value, however, their protective action is comparatively low.

It is possible to improve the efficiency of HEDPZn by different additives, such as oxidizers, carboxylates or heterocyclic compounds. The problem of selection of additives lies in the fact that many of them can deteriorate the complexonate, causing its deposition in the solution. In this connection it is impossible to use some salts of higher fatty acids, for example, which also able to turn steel to passive state. Nonetheless some compounds can essentially enhance the protective properties of HEDPZn and the forming films have a high resistance in humid atmosphere. Some formulations based on HEDPZn with carboxylates and heterocyclic compounds was developed and investigated. The efficiency of steel protection by the formulations was 10 times higher than complexonate in itself, although the thickness passive layer was not over than a several tens of nanometers.

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**ELECTRODEPOSITION OF NICKEL COATINGS FROM LOW-CONCENTRATED GLYCINE-CONTAINING ELECTROLYTES****Dolgikh O.V., Vu Thi Duyen, Sotikaya N.V., Lytkina A.A.***Voronezh State University, Voronezh, Russia*

The purpose of this work was to study the possibility of using low-concentrated chloride, sulfate and acetate glycine-containing electrolytes for the electrodeposition of nickel coatings of high quality with a given set of properties.

The buffer properties of the investigated electrolytes were studied. It was found that the maximum buffer effect, they are display in acidic (pH 2.3) and subacidic (pH 4..6) media. The best buffer action have the acetate electrolytes which buffer capacity in the range of pH 4..5 exceeds that for the standard Watts electrolyte more than 350 times.

The influence of the nature of the background anion on the life duration of the nickel plating electrolytes was estimated. In the process of deposition pH and deposit appearance were controlled. The experiment was stopped when a pH of hydrate formation ( $pH_H$ ) was reached, as judged by the turbidity of the solution. It was found that the life duration of the investigated electrolytes correlates with their buffer properties:  $pH_H$  increases during the transition from glycinate-chloride to the glycinate-acetate solutions; increase in the concentration of glycine in the solution to a certain limit also improves  $pH_H$ .

We considered the impact caused by the anionic composition of the electrolyte on the peculiarities of the nickel coatings electrodeposition, their structure and properties. It was found that at low cathode current density ( $i \approx -5 \text{ mA/cm}^2$ ), the maximum current yield (CY) provides the chloride electrolyte, and the minimum – acetate electrolyte. This is due to the high polarization of the nickel ions reduction from acetate solutions. At the same time, in an acetate electrolyte we could receive the highest current yield when the current density was increased by 10 times due to its good buffer properties.

The role of the nature of buffer additives in the formation of surface morphology was investigated. Coatings deposited from chloride solution, are characterized by the presence of the largest spherical clusters of homogeneous size with distinct grain boundaries. In the sulfate solutions coating surface becomes smoother with separate spheroids of different sizes. On the coatings deposited from acetate electrolyte, there are virtually no traces of individual grains, but they are characterized by the presence of cracks, indicating considerable internal stresses.

This difference in the deposits morphology affects their properties. We estimated the catalytic properties of Ni-coatings deposited from electrolytes of various anionic composition, as well as their porosity, which determines the corrosion resistance. As a model reactions anodic oxidation of hypophosphite ion and cathodic hydrogen evolution were selected. It was found that the catalytic activity of coatings deposited from chloride electrolyte is very low, especially in the anodic process. Deposits received from the acetate solution, by contrast, exhibit good catalytic properties, due probably to their specific morphology.

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**ANODIC DISSOLUTION AND PASSIVATION OF SOME METALS AND HETEROGENEOUS ALLOYS DEPENDING ON ANION COMPOSITION OF MEDIA AND ORGANIC ADDITIVES****Ehlik V.Y., Berezanaya A.G., Tikhonileva K.S., Ogarev P.L., Misharov V.I.***Southern Federal University, Rostov-on-Don, Russia*

The anodic dissolution of lead, bismuth, tin, zinc, cadmium as well as of PbSn, CdBi, SnZn alloys has been studied by using non-steady-state and quasi-steady-state measurements depending on anion composition of media and on potassium oleate (PO), benzotriazole, and benzimidazole additives.

During the anodic polarization it can be observed a possibility of lead oxide passivation followed by sulphate depassivation and repassivation which is connected with a change of potential and pH value at the metal solution interface. The parts of the current allocated to lead dissolution, oxide and salt film formations have been determined. The information on a specific effect of additives has been obtained depending on their nature and on a type of film formed. The similarity and the difference between the anodic behaviours of lead and bismuth in the solutions without additives and with the organic compounds added has been determined and analyzed.

It has been shown that anodic processes on eutectic bismuth-tin alloy and additives effect are mainly determined by the second alloy component. Passive film composition is changed with an increase of  $\text{Na}_2\text{SO}_4$  concentration, therefore co-ordinate of anodic polarization peaks observed in sulphate solutions are changed accordingly. The organic additives have been found to be more effective inhibitors of eutectic alloy dissolution compared with pure bismuth dissolution.

It has been found that the rate of cadmium, bismuth and their alloy anodic dissolution rises with an increase of boron containing ions concentration ( $\Sigma\text{C}_\text{B}$ ) in borate buffer. Bismuth corrosion potential is decreased with increasing of  $\Sigma\text{C}_\text{B}$ . At the highest concentrations, the peak of the anodic polarization curve is revealed, and the currents of total passivation and transpassivation increase. However the potential of transpassivation is not practically changed. The anodic behaviour of alloy is similar to that of cadmium. Passive films are not destroyed, but on the contrary are tightened when the direction of polarization is changed. This is confirmed by the larger values of corrosion potential on bismuth and alloy.

It has been shown that an increase of tin content in SnZn alloys changes characteristics of the anodic polarization curve. The critical current of passivation and the current of total passivation decrease. Meanwhile, the current in passive range is more stable and is lower for alloys than that for pure tin. Inhibiting effect of PO is observed in the range of tin active dissolution only, while inhibition of alloys is observed both in active and in passive ranges. PO stimulates the active zinc dissolution. Protective effect of PO in passive range somewhat decreases with time. The time dependence of it in active dissolution range has a nonlinear character. The reasons of a difference in an influence of alloy components nature on the anodic behaviour of homogeneous as well as heterogeneous binary alloys and on the effectiveness of organic additives have been analyzed.

**ANALYSIS OF WETTING DYNAMICS AS A TOOL  
TO STUDY CORROSION PROCESSES****Bolnovich L.B., Rumyantsev A.M.***A.N. Frumkin Institute of Physical Chemistry and Electrochemistry,  
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The demanding problem for evaluating the efficiency of anticorrosive protection by various protective coatings is the creation of express methods allowing one to recover even very early stages of corrosion processes at metal surfaces.

One of the most promising methods is the analysis of the wetting dynamics. The contact angle value is determined by the structure and the state of the topmost material layer with tens of nanometers thickness, as well as by the structure of electric double layer at the metal/solution interface. Therefore any variation in the state of the surface due to electrochemical reaction, associated with a corrosion process, will immediately be reflected in the change of contact angle, allowing thus analysing the character of interaction between the metal surface and the corrosion-active media in situ. The sensitivity of contact angle value to processes at the surfaces essentially exceeds the sensitivity of many other analytical methods. The important advantage of the method presented here in its application to the problem discussed in this paper consists in the possibility to infer the conclusions on the mechanisms of reactions, taking place at the surface, on the basis of combined analysis of the behaviour of contact angle and contact diameter of the drop of testing liquid. Besides, it is possible to investigate the corrosion processes in various media by the appropriate choice of the test liquid.

The method based on the analysis of wetting dynamics was employed in our work to study the kinetics of corrosion and the protective efficiency of the coatings developed in A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences.

## MAGNETIC FIELD OF CORROSION PROTECTOR ELEMENTS

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The development of the methods of the finding and control of magnetic field promoted the reanimations of the interest to questions of the influence of the magnetic phenomena on electrochemical and corrosion processes. It's considered for a long time that in consequence of small value of magnetic forces, acting on ion components, magnetic fields not capable to cause essential change of kinetic of physical and chemical processes on metal/solution interface.

This opinion was connected first of all with relatively weak magnetic fields, used in study. For example, magnetic inductions ( $B$ ) of natural and technical magnets using in most measurements falls into category of weak ( $B \sim 10^{-4} - 10^{-2}$  T). The appearance ferrite magnet on base Nd-Fe-B-powder materials has allowed to use in scientific study magnetic fields with  $B$  to 1.5 T. In new modern plants (similar to Large Hadron Collider ( $B \sim 10$  T) or separators of mineral-concentrating plants ( $B \geq 10^3$  T)) magnetic forces are more important. In such cases the possible influence of magnetic field on electrochemical and corrosion processes are very essential.

The renewal of the interest to corrosion process in magnetic field is bound with appearance sensitive magnetometers also, capable to register the magnetic induction  $B$  in intervals  $10^{-10}$  nT (IMP-04) and  $10^{-6} - 10^{-9}$  nT (SQUID-magnetometer). SQUID-magnetometer, using fine measurements Josephson junctions current, successfully lead, in particular, at study of very small magnetic fields of biological objects and processes, accompanying change of metal films structure.

Use protector, i.e. material with electronegative potential  $E_p$  to the stationary potential  $E_s$  of the protectable metal, brings about appearance on surfaces of the metal galvanic couple and electric current in corrosion environment. The density of this current  $i$  (on order of the value) is equal  $i \sim \sigma(E_p - E_s)/r_s$ . Here  $\sigma$  – electro-conductivity of environment, and  $r_s$  – a typical size of the protector. The electric current in corrosion environment is accompanied the appearance of the magnetic field strength  $H$ . For quantitative estimation of the strength appearing magnetic field use the calculation for magnetic field of conductor with current.

So, assuming that side-boundary of the protector similar solenoid with current, for value of the induction appearing magnetic field it's possible to write  $B \sim \mu_0 \mu \sigma \Delta E$ . Here  $\mu_0$  and  $\mu$  – magnetic constant and magnetic permittivity of the environment, accordingly. Having substituted in brought formula of importance  $\mu_0 \sim 1.26 \times 10^{-6}$  H/A<sup>2</sup>,  $\mu \sim 2$ ,  $\sigma \sim 3$  Sm/m,  $\Delta E \sim 1$  B), shall get  $B \sim 7.5 \times 10^{-6}$  T that is found within possibilities modern magnetometers.

The more strict calculations executed for two wide-spread types protector (circular and striped), confirm the brought estimations of the magnetic induction value.

In below-mentioned publications [1] are brought some of the result of the use SQUID-magnetometer for study corrosion processes.

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## THE FEATURES OF STEEL PROTECTION AGAINST HYDROGEN SULFIDE CORROSION BY VOLATILE AMINES

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In the case of new fields design and rise necessity of working life of old fields the important task remains the most reliable and safety operation of hardware in oil-and-gas industry. Inside corrosion of field equipment and pipelines causes significant financial costs, that is more serious in the presence of sour components in hydrocarbon raw materials ( $H_2S$ ,  $CO_2$  etc.). It is inhibitor protection that is the most efficient way to struggle against corrosion under corresponding condition. However, widely used contact inhibitors are able to protect steel against  $H_2S$ -corrosion (HSC) in case of its preliminary coating on protected surface only. Such inhibitor layers are not able to self-recover on conditions of integrity breaking, for instance by gas stream. Volatile corrosion inhibitors (VCI) are possessed of that property, so they are able to vaporize, saturate a gas phase and adsorb from it on a steel surface [1].

In view of the design priority of efficient and accessible VCIs against HSC for native oil-and-gas industry the protective properties of more than 30 volatile compounds were studied by us. Investigations were carried out in media modeling the real environment of gas-condensate field.  $H_2S$  concentration in vapour phase was 2–15 vol. %, range of studied media pH 3.6–8.4. It is assign that aliphatic secondary and tertiary amines demonstrate better protective action among compounds under consideration. But demand level of protection found in specific range of  $C(H_2S)$  and pH only [2]. Protection by the amines is considerably reduces under low  $H_2S$  content in vapour phase and/or alkaline region of pH values. It is caused by appearance of modification in sulfide film structure which is able to possess a protective role in some degree and promote the amine adsorption. It is known [3–5] that electrochemical impedance spectroscopy (EIS) are one of the *in situ* methods to evaluate properties of different films on metal and inhibitor adsorption on it. Try to apply EIS to detection of some VCIs action features has been undertaken by us in this work.

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**ELECTROCHEMICAL SYNTHESIS OF COATINGS IN MOLTEN SALTS  
FOR PROTECTION OF MATERIALS FROM OXIDATION****Kuznetsov S.A.***Institute of Chemistry, Kola Science Centre of Russian Academy of Sciences,  
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Materials based on graphite are widely used in present-day technology, mostly in aerospace techniques, because of the unique properties of graphite. However, a drawback of graphite is its low heat resistance in oxidizing atmospheres. To increase this heat resistance, siliciding and borosiliciding are currently used. Such articles are operable in a limited period of time at temperature up to 1200 °C only.

By electrochemical synthesis in NaCl-KCl-NaF-K<sub>2</sub>HfF<sub>6</sub>-K<sub>2</sub>NbF<sub>7</sub> melt HF-Nb coatings of the  $\alpha$ - $\beta$ -composition with the thickness 20-40  $\mu$ m were obtained on articles from borosilicizing graphite. It was found that niobium in hafnium-niobium alloys stabilize the low temperature monoclinic modification of HfO<sub>2</sub> formed during oxidation. Due to this the exploitation of graphite articles with HF-Nb coatings can be increased up to 2100-2200 °C.

The results of electrochemical synthesis in molten salts of hafnium, zirconium, niobium, tantalum borides are discussed too. It was shown that these compounds are promising materials for protection of graphite from high temperature oxidation.

Protective Mo-Si-B coatings were obtained on molybdenum substrate by synthesis in molten salts. In this process, the Mo substrate was first silicided to produce a MoSi<sub>2</sub> layer, which was boronized in a subsequent step. It was determined that during boronizing of MoSi<sub>2</sub> several boride phases are formed and heat resistance of the composition Mo<sub>2</sub>B<sub>3</sub>-MoSi<sub>2</sub>/Mo increases in the next row: MoB<sub>4</sub>>Mo<sub>2</sub>B<sub>3</sub>>MoB<sub>2</sub>>MoB. The optimal regimes of boronizing, which led to the formation of MoB<sub>4</sub> in the bulk MoSi<sub>2</sub> phase were found. Study of composition materials MoB<sub>4</sub>(12-15 wt.%) - MoSi<sub>2</sub>/Mo with the coating thickness 5-7  $\mu$ m, obtained at current density 5 mA cm<sup>-2</sup> and temperature 800 °C showed that no pest disintegration of the molybdenum substrate was observed in an air-water mixture at 900 °C after 700 hours.

A new generation of highly active and stable catalytic coatings Mo<sub>2</sub>C/Mo for the water-gas shift reaction by high-temperature electrochemical synthesis in molten salts has been developed. This catalytic coatings can be used both for the low and high temperature water-gas shift reaction. The coatings were stable at 450 °C during the thermal cycling, while the activity of commercial catalysts tends to decrease with time.

## SOME PERSONAL ADVENTURES IN EXPLORING THE PASSIVE STATE

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All reactive metals that are used for structural, electronic, or decorative purposes, such as aluminum, chromium, nickel, iron, zirconium, magnesium, and many others, and the alloys of these elements, owe their kinetic stabilities to the formation and continued existence of a "passive" oxide film on the surface that effectively separates the reactive metal from the corrosive environment. This film was initially detected by Michael Faraday in 1833 as the result of his famous "iron in nitric acid" experiment. Since that time, numerous models have been devised to describe the properties of the passive film, which commonly forms as a bilayer structure comprising a point-defective barrier layer and a porous, precipitated outer layer. In the case of all metals and their alloys, the barrier layer, which grows directly from the metal and which is usually designated as MO (e.g., NiO), has a accurate formula of  $M_{1+x}O_y$ , where  $x$  and  $y$  describe the non-stoichiometry of the phase, with  $y > 0$  for an oxygen-deficient phase, due to the existence of oxygen vacancies, and  $x > 0$  for a metal-rich phase due to the existence of cation interstitials or cation vacancies (in which case  $x$  is negative). The first two defects dope the barrier layer n-type in electronic character. Contrariwise, if  $x < 0$ , corresponding to a cation-deficient phase, due to the existence of vacancies on the metal sub-lattice, the oxide is doped p-type in electronic character and hence the electronic properties of the barrier layer can be used to ascertain the dominant defect in the system. On the other hand, the outer layer forms via the hydrolysis of metal cations that are ejected from the barrier layer and the subsequent precipitation of a hydroxide, oxyhydroxide, or oxide, often in the form of a porous film that contains species from the solution (e.g., borate). These species are never found to be present in the barrier layer, whereas alloying elements present in the substrate metal are generally found in both the barrier and outer layers. These observations are consistent with the origins of the barrier and outer layers being direct growth from the metal and precipitation, respectively. The present talk will review what is known about the passive film that forms on metals and alloys under anodizing conditions and will show that the formation and breakdown of the film is well-described by the Point Defect Model (PDM) that has been developed by the author over the past three decades. The PDM also identifies strategies for producing more corrosion resistant surfaces via chemical or physical modification of the outer layer. Some of these strategies are already practiced in the anodizing industry (e.g., sealing, chromate conversion coatings), but others are less-well developed (e.g., photoinhibition of passivity breakdown). Modification of the barrier layer in terms of interaction of mobile point defects (e.g., cation vacancies) with immobile foreign cations on the cation sublattice is also an attractive strategy, particularly for improving pitting resistance, but it has not been explored in a comprehensive manner.

**DEVELOPMENT OF CHEMICAL-GALVANIC PROCESSES FOR LITHOGRAPHIC PRODUCTION OF 3D MICROSTRUCTURES**

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The paper discusses lithographic and galvanic processes, which are the major components of LIGA techniques. The fabrication of X-ray masks (XRM) and the copying of the diffractive optical lens are used as examples.

The fabrication of XRM is an obligatory initial stage of LIGA-technology for production of any microstructure with deep channels (up to 200  $\mu\text{m}$ ) and a high aspect ratio (up to 100:1). An XRM is an X-ray opaque pattern of the future microstructure supported by an X-ray transparent wafer, for example, a glassy carbon one. Contrast ratios of the XRM to different absorbers were calculated for the radiation source (X-ray synchrotron radiation, a VEPP-3 accelerator, Budker Institute of Nuclear Physics SB RAS, Novosibirsk), and Re and Au were demonstrated to be the best absorbers.

The paper reports the results of the electrodeposition of a Re-Ni alloy (90-95 wt % Re) from sulfate and acetate electrolytes onto XRM blanks. In the first case, if current density is 5-10  $\text{A}/\text{dm}^2$ , the average deposition rate about 8  $\mu\text{m}/\text{h}$ , current efficiency 20-30%, and the final coating thickness 20  $\mu\text{m}$ , the coatings are gray, undulating, very high-stressed, and with a continuous network of large microcracks. Using an acetate electrolyte allowed us to stabilize solution pH during the electrodeposition and to obtain light gray, lower stressed coatings with a Re-Ni alloy. Nevertheless, microcracks cannot be fully eliminated from a 20- $\mu\text{m}$ -thick cathode deposit even in this case.

Gold is a more promising absorber for XRM. It was deposited onto XRM blanks from sulfite-thiosulfate and citrate-cyanide electrolytes. As is not the case with Re, both electrolytes yield continuous and dense Au deposits, which assure the required high contrast (100-150) if they are 20-30  $\mu\text{m}$  thick. A citrate electrolyte produces higher quality and more fine-crystalline Au coatings.

The central problem in copying the flat diffractive element was high internal stress inside the electrodeposits (especially Ni ones). It results in local separation of the conducting strike layer (chemical silvering) and distortion of the copy microtopography. A flat copy can be obtained with the required accuracy in the following way. First, a thick (40-50  $\mu\text{m}$ ), low-stressed copper layer is deposited onto a silver sublayer. After that, the flat copper copy is separated from the original (together with the sublayer), and a thin (1-2  $\mu\text{m}$ ) functional Ni layer is deposited onto its face from a sulfamate electrolyte.

*The study was conducted under integration project No. 55 of the Siberian Branch of the Russian Academy of Sciences "X-ray LIGA Techniques for Synthesis of 3D Diffraction Structures"*

# INFLUENCE OF CONCENTRATION OF SODIUM HYDROXIDE ON ELECTROCHEMICAL DESTRUCTION OF NICKEL ALTERNATING CURRENT

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The method of cyclic voltammetry (CVA) and preparative electrolyses for electrochemical behavior of nickel was studied in solutions of sodium hydroxide with a concentration of 1 to 17 M for the imposition of a sinusoidal alternating current of industrial frequency. CVA were obtained on a stationary disk, using a nickel microelectrode, generator GZ-113, potentiostat EP 22, ADC-DAC module 16/16 Sigma USB and PC.

It is shown that as a result of anodic polarization in alkaline solutions Origin of walk-forming oxides of variable composition of nickel  $Ni \rightarrow NiO \rightarrow Ni_3O_4 \rightarrow Ni_2O_3 \rightarrow NiO_2$ . In the cathodic half-cycle is a restoration of the surface oxide layer, and mechanical sloughing does not restore some oxide with gaseous hydrogen. It formed ultramicrodispersy powder the oxide of nickel black.

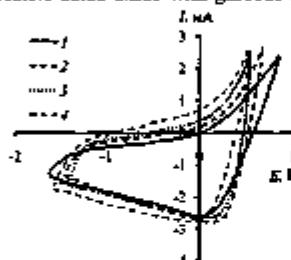


Fig. 1. CVA, taken on a nickel electrode in sodium hydroxide solution at  $T = 70\text{ }^{\circ}\text{C}$ , 50 Hz and concentrations: 1 - 1 M, 2 - 5 M, 3 - 10 M, 4 - 17 M.

With increasing concentration of sodium hydroxide, other things being equal, there is an increase rate of destruction of nickel electrode. Increasing the concentration of sodium hydroxide leads to a shift in the anodic half-cycle of achievable current capacity in the negative direction (Fig. 1). In solutions of sodium hydroxide with a concentration of 1...5 M at the electrode surface forming dense, thin oxide films, but 10...17 M solution on the electrode surface formed unconsolidated porous layers of oxide, which facilitates the removal of hydrogen excreted in the cathodic half-cycle current. The time required for the accumulation of significant oxide layer and the beginning of the destruction of the electrode with increasing concentration of alkali markedly reduced.

When the polarization of nickel with the potential scan rate 2 V/s in 1 M solution of sodium hydroxide amount of electricity recycled in the anodic process ( $Q_a$ ) formation of oxides  $Ni_3O_4$  and  $Ni_2O_3$  commensurate with the amount of electricity recycled in the recovery of these oxides ( $Q_k$ ). Increasing the concentration of sodium hydroxide leads to an increase in the ratio  $Q_a/Q_k$  and alkali concentration is 17 M it reaches 4.94.

Obtained by us ultramicrodispersy powder of nickel oxide was tested in the catalytic synthesis of carbon nanomaterials.

The work was done in the framework of the analytical departmental for special purpose program of the FSPP "Scientific and scientific-pedagogical cadres Innovative Russia" in 2009-2013 years.

## CORROSION OF METALS AND ALLOYS IN IONIC LIQUIDS

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Ionic Liquids (ILs) are salts composed of large and non symmetrical ions [1]. Such irregular shapes prevent the ions packing neatly, so that the salts are liquids even at room and lower temperatures. The own conductivity permits the electrons transfer from metallic material to the media, and, potentially, corrosion phenomena may occur. During the last few years, they have been widely investigated for a variety of applications: the use as solvents for chemical synthesis [2, 3], media for electrodeposition of metals [4–6], electrolyte for electrochemical devices such as batteries [7], supercapacitors [8], fluids for thermal storage and exchange in solar concentrating power plants [9], as additives to prevent corrosion in aqueous solutions [10]. Many of such industrial applications have required investigating the interactions between metals and alloys and the ILs to establish their chemical activity as possible corrosive agents. The study is resulted challenger because of both the not trivial chemical-physical characterization of the room temperature molten salts (thermal stability, conductivity, viscosity, vapor pressure, mass transport issues and so on) as well as the need of a deep revision of the application of the model and the methods of the corrosion study used in aqueous solution or in molecular liquids solvents.

The corrosion behavior of several ILs, especially based on bis(trifluoromethylsulfonyl)imide anion were investigated in contact with a variety of metals and alloys (copper, nickel, brass, carbon and stainless steels, Inconel) by room temperature electrochemistry techniques and by immersion tests up to 200 °C. The nature of corrosion morphology has been deeply investigated by SEM and EDAX analysis and the depth profile of the interaction layer by SIMS spectrometry. All the investigations were conducted in the ILs 'as purchased' and in open to air conditions. The results show a complex behavior of the different combinations of substrate and ILs. In several cases, important corrosion phenomena were observed that can be attributed at the presence of ILs impurities and at the presence of dissolved oxygen (from air). The investigated topics will be the object of future studies being crucial in the path for the characterization of the ILs corrosion behaviors.

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## SELF-ORGANIZATION PHENOMENA IN THE PROCESSES OF GROWS AND CORROSION OF Ni-P COATINGS

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The analysis of the topography and microstructure of growing Ni-P coatings as well as the analysis of the spectra of oscillations of the plating potential during the electroless nickel plating revealed the elements of self-organization of the electroless nickel plating process.

The topography and microrelief of Ni-P coatings obtained by the electroless nickel plating were investigated by using the methods of the 3D non-contact profilography, interferential microscopy (New view 5000, Zygo) as well as by scanning electron microscopy (Hitachi S-3400N).

The study of the microstructure and microrelief of the growing Ni-P coatings revealed that depending upon the conditions of plating the growth of the coatings may occur by either the lateral or normal growth mechanisms. The former mechanism results in the formation of spheroids, which are highly elongated in the plane of the base plate, while the later mechanism leads to the formation of spheroids with the axial ratio less than 10. The transition from the former to the later mechanism occurs due to a decrease of nickel ion concentration at the growth front and an increase in the catalytic activity of the coating surface for the anodic reaction of oxidation of  $\text{NaH}_2\text{PO}_2$ . The limiting case of the normal growth mechanism is the formation of globular dendrites followed by a "decomposition" of the electroless nickel plating solution.

Self-organization upon the nickel plating is also revealed by monitoring the periodic oscillations of the plating potential, the amplitude and frequency of which are depend upon the chemical composition of the plating solution as well as the plating conditions.

The electrochemical studies were carried out using Solartron-1255A device with the electrochemical interface 1287. To analyze the oscillations, the frequency spectrum was obtained by the fast Fourier transform of the oscillations of the plating potential using packages MATLAB 7.4 and Origin 8. We found that the low frequency oscillations (with the oscillation period  $> 100$  s) are related to the formation of the lamellar structure of the coatings and change in the catalytic activity of the coating surface for the anodic reaction of oxidation of  $\text{NaH}_2\text{PO}_2$ . The oscillations with shorter periods (10–100 s) are predominantly caused by the cathodic reactions of formation of nickel and hydrogen. Thus, the oscillations of the plating potential and change of the coating growth mechanism depending on the conditions of the electroless nickel plating reveal the elements of self-organization of the studied system.

The phenomenon of self-organization could also be revealed in the corrosion-electrochemical behavior of Ni-P coatings, which has been investigated in the neutral chloride- and sulfate-containing media as well as in the acidic sulfate-containing media ( $\text{pH} = 0.5\text{--}3.0$ ). Self-organization is revealed in a complex dependence of the corrosion rate on time in the acidic sulfate-containing media and in some peculiarities of the anodic dissolution of the coatings. This happens because of formation of the phosphorous enriched boundary layer at the surface, which is followed by its degradation upon further anodic dissolution of the coating.

## SYNTHETIC DIAMOND ELECTRODES: THE STRUCTURAL AND SEMICONDUCTOR EFFECTS

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Owing to its extraordinary chemical stability, diamond is a perspective electrode material for using in the theoretical and applied electrochemistry. The electrochemical behavior of diamond electrodes was studied by electrochemical impedance, cyclic voltammetry, and spectroscopy techniques.

The electrode activity in electrolyte solutions was measured for homoepitaxial boron-doped CVD diamond thin films, grown by hot-filament technique on (111)-, (110)-, and (100)-orientated dielectric diamond substrates. The acceptor concentration, determined from the slope of Mott-Schottky plots, decreased in the sequence [polycrystalline]  $\sim$  (111) > (110) > (100), which can be explained by different intensity of the dopant (boron) incorporation into differently orientated diamond crystal faces during the film (or single crystal) growth. The rate of electrochemical reactions in the  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  redox systems decreases in the same sequence, in full agreement with the recently found interrelation between the kinetics of electrochemical reactions on diamond electrodes and their doping level [1]. By and large, the effect of crystal face orientation on the diamond electrode electrochemical activity boils down to the variation of dopant concentration in the electrodes.

Electrochemical properties of the *n*-type diamond films are studied for the first time. The films of sulfur-doped synthetic diamond were chemical-vapor-deposited using co-doping with sulfur and boron. Electrochemical, thermoelectric and Hall measurements showed that the sulfur-containing films grown from a gas phase lean in boron are *n*-type, whereas those grown with higher boron content are overcompensated, hence, *p*-type. The Mott-Schottky plots and cyclic voltammograms of the *n*-type semiconductor diamond electrodes are mirror-symmetrical to those of *p*-type diamond [2].

The effect of the surface morphology, in particular, surface roughness (which varied from 0.1 to  $\sim 10 \mu\text{m}$ , the true-to-geometrical surface area ratio, up to  $\sim 3$ ) was investigated. Generally, the differential capacitance followed the true surface area of the electrodes. The electrode reversibility in the  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  redox system increased with increasing surface roughness: the transfer coefficients increased, the potential difference for the anodic and cathodic current peaks in cyclic voltammograms decreased. The apparent increase in the reversibility of the reaction can be explained by the decrease in the true current density [3].

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**CORROSION AND ELECTROCHEMICAL BEHAVIOUR OF MOLYBDENUM AND TITANIUM SILICIDES IN DIFFERENT AGGRESSIVE MEDIA****Rakityanskaya I.L., Patokina O.U.***Perm State University Perm, Russia*

Metal silicides are the wide class of the substances which have interesting electric and magnetic characteristics. They are very prospective new materials for science and technique because of their chemical stability, the corrosion and mechanical resistance and the possibility of formation in low temperature conditions.

The investigation of anodic behavior of the molybdenum disilicide  $\text{MoSi}_2$  and titanium disilicide  $\text{TiSi}_2$  was done using voltammetry and CV curves, SEM and micro X-ray spectroscopy. The corrosive media were the solutions of  $\text{NaOH}$  and  $\text{H}_2\text{SO}_4$  having different concentrations.

In 0.1–3 M  $\text{NaOH}$   $\text{MoSi}_2$  is more resistive against corrosion than his pure components – molybdenum and silicon. The potentiostatic curve has the peak of active dissolution at 0.17V. After it the interval of passivity was registered. The reason of passivity is the formation of the protective layer on the surface of material which contains the mixture of molybdenum oxide and silicon oxide. In 0.05–2.5 M  $\text{H}_2\text{SO}_4$  the corrosion resistance of  $\text{MoSi}_2$  is higher in comparison with pure Mo also. The main reason of high corrosion stability is the formation of surface protective layer consisted of  $\text{SiO}_2$ . The addition of the fluoride-ions in the solution decrease the corrosion stability of  $\text{MoSi}_2$ , in comparison with solution containing only sulphuric acid, because of desolating the protective layer from the surface. The content of the elements in surface layer after anodic polarisation was fixed by SEM and micro X-ray spectroscopy. In both acid and alkaline solutions the percentage of molybdenum on the surface is decreasing and the percentage of silicon is increasing. Most likely that silicon on the surface is in  $\text{SiO}_2$  form protecting the material from the dissolution.

The corrosion resistance of  $\text{TiSi}_2$  in the 1 M  $\text{NaOH}$  is between the same characteristics for the pure silicon and pure titanium. For  $\text{TiSi}_2$  the current density on the voltammetry curve in the passive interval of potentials is three orders less then for pure silicon and one order higher then for pure titanium. In sulfuric acid the dissolution rate for  $\text{TiSi}_2$  is like for pure Ti. The current density on this curve is five order less then for silicon. SEM and micro X-ray spectroscopy demonstrate that ratio of titanium and silicon is equal after anodic polarisation  $\text{TiSi}_2$  in different electrolytes. This fact shows that the both components of material take the equal participation in interaction with corrosion media.

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# FORMATION AND SOME PROPERTIES OF PLASMA-ELECTROLYTIC PROTECTIVE OXIDE COATINGS ON ALUMINUM AND TITANIUM

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The method of electrolytic formation of oxide surface layers on conducting materials under anodic, alternating anodic-cathodic, and cathodic polarization conditions as a result of spark, arc, or propagating electric discharges in the near-electrode region is called the microarc, microplasma, or the plasma-electrolytic oxidation (in the further text, PEO).

Alumina protective coatings on aluminum alloys were prepared by PEO technique in electrolyte with  $\text{Na}_2\text{B}_4\text{O}_7$ . The microstructure, phase composition, elemental distribution, and micro-hardness of alumina ceramic coatings were investigated. The fabricated samples were composed of  $\gamma\text{-Al}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3$ . Micro-hardness test shows that the prepared coatings are of high hardness, which can satisfy the requirements for the mechanical application, Fig. a).

The films formed on titanium in aqueous solutions of  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  under galvanostatic conditions by PEO method contained considerable amounts of zirconium and, correspondingly, crystalline zirconium oxides. The films had a small number of pores, were dense and poorly wetted with water, Fig b) and c). They are of interest as candidates for protective systems.

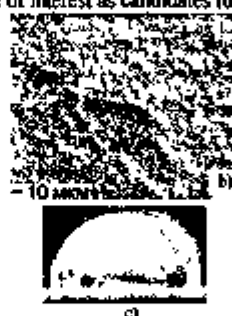
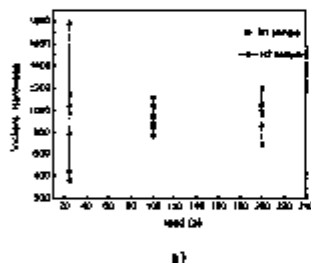


Fig. Micro-hardness of some samples measured under different loads (a). Surface organization (electron-microscopic images) (b) and the profile of a drop of distilled water placed at the film surface (c).

Oxide-phosphate layers with a thickness of 20-150  $\mu\text{m}$  were obtained on titanium by PEO in aqueous electrolytes with polyphosphate complexes of zirconium (IV). The coatings contained  $\text{ZrP}_2\text{O}_7$ . These coatings are of interest as thermal-resistant ones.

The coatings containing titan, zirconium and cerium oxides were formed on the titanium. The coatings contained 2-3 at. % of the cerium. The addition of the barium salt to the used electrolytes promoted crystallization of the cerium oxides. The coatings obtained were smooth and dense; they practically were not moistened of the water. The compositions  $\text{TiO}_2 + \text{ZrO}_2 + \text{Ce}_2\text{O}_3/\text{Ti}$  can be perspective as candidates for corrosion protection and catalytic application. The approach described can be applied for formation of coatings with various rare-earth metals.

The iron-containing oxide coatings on aluminum produced by PEO had ferromagnetic properties. The coatings with a thickness of 30-120  $\mu\text{m}$  contained up to 20 at. % Fe. The measured coercive force, 40-100 Oe, was closer to the values corresponding to magnetically hard materials. Temperature dependences of remnant magnetic moments were evidence of some ferromagnetic order in the oxidized surface layer.

## NANOSTRUCTURAL OXIDES FORMATION ON ALUMINIUM AND TITANIUM

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New possibility of use for oxide films, formed on aluminium and titanium with an anodizing treatment have been found recently. Anodizing allows through the self-organizing oxide formation to create the regular and coherent superficial structures with the cells sizes about 200 nanometers.

Formated with anodizing technique oxide may have a regular porous structure with poros diameter from several to tens nanometers. It may be employed as a catalyst carrier for further fills with various additives and give the nanostructural material with unique physical properties. First of all, it concerns the creation of new type of semi-conductor, optical, and also magnetic sensors. In any case the purpose is to obtain a regular nanoscale porous oxide on the surface of aluminium and titanium.

Oxide films consist of two layers: -thin porousless oxide layer of barrier type (the thickness about 0.01-0.03 microns), directly contacting with a metal, and the porous layer representing the basic oxide body. The oxide film on aluminium is not a monolithic oxide, chaotically penetrated by channels, but consists of dense packing oxide cells in a form of hexagonal prisms with the coaxial pores, normally directed to a surface and soldered on lateral sides.

The sizes and regularity of pores depend on an anodizing solution composition and the electrochemical regimes and the temperature. The cleanliness and structure of aluminium and titanium are also have an important effect for the cells regularity. A surface of the films was investigated by means of atomic force microscopy (AFM).

The samples of aluminium, anodized in 10 %  $H_2SO_4$  at 5-20 mA/cm<sup>2</sup>, form the nanotexture of hexahedral pores, surrounded with hexahedral oxide ledges. The minimum pores size is about 15 nanometers. Photo-electric polarization technique was used to study the mechanism of the phenomenon. It has been shown that the pores initiation is caused by the cation vacancies supersaturation in the surface layer and their segregation with pores germs generation.

The porous titanium oxide formation occurs in the fluoride-ion containing environments (1 M  $H_2SO_4$  + 0.15 % HF). Well prepared titanium surface started to polarize from the corrosion potential up to 20V with the scan rate of 100 mV/s. Then the potential maintained at this level. The current thus decreases with a time and some oscillations were observed. The oxide of nanotubular structure formed as a result. Such prepared samples were coated with platinum microparticles. For comparison the same treatment was employed to the oxidized titanium with smooth oxide. Platinization in both cases improves, both anodic and cathodic electrochemical properties of the surface. However the efficiency of the platinized sample with nanotubular oxide is better.

**CORROSION STABILITY OF ALUMINIUM AND TITANIUM ALLOYS WITH MICROARC COATINGS**

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One of the modern and perspective methods of prescribed composition oxide coatings formation on metals is microarc oxidizing carried out under anodic polarization and electrical and thermal breakdown of barrier films in water and water free electrolytes

Microarc oxidizing technology allows forming coatings with various unique properties high hardness, corrosion stability, wear resistance, etc

Titanium and aluminum alloys possess many valuable technological and operation qualities, therefore essential interest represent oxide coatings which contain dopants compounds of d- and f-elements

Variation of corresponding electrolysis modes, electrolyte composition, the polarization current form allows to change the qualitative composition of coatings in a wide range and to improve their functional properties essentially

This work reports the experimental results and the analysis of microarc coatings formation kinetics in galvanostatic and pulse modes from the electrolytes containing the compounds of vanadium, tungsten, molybdenum, manganese, cobalt and cerium. Dependence of composition, morphology, thickness, durability of adhesive bond and other properties of oxide coatings from modes microarc oxidizing is established. Influence of the above mentioned compounds on phase and element structure of the received coatings on titanium and aluminum alloys is defined. The composition of electrolytes and modes of microarc electrolysis on the specified alloys for the purpose of obtaining oxide coatings with high wear resistant and corrosion stability is optimized.

The corrosion behavior of titanium and aluminum alloys with oxide coatings obtained by microarc oxidizing is investigated by impedance spectroscopy method in solutions of sulfuric acid, sodium chloride and sodium hydroxide. Impedance frequency dependences received at the exposition in sodium chloride solution are alike the semicircle and are characterized by high values of charge transfer resistance both for microarc oxide coatings and for the anodic coatings received by classical oxidizing technology. The geometry of impedance hodographs on titanium alloys with a film of natural oxides in the concentrated sulfuric acid solution has a classical appearance of two semicircles with the centre on a material axis. The microarc coatings presence on titanium and aluminum alloys surfaces essentially changes a kind of sample's frequency dependences: the charge transfer resistance increases on three orders of magnitude that specifies on high corrosion stability. Microarc oxidizing leads to increase titanium and aluminum alloys open circuit potentials in comparison to samples with natural oxide films and classical anodic coatings.

Thus, as a result of researches it is established that microarc oxide coatings and coatings received by classical oxidizing under exposition in neutral environments possess high anticorrosive properties, however microarc oxidizing leads to substantial increase in corrosion stability of titanium and aluminum alloys in sulfuric acid and sodium hydroxide solutions.

## **CORROSIVE-ELECTROCHEMICAL PROPERTIES OF NANOCOMPOSITE MATERIALS ON THE BASIS OF IRON AND CARBIDES OF TRANSITIONAL METALS**

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Carbides steels, which are composites with a carbide consolidating phase in a viscid metallic matrix, belong to perspective composition materials. Physical and chemical properties of carbides steels are determined by dispersion and by volume contents of carbide phase. From this point of view production and research of nanostructured analogues of carbides steels obtained by the method of mechanical alloying presents some interest. Research objects were compactive composition materials  $\alpha$ -Fe carbides of iron, titanium, vanadium and niobium, got by the dynamic pressing of the powder-like systems, prepared by the method of mechanical synthesis. The synthesis was conducted in the ball planetary mill by different ways: mechanical alloying of mixtures of powders and iron with the prepared carbide in the environment of argon, mechanical activation of metals in liquid organic environments, including different additons.

In all cases nanocrystalline materials were formed with the size of grain  $\alpha$ -Fe from 10 to 40 nm. Substantial influence of terms of mechanical chemical synthesis on the amount and morphology (sizes and mutual location) of including of carbide phases was established. In particular, carbides being milled in organic environments form the nanosized reticulated structure.

Electrochemical properties of the obtained composites are investigated in the wide range of environments, modeling the most widespread cases of corrosion: sulfuric (pH = 0.4–2.9), sulfate-alkaline (pH = 12–13.7), borate solutions (pH = 6.3–9.0), neutral chloride solutions (10–4–0.5M NaCl).

The most meaningful factor in the corrosive conduct of composites is the content of cementite, characterized by the higher over voltage of dissolution. Due to this factor with the height of his maintenance rises pitting resistance of the composites is increasing, and the interval of concentrations of chlorides when the formation of pitting is possible is decreasing. High activity of cementite is shown during the cathode selection of hydrogen in acid environments, especially at the size diminishing. Incorporations and formation of the cementite reticulated structures.

The influence of the nanocrystalline state is revealed only in the processes of active dissolution of the composites and only in acid environments. The protective ability of passive films does not depend on the presence of plenty of borders of grains ferrite/ferrite and ferrite/cementite, but carbon accumulated on the surface at dissolution. If there is carbide of titanium in the composites, their passivation in neutral environments is conditioned mainly by forming mixed oxides of  $\text{FeO-TiO}_2$  on the surface.

*The work is supported by the programs "Physics of new materials and structures" "Scientific bases of creation of by volume nanocomposite corrosive-proof materials on the basis of iron with the refractory phases of introduction"*

# CORROSION BEHAVIOR OF SINTERED NdFeB MAGNETS ALLOYED WITH COBALT AND DYSPROSIUM

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High energy products NdFeB-based magnets find a rapidly growing variety of applications. However, strong galvanic interaction among phases constituting magnet, oxidation tendency, as well as hydrogen absorption capability of the rare earth elements are the causes of the poor corrosion resistance. Addition of dysprosium improves the intrinsic coercivity of NdFeB magnets at the expense of remanence, with the increase of Dy and Nb contents more stable intermetallic phases develop within the intergranular regions [1]. Co and Ga additions reduce the rate of initiation and propagation of pitting corrosion of NdFeB based magnets [2].

Besides the change in the composition of a magnetic material for magnification of its corrosion resistance and mechanical characteristics, protective plating is also used. Plating is carried out in rather aggressive solutions.

Studies of magnets corrosion behavior were carried out in the solutions containing background components of acid and alkaline electrolytes for plating. These solutions corresponded to the electrolytes based on simple metal salts, as well as complex compounds. Disc specimens of 15 mm diameter and 3 mm thickness were cut out from the sintered alloys of the nominal composition  $Nd_{10}Fe_{70}B_6$  and  $Nd_{15}Dy_{12}Fe_{73}Co_{5}B_6$ . All magnets specimens were in demagnetized state. Electrochemical corrosion studies were performed in terms of quasistationary anodic and cathodic potentiodynamic polarization measurements at the open circuit potential at a scan rate of 0.5 mV/s. The corrosion studies were carried out in aerated solutions, no-stirring.

The potentials of corrosion for the alloyed magnets in all the studied background solutions showed more positive values (by 25–200 mV, depending on a composition of the solution and magnets immersion time in it), as compared to the magnets without dysprosium and cobalt additives. The corrosion currents in weakly alkaline (pH 8.5) background solutions are lower for the alloyed magnets. The slowly formed products of corrosion were strongly bound to the substrate; the weight of the magnets increased at the initial immersion period under certain circumstances. However, the corrosion rate of the alloyed magnets was 2–3 times higher in the weakly acidic solutions (pH 4.5). Both in the weakly acidic, and in the weakly alkaline solutions, the presence of the ligands forming strong solvable complexes with the components of magnets, led to the considerable growth of corrosion rate for both magnet types (by 1–2 orders).

The results of studies can be used for the selection of electrolytes for electroplating of magnets, as well as for the surface treatment before plating without degradation of magnetic properties of the material.

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## EFFECT OF ENVIRONMENT EXTERNAL FACTORS ON CORROSION CRACKING OF LOW ALLOY AND AUSTENITIC STEELS WITH SLOW STRAIN RATE IN HIGH PARAMETERS WATER

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In long-term nuclear power plant practice service with water-cooled and water-moderated nuclear reactors it is occurred damages of equipment elements which contact with deionized water with 200–300°C and equilibrium pressure

Metallographic analysis of damage character establish that they are caused by the simultaneous influence on metal process of stress under slow rate of deformation and corrosive environment and identified as metal corrosion degradation by slow strain corrosion cracking mechanism (SSCC)

Electrochemical nature of corrosion cracking depends on combination numerous external and internal factors which determine metal stationary potential in each metal-environment system

The report consider the influence of temperature in the range of 200–340°C dissolved oxygen concentration, chloride-ions content, pH value of environment on steel corrosion cracking under load with slow strain rate ( $1.4 \times 10^{-7} \text{ s}^{-1}$ )

It was researched the behavior of secondary coolant circuit basic constructional metal RU VVER – of low alloy steel 10GN2MFA and austenitic steel 08H18N10T in conditions of SSCC

Low alloy and austenitic steels are inclined to SSCC under the strain rate of  $1.4 \times 10^{-7} \text{ s}^{-1}$  in deionized water and containing chloride-ions high parameters solution

Extreme decrease of ductility for these steels is typical in 200–290 °C environmental temperature range

The degree of sensitivity to SSCC is evaluated by complex metal structure combination, parameters and environmental oxidizing properties, chemical potential of metal

Nature of experimentally received destructions is identical to destruction which are observed in real service conditions

# THE MODERN APPROACH TO THE TASKS SOLUTION OF ANTICORROSIVE PROTECTION OF FIELD PIPELINES

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Corrosion of the industrial equipment and pipelines is one of the principal causes of decrease of their operational resource. Nowadays the solution of effective decrease of corrosion rate task requires development of new approaches such as modeling of corrosion processes and development of computer systems of decision support of estimation of corrosion risk and protection problems. There are some types of corrosion, the contribution of carbon dioxide corrosion in destruction of pipelines under influence of the transported media (stratal water) is considerable. At the same time along with this process occurs parallel proceeding process of salt deposition ( $\text{CaCO}_3$ ) which has considerable influence on steel corrosion rate. The authors developed corrosion models for the information computing system and the algorithm of corrosion rate calculation  $V_{\text{cor}}$  on the basis of these models, the parallel proceeding process of salt deposition was taken into account. At the same time there is no need to carry out expensive monitoring of witness samples for calculation of  $V_{\text{cor}}$ , it is enough to determine chemical indicators (pH, the general mineralization ( $M$ ), concentration of elements ( $C_{\text{Cl}^-}$ ,  $C_{\text{HCO}_3^-}$ ,  $C_{\text{CO}_3^{2-}}$ ,  $C_{\text{Ca}^{2+}}$ ,  $C_{\text{Mg}^{2+}}$ ,  $C_{\text{Na}^+}$ )) and technological parameters (flow rate ( $V_{\text{max}}$ ) and temperature ( $T$ )) in the corrosion media sample. Use of this system will allow receive data on a corrosion situation in on-line a mode that will help to prevent breakouts connected with considerable emissions, the material losses causing an economic and ecological damage on the objects in proper time.

The following transformed model of  $V_{\text{cor}}$  calculation which takes proceeding process of salt deposition into account is suggested:

$$\lg V_{\text{cor}} = 3.996 - \frac{1730}{273.2 + t} + k_s + 0.365 \cdot \lg P_{\text{CO}_2}, \quad (1)$$

where  $k_s$  – state factor of system's pH in case of salt deposition.

In the suggested model the influence of the limited number of factors of the media on processes of corrosion and salt deposition is considered. With the reference to field objects for account of more significant factors another model of  $V_{\text{cor}}$  calculation formalized as follows is suggested:

$$V_{\text{cor}} = \frac{F(Y) - F(Y)_{\text{min}}}{F(Y)_{\text{max}} - F(Y)_{\text{min}}} \cdot V_{\text{max}}, \text{ mm/year}, \quad (2)$$

where  $V_{\text{cor}}$  – corrosion rate calculated by the results of the factor analysis of the media on the basis of stratal water (chemical and technological indicators), mm/year,  $V_{\text{max}}$  – maximum corrosion rate measured on object (real), mm/year,  $F(Y)$  – estimator.

The category of media corrosion power is determined on the basis of the results of calculated  $V_{\text{cor}}$  and the decision on the necessity of protective actions (inhibition) is issued.

The information computing system developed by authors is applicable for objects of gas and oil producing industry where there is a problem of carbon dioxide corrosion.

## PERCOLATION EFFECTS INTO METAL-ION EXCHANGER NANOCOMPOSITES

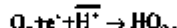
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An interest to nanostructured electrodes is concerned with the presence of the numerous interfaces allowing essentially to intensify electrochemical processes. To increase an aggregate durability and stabilization of metal nanoparticles various polymeric and coal materials are used. A special class of carriers is represented by ion-exchanging matrixes (membranes, fibers, granules). On it's basis composites with volume distributed metal in the set quantity can be created.

In this work the condition of chemically deposited copper in macroporous sulfocation-exchanger CU-23 15/100 is studied. Data obtained with the use of scanning electron microscopy (SEM) has shown particles of copper in the size of 300–600 nanometers, which are ensembles of smaller particles with approximate value of 36–52 nanometers defined by the X-ray analysis. In its turn, large metal formations, revealed by SEM, represent the ensembles consisting of crystals with diameter of about tens nanometers, and that allows to speak about nanostructured copper condition in ion-exchanging matrixes. Electronic conductivity of nanocomposite metal-ion-exchanger is defined. Dependence of conductivity and quantity of chemically besieged metal has a percolation character [1].

Electrochemical activity of a composite copper-ion-exchanger is studied in reaction with oxygen electroreduction. It was found that a high proton concentration in the ion-exchange matrix causes a decrease in the oxygen reaction overvoltage in comparison with a neutral solution by ~0.2 V due to the ion involvements in the slow stage



We have worked out the similar effect at oxygen reaction on the dispersed silver – ion exchanger CU-23 and metal ( $Cu^0$ ,  $Ag^0$ ) – ion-exchange membrane MC-40 composites. This very effect does not depend on the nature of the deposited metal and is caused only by the ion-exchange matrix property such as high cation-exchange capacity.

The nanostructured state of copper particles causes stabilization of the intermediate product, i.e., hydrogen peroxide. As opposed to the compact copper electrode the polarisation curve of oxygen electroreduction on the copper – ion exchangers nanocomposites possesses two waves in the neutral solution. At the nanostructured copper particles stabilized by the ion-exchange matrix, the parity of speeds of formation and reduction of hydrogen peroxide, which is the intermediate product of oxygen reaction, is changing that leads to its accumulation in the near-surface layer. It is important that the additional wave on the polarisation curve is not observed at oxygen electroreduction on the silver-containing composite in which metal particles are not the nanostructured formations (more than 100 nm). The electrochemical response of such electrode material is similar to the response of the compact metal electrode. Using the rotating disk electrode method, it was detected that the process is limited by external diffusion of oxygen to composite grains. The oxygen reaction is mostly concentrated on the grain surface and surface layers; oxygen is reduced in the bulk due to dispersed copper oxidation [2].

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**ELECTRODEPOSITED Ni-P-COATINGS AS CATALYSTS  
FOR HYDROGEN EVOLUTION REACTION****Dolnik O.V., Sotskaya N.V., Kravtsova Yu.G.***Voronezh State University, Voronezh, Russia*

Ni-P alloys are of undoubted interest to researchers as an electrode material having a good catalytic activity in the hydrogen evolution reaction (HER), but data on their catalytic properties are few and contradictory. The aim of this work was a detailed study of the catalytic activity of electrodeposited nickel-phosphorous coatings in a wide range of compositions in the reaction of hydrogen evolution from solutions of sulfuric acid.

For Ni-P-coatings deposition we applied glycine-acetate electrolytes with different sodium hypophosphite concentration, allowing to obtain Ni-P deposits with phosphorus content from 0 to 12.6 wt.%. Coatings were deposited in the galvanostatic mode at room temperature.

The structure and morphology of freshly deposited Ni-P alloys of different composition were investigated. It was established that all of them have primary texture (200), the fraction of which reaches 1 when the phosphorus content is 7.2 wt.%. There are some cracks on the surface of Ni-P-coatings whose grid becomes more pronounced with increasing of the non-metallic component content.

The main parameters of hydrogen evolution reaction from acidic solutions on Ni-P-alloys were found. Namely, the reaction rate at constant overpotential  $i_H$ , and hydrogen overpotential  $\eta_H$ . It was established that the inclusion of phosphorus in electrolytic nickel in an amount up to 6.5 wt. % had almost no effect on the rate and overpotential of the investigated reaction. Further increase of phosphorus content in the alloy causes drop of  $\eta_H$  and acceleration of  $i_H$ .

The contribution of the surface development and actual catalytic properties of the studied materials in the acceleration of hydrogen evolution was estimated. To this purpose we normalized  $i_H$  values to the corresponding values of relative roughness factors. It was found that Ni- and Ni-P-coatings containing small amounts of phosphorus (1 %) show extremely high catalytic activity in hydrogen evolution reaction: the speed of the process is more than an order of magnitude higher than that on compact nickel. With increasing of phosphorus content catalytic properties of the coatings become worse, and when the phosphorus content is more than 6.5% the reaction rate goes to the level of compact nickel and does not change with further changes in the alloy composition.

Thus, the nature of the acceleration of HER by alloys of various composition is different: the actual catalytic activity have only coatings containing up to 6 wt. % of phosphorus; for Ni-P-coatings enriched by phosphorus reaction acceleration is achieved only through significant development of the surface, which, however, does not prevent them use as electrode materials.

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## COMPARISON STUDY OF THE CURRENT-VOLTAGE CURVES PARAMETERS OF DIFFERENT COMPOSITE MEMBRANES ON THE MF-4SC BASE

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Methods of perfluorinated membranes modification for fuel cells are intensively developed now. The various additives lead to water immobilization in the membrane increase of thermostability of polymer, and also preparation of composite catalyst systems. The comparison study of composites on the base of MF-4SC membrane and modifying additives of organic and inorganic type was carried out by membrane voltammetry method. Polyvinyl alcohol, polyvinyl butyral, sulphonated polysulphon, hydrogen zirconium phosphate, polyaniline and nanodispersion of platinum were used as modifying agents. The current-voltage characteristics (CVC) of composites in the "free standing" state were measured by method described elsewhere [1]. The CVC of the initial MF-4SC samples with various exchange capacity, water content and thickness were measured to estimate of influence effects of the various modifying additives. The parameters of CVC to be used for testing of membrane are as follows: the slope of the ohmic portion ( $\Delta E$ , S/m<sup>2</sup>), the limiting current value ( $i_{lim}$ , A/m<sup>2</sup>), the length of limiting current plateau ( $\Delta$ , V), and the potentials of the transitions into limiting ( $\Delta E_{lim}$ , V) and overlimiting ( $\Delta E_{ov}$ , V) state.

It was revealed that the  $\Delta E$  value is the same for membranes modified by hydrophilic polymers because the membrane contribution in the general resistance of system is not essential. It was discovered the  $i_{lim}$  value decrease on 10–15 % after inclusion of hydrogen zirconium phosphate and the platinum dispersion. The parameter  $\Delta E_{ov}$  of hybrid membranes is above 1.3 V in the case of hydrogen zirconium phosphate and above 1.0 V in the case of the platinum coating, whereas for the initial membrane this value is 0.8 V. More essential effects of the CVC parameters change were discovered in the case of MF-4SC membrane modified by polyaniline. The polyaniline intercalation in the template matrix leads to the change of the  $\Delta E_{ov}$  parameter from 0.8 up to 3.2 V [2]. It has been shown that the plateau length depends on the type and concentration of solution, characteristics of the initial membrane and polyaniline oxidation degree.

The asymmetry of CVC at the current reverse is found in the case of MF-4SC after surface modification by polyaniline [3]. The effect of asymmetry is the most essential for parameters  $\Delta E$ ,  $\Delta E_{ov}$  and  $\Delta$  in HCl solutions. The asymmetry of CVC is observed for platinum-coated MF-4SC also. The reasons of these effects are discussed taking into consideration the chemical type of additives, the water reorganization in the membrane nanostructure, and the formation of concentration profile inside the membrane.

*The work is supported by Russian Foundation for Basic Research (project # 09-08-00609).*

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# SELF-ORGANIZING CATALYTICALLY ACTIVE LAYERS OF OPPOSITELY CHARGED COMPONENTS

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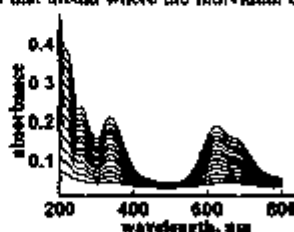
One of the most effective ways of surface modification is the method of the electrostatic coverage by the layer of oppositely charged substances (layer-by-layer technique, LbL-method). Formerly we have synthesized polylayer composition of ultrathin anionic layers of silicododecamolybdate ( $\text{SiMo}$ ) and cationic ones of polyallyl ammonium or palladium [1, 2]. This LbL-composition has catalytic activity at the electrochemical reduction of  $\text{HNO}_2$ .

The formation of self-organizing layers from oppositely charged components is possible for phthalocyanines, containing anionic or cationic substituents. But in contrary to self-formation of silicododecamolybdate film on glassy carbon surface the pretreatment of glass is necessary for formation of phthalocyanine self-organizing film on it. It was shown that after such pretreatment in polystyrenesulfonate (PSS) solution it is possible to form up to 30 bilayers of copper(II) phthalocyaninetetrasulfonic acids ( $\text{CuTsPc}$ ) – polydiallyldimethylammonium (PDDA) on glass, conducting glass and quartz ( $\text{CuTsPc}$  is an anionic component, PDDA is a cationic one).

The possibility of synthesis of layers by LbL-method for cationic phthalocyanine Alcon blue, pyridine variant (AB) and PSS (anionic component) is shown at the figure. Nafion can also be used as anionic component.

The formation of the layers by LbL-method is a rather hard process. This is why we have developed a simpler method – the formation of salts between cationic and anionic components in the process of pouring the solution at the surface. The interaction between components of salt gives rise to loss of solubility in that media where the individual components are soluble (table).

Film	Medium		
	$\text{H}_2\text{O}$	$\text{H}_2\text{SO}_4/\text{H}_2\text{O}$	DMF
$\text{CuTsPc}$	+	+	–
AB	+	+	+
$\text{CuTsPc-AB}$	–	–	–
PSS-AB	–	–	–
PDDA- $\text{CuTsPc}$	–	–	–
$\text{CuTsPc-PdCl}_2$	–	–	–
AB- $\text{SiMo}$	–	–	–



Electronic absorption spectrum of composite Alcon blue formed through polystyrenesulfonate at quartz (13 bilayers)

The films containing phthalocyanine salts are electrochemically active in the solution of DMF,  $\text{Bu}_4\text{BF}_4$  in the potential region from 0 to  $-1600$  mV (s.e.). The film formed from two phthalocyanines has the most reversibility.

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# **SYNTHESIS OF POLYMERIC FILMS BY INITIATION OF POLYMERIZATION OF ACRYLIC MONOMERS BY METAL ZINC IN AQUEOUS MEDIUM**

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Electrochemical initiation of polymerization (EIP) of monomers is one of the perspective methods for creation of functional materials and coatings. It lets to form electro isolating, antifriction, protective, decorative, immobilizing and composite coatings. Moreover, it is also efficient for obtaining of double-layer asymmetric porous membranes for ultrafiltration, nanofiltration and reverse osmosis. Such membranes were synthesized on the base of cross-linked co-polymers obtained by polymerization of acrylamide, formaldehyde or N,N'-methylene-bis-acrylamide and zinc chloride was used as an initiator [1-3].

We stated that metal zinc may be used as an alternative polymerization initiator of the above-mentioned monomer composition in the currentless regime. In order to form polymeric films, a steel plate was covered by layer of electrodeposited zinc. After immersion of such an electrode into a monomer aqueous solution, the former is covered with a uniform and transparent polymeric film. Dynamics of the polymeric layer growth is investigated. It is stated that at first the speed of the coating growth is comparable with EIP kinetics or even somewhat higher than the latter. Then, the process is retarded and becomes stationary, and thickness of the film does not practically change.

The mechanism of initiation is studied. It is stated that chemical interaction between zinc and acrylamide in aqueous medium results in formation of the hydrated complex [acrylamide- $\text{ZnOH}^+$ ]. The standard exchange current of zinc is known to be equal to  $i_0 = 7 \times 10^{-1} \text{ A cm}^{-2}$ . This value is comparable with that of the cathode current density in the EIP process. Therefore, the current density of zinc exchange is sufficient to provide the complex discharge producing acrylamide radicals  $[A^\cdot]$  which initiates monomer polymerization. Thus, initiation of polymerization of acrylic monomers with metal zinc in aqueous medium in the currentless regime has electrochemical nature. And polymerization proceeds in the conditions similar to potentiostatic regime.

The structure of polymeric films obtained under influence of metal zinc is studied using the light microscopy method with differential-interference contrast. It is stated the film contains a morphologically isolated thin dense layer at the side adjacent to metal in the process of synthesis. The size of this layer was about 12-13 microns; the total film thickness equalled ~480 microns. Formation of the dense layer is conditioned by specific adsorption of acrylamide on metal. Thus, initiation of acrylic monomer polymerization with metal zinc lets to form the films with asymmetric structure which may be used as membranes for biocompatible processes.

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## CATALYTIC ACTIVITY OF PEDOT/Pd COMPOSITES IN RESPECT TO HYDROGEN PEROXIDE ELECTROREDUCTION

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Poly-3,4-ethylenedioxythiophene (PEDOT) is one of the most promising conducting polymers which possess high electrical conductivity and good chemical stability. In p-doped state this polymer is well suited as a conducting polymer matrix for loading of small particles of metals for fabrication of novel composites with interesting electrocatalytic, electroanalytical and optical properties.

In this work, the spontaneous deposition of palladium nanoparticles into PEDOT films is ascribed to the redox reaction between reduced fragments of PEDOT and  $\text{Pd}^{2+}$  ions due to their high oxidation potential.

X-ray photoelectron spectroscopy (XPS) data confirmed the presence of metallic palladium in the polymer. Morphology of the pristine and composite films, as well as the size of Pd nanoparticles and their distribution were characterized by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The electrochemical properties of composite materials obtained were investigated by cyclic voltammetry, EQCM and electrochemical impedance spectroscopy.

The systematic study of test electrode processes such as reduction of hydrogen peroxide on PEDOT/Pd-electrodes has been performed. It was found that the electroreduction process predominantly proceeds on palladium nanoparticles acting as nanoelectrode array. The obtained kinetic data show that with an increase of density of Pd particles in composite films the limiting currents of electroreduction are increased and reach a saturation at highest Pd-loading. It was suggested that the rate of hydrogen peroxide reduction proceeding on Pd nanoparticles in acid and neutral electrolytes, is controlled by diffusion and by electron-transfer steps. The porous network structure of PEDOT supports an effective dispersion of Pd particles and facilitates an easy access of reagents to the catalytic sites.

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## **SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF PEDOT/Au NANOCOMPOSITES**

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Poly-3,4-ethylenedioxythiophene/Au (PEDOT/Au) composite films were obtained by electroless deposition of highly dispersed gold particles into PEDOT film from solution of  $\text{HAuCl}_4$  with varied concentration ( $5 \times 10^{-2}$ – $5 \times 10^{-3}$  M) in 0.1 M  $\text{H}_2\text{SO}_4$ . Spontaneous deposition of gold takes place due to the redox reaction of reduced fragments of PEDOT film with  $\text{AuCl}_4^-$ -ions acting as oxidizing agent.

The EQCM measurements were applied for the observation of Au-loading processes and estimation of amount of gold incorporated into PEDOT film. The fact of inclusion of gold particles into PEDOT films with formation of PEDOT/Au composite was also confirmed by means of EDX analysis. The morphology of PEDOT/Au nanocomposite was investigated by scanning electron microscopy (SEM). SEM images show highly microporous structure of both pristine and composite films. The surface of polymer is covered by gold nanoparticles in the case of composite film. Transmission electron microscopy (TEM) revealed more details about the size and distribution of gold nanoparticles. As was found from TEM images, the mean size of the particles and degree of their agglomeration is dependent on synthesis conditions.

The electrochemical characterization of PEDOT/Au composites was performed by using cyclic voltammetry measurements in solutions of 0.1 M  $\text{H}_2\text{SO}_4$  and the same solutions with addition of various concentrations of chloride ions. CVs of pristine PEDOT and composite PEDOT/Au films recorded in 0.1 M  $\text{H}_2\text{SO}_4$  show that the values of oxidation/reduction currents practically coincide in the potential range from -0.3 to 1.0 V and they are determined by the film charge/discharge processes, while the participation of gold nanoparticles in charging processes is not observed. Introduction of chloride-ions into electrolyte solution caused the appearance of a new couple of redox peaks which are associated with formation of gold oxidation product and its reduction. The oxidation process of gold particles was found to be of the first order with respect to chloride-ions. The parallel CV and EQCM data suggest that approximately one chloride-ion is transferred per one electron during the process of oxidation of gold with formation of gold(III) chloride complexes as a product.

Based on the mass changes and electrode kinetic data it was proposed that gold clusters in PEDOT/Au composite have porous or dendrite-like structure. It is consistent with TEM-images of some gold clusters at higher magnifications – agglomerate structures, formed with smaller metal clusters of approximately 10 nm diameter are observed. The electrocatalytic effects of Au nanoparticles incorporated into PEDOT matrix were studied for some test electrode reactions such as oxidation of ascorbic acid and dopamine and reduction of hydrogen peroxide in phosphate buffer solutions.

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**ELECTROCHEMICAL SYNTHESIS OF FUNCTIONAL AND CONSTRUCTIONAL COMPOSITION MATERIALS ON THE BASED OF TUNGSTEN AND MOLYBDENUM CARBIDES AND METALS OF IRON TRIAD**

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Cemented tungsten and molybdenum carbides are commercially one of the oldest and most successful powder metallurgy products [1]. These composites are essentially aggregates of particles of tungsten (molybdenum) carbides bonded with cobalt (iron, nickel) metal via liquid-phase sintering.

There are few methods of refractory metals carbides synthesis. The method of high-temperature electrochemical synthesis is one of more effective method of refractory metals carbides synthesis. On the basis of high-temperature electrochemical synthesis of tungsten and molybdenum carbides [2] are multielectronic electrochemical processes of joint electrodeposition of tungsten, molybdenum and carbon on the cathode and their subsequent interaction at atomic level with formation nanosized powders of tungsten and molybdenum carbides.

In this work results on joint electrochemical electroreduction of tungsten (molybdenum) with cobalt (iron, nickel) and carbon in ionic melts are presented at temperature 900 °C.

By methods for research of joint electroreduction of refractory metals with iron triad metals and carbon have been chosen: cyclic voltammetry, potentiometry and also X-ray, X-Ray fluorescence methods of analysis.

The dependence of cathodic deposits structure on electrolysis conditions were investigated by methods of one  $\tau$ -stem and cyclic voltammetry.

Electrochemical systems are developed for synthesis hard-alloyed ceramic composites of carbides of tungsten, molybdenum and metals of a triad of iron on the basis of these processes.

Optimum conditions of the nanosized powders obtaining of double tungsten and molybdenum carbides with iron metals triad (current density, melt composites, temperature) are found.

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# INFLUENCE OF INTERFACE BETWEEN LAYERS IN POLY(DIPHENYLENEPHTHALIDE) FILM ON ELECTRON TRANSPORT

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Sequential deposition of poly(diphenyleneophthalide) (PDP) layers was shown to form a polymer film with a well clear interface between the layers which exhibits unique electronic properties [1]. In particular, abnormal high electronic conductivity was found along the interface, while the rest of the polymer bulk remained in dielectric state. Such a multilayered PDP film with the embedded interfaces can be evidently considered as a polymer composite material.

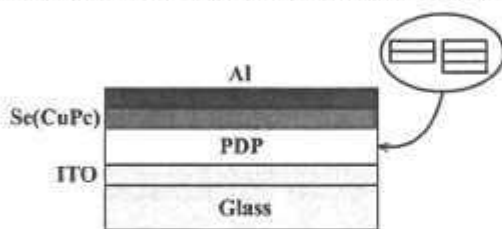


Fig. 1. Experimental sample for TOF measurements. ITO – clean indium tin oxide; PDP – polymer films; Se(CuPc) – photogeneration layer; Al – top electrode

In this work, an influence of the interface between the PDP layers on the charge carrier transport in the normal to the film plane direction was investigated. The study was carried out with specimens of the structure shown in Fig. 1 by the use of a conventional time-of-flight technique. The films consisted of one through three layers.

The transient current measurements showed that the transit time  $t_T$  for electrons is equal to 4 ms, 2 ms and 3 ms in a

2.4  $\mu\text{m}$  thick single-layer film, 5.4  $\mu\text{m}$  thick double-layer film and 7.5  $\mu\text{m}$  thick three-layer film, respectively. It is seen, that the transit time does not increase with the thickness of layered films. By contrast, the transit time is known to increase with the film thickness for polymer films formed by single layer [2]. Thus it is established experimentally that the electron transport behavior is significantly influenced by the interface between the layers of a PDP film, and the transient current decay time reduces.

In the report, the obtained data and electronic processes (generation and recombination of charge carriers) which allow us to interpret the electron transport through the interfaced layers are discussed.

The study was supported by Russian Foundation for Basic Research (project 09-03-00616-a)

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# NEW ELECTROCHEMICAL ROUTE FOR THE SYNTHESIS OF NICKEL CARBONIC COMPOSITE

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The nickel-oxide electrode have been widely used in organic electrosynthesis, due to high efficiency and selectivity of the process, as well as low cost electrode material and the simplicity of its manufacturing technology. In recent years, for these purposes are investigated nickel-carbon composite (NiO/C).

In this work we proposed a novel method of electrochemical synthesis of NiO/C composites. Our method is based on the dispergation of metal under asymmetric alternating current with simultaneous deposition on the carbon support (Vulcan XC-72). Such technique allows to obtain nanosized particles NiO and prevent trace-element contamination as well.

Interestingly, that XRD pattern of synthesized material show the five broadened characteristic peaks of the face-centered cubic crystalline structure of  $\beta$ -NiO. The average grain size of synthesized materials estimated using Scherrer equation was 3 nm. However, as indicates SEM image (Fig.1a) the average particle size according to SEM was 500-800 nm. The inconsistency between XRD and SEM results suggested that the observed nano-sheets were possibly formed by stacking of NiO nano-grains.

The formation of the  $\beta$ -form has also confirmed by our results of the cyclic voltammetry (Fig 1b). The potentials of nickel higher oxides formation (anodic peak) and potentials of their reduce (cathodic peak) for NiO/C composite close to typical for  $\beta$ -Ni(OH)<sub>2</sub>, while nickel-oxide electrode synthesized using conventional electrochemical method close to typical for  $\alpha$ -Ni(OH)<sub>2</sub> [1].

We suppose that these synthesized NiO/C composites could be very promising for use in electrocatalytic processes, as well as Ni/MH batteries.

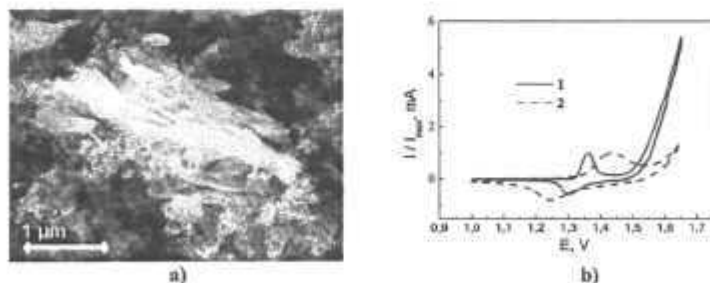


Fig. 1. a – SEM image synthesized NiO/C composite;  
b – cyclic voltammogram (1M NaOH) of the nickel-oxide electrode (1), NiO/C (2)

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## HOPPING CHARGE TRANSPORT IN ORGANIC MATERIALS

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Most disordered organic materials are molecular glasses having very low concentration of intrinsic movable charge carriers. They demonstrate measurable conductivity only after injection of carriers by the action of the laser pulse or strong electric field. At the same time, organic glasses usually have high concentration of dipoles and quadrupoles. Due to almost zero concentration of free carriers and lack of screening such molecules provide long range electrostatic contribution to the overall energetic disorder for charge carriers. Usually, the resulting random energy landscape  $U(r)$  could be accurately approximated by the random Gaussian field with the typical magnitude of energetic disorder close to 0.1 eV. Long range sources inevitably lead to the strong spatial correlation of random energy  $U(r)$ : in organic polar materials (dipolar glasses) correlation function of random energy  $C(r) = \langle U(r)U(0) \rangle$  decays as  $1/r$  and in nonpolar materials (quadrupolar glasses) it decays as  $1/r^3$  [1,2].

Long range correlations mean that sites with close values of random energy tend to group together and form clusters (cluster is defined as a set of connected sites, where all of them have site energy  $U$  greater than some boundary energy  $U_0$ ). Hence, organic glasses have a natural cluster structure and the probability to find large clusters is greater than the corresponding probability in non-correlated random landscape by many orders of magnitude. For example, in dipolar glass the asymptotics of the cluster numbers  $n_s$  for clusters having large random energy is  $\ln n_s \propto -s^{1/3}$ , while for the non-correlated Gaussian field  $\ln n_s \propto -s$  (here  $s$  is the number of sites in a cluster) [3].

Spatial correlations directly govern the field dependence of the hopping mobility of charge carriers in organic glasses. For 1D model the power-law asymptotics  $C(r) \propto 1/r^3$  leads to the field dependence of the mobility  $\ln \mu \propto E^{-(s+1)}$  [4], and this result is supported by the 3D computer simulation [2]. This means that in polar glasses the mobility field dependence has a form  $\ln \mu \propto E^{-1/2}$ , and in nonpolar glasses the corresponding dependence is  $\ln \mu \propto E^{-3/4}$ .

Electrostatic contribution to the total random energy is significantly modified at the surface of the electrode. Indeed, electrostatic energetic disorder in organic glasses is just a reflection of the disorder in the spatial distribution of electrostatic potential, generated by randomly situated and oriented dipoles and quadrupoles. In the organic layer bounded by conducting electrodes this spatial distribution must obey a boundary condition at the electrode surface: at this surface the potential should be a constant. Thus, at the electrode surface there is no energetic disorder at all, irrespectively to how disordered is the material in the bulk, far away from the interface. This means that the magnitude of electrostatic disorder increases while going away from the electrode, asymptotically reaching its bulk value. Behavior of the correlation function  $C(r)$  is different in the vicinity of the electrode, too [5]. This effect leads to the significant decrease of channeling of the injected current in organic electroactive devices. Hence, it decreases local overheating and improves stability of organic devices.

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## SOLID POLYMER MEMBRANE WITH PROTON CONDUCTIVITY

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We studied the following three-component copolymers: (1) butylacrylate (BA)–styrene–methacrylic acid (MAA) ( $C_{16}H_{22}O_6$ ) with an interstitial anionic surfactant, a hydrophobic anionic polymer with a monomer mass equivalent of 300 g/mol; (2) BA–butylmethacrylate (BMA)–MAA ( $C_{16}H_{22}O_6$ ) with an interstitial anionic surfactant ( $RSO_3^-Na^+$ ), a hydrophilic anionic polymer with a monomer mass equivalent of 314 g/mol; (3) BA–methacrylate (MA)–MAA ( $C_{11}H_{18}O_6$ ) with an interstitial cationic surfactant ( $R-NCl$ ), a cationic polymer (aqueous emulsions) with a monomer mass equivalent of 300 g/mol; and (4) acrylic acid (AA)–styrene–MAA (nonaqueous copolymer). Dimensions of the emulsion particles varied within the range 50–300 nm.

With a thickness of 0.03–0.5 mm, these membranes were optically transparent; chemically resistant to concentrated solutions of bases and nitric, sulfuric, and hydrochloric acids; and soluble in acetic acid. They could also be safely heated to a temperature of 333 K. Their tensile strength was 50 kgf/cm<sup>2</sup> with a relative elongation of 600 %. Electrical conductivity of the film with the anionic surfactant was  $1 \times 10^{-3} \text{ S cm}^{-1}$  at 298 K and 52 % humidity.

Aparicio et al. have noted that for polymers based on perfluorosulfonic acid (PFSA), which contain hydrophilic and hydrophobic groups, the hydrophilic region of the nanostructure is hydrated in the presence of water and thus supports conductivity, while the hydrophobic regions provide mechanical strength. The highest conductivity of  $1 \text{ S cm}^{-2}$  was observed at 393–403 K for membranes prepared by modifying the PFSA with a styrenemethacrylate composite with  $SiO_2$  with incorporated phosphotungstic acid (PTA). SPE based on acrylates soluble in benzene, toluene, and petroleum ether are hydrophilic in ethyl alcohol, ethyl acetate, and tetrahydrofuran (THF). This property makes it possible to prepare thin SPE films by applying a solution to electrode surfaces in various electrochemical systems and evaporating the solvent with a small amount of heating. These are termed polymer electrodes.

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## ELECTROACTIVE ANION-MODIFIED POLYANILINE

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Large electroactive anion-dopants ( $d \geq 1$  nm) are immobilized in a polyaniline (PANI) matrix in the course of the electrochemical or chemical PANI synthesis. These anions can serve as effective modifiers for PANI [1–3] affecting its electrochemical, electrochromic and catalytic properties.

To modify PANI we used four-charged anions of copper tetrasulfophthalocyanine (CuTSPc, anion 1) and silicododecamolybdate (SiMo, anion 2). It is shown that the electrosynthesis of PANI from 1 M  $H_2SO_4$  aqueous solutions containing the modifiers is complicated by the reaction between anilinium cations and modifier anions yielding insoluble salt. Only solutions with low concentrations of precursors are stable in time and provide reproducible kinetics of anodic synthesis of PANI-anionic modifier composite. As follows from spectral (anion 1) and electrochemical (anion 2) data, both modifiers enhance significantly the rate of PANI polymerization (see, for example, Fig. 1) and incorporate into the polymeric matrix. As shown in Fig. 2, a cyclic voltammogram for the PANI-SiMo composite is not a simple combination of those for PANI and SiMo/multi-walled carbon nanotubes (MWNTs) thus pointing to the polymer-modifier interaction.

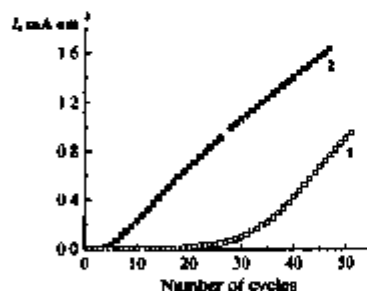


Fig. 1. Redox activity for (1) PANI and (2) PANI-CuTSPc composite as a function of number of cycles of anodic synthesis. Films were synthesized on ITO glass;  $v = 0.02$  V  $s^{-1}$ .

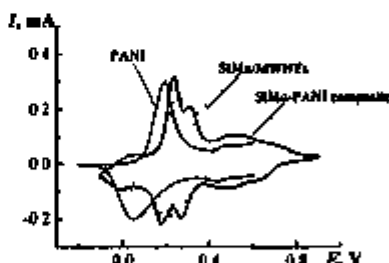


Fig. 2. Redox transitions of PANI, SiMo, and SiMo-PANI composite. PANI and SiMo-PANI films were synthesized on ITO glass, SiMo was adsorbed on MWNT,  $v = 0.02$  V  $s^{-1}$ .

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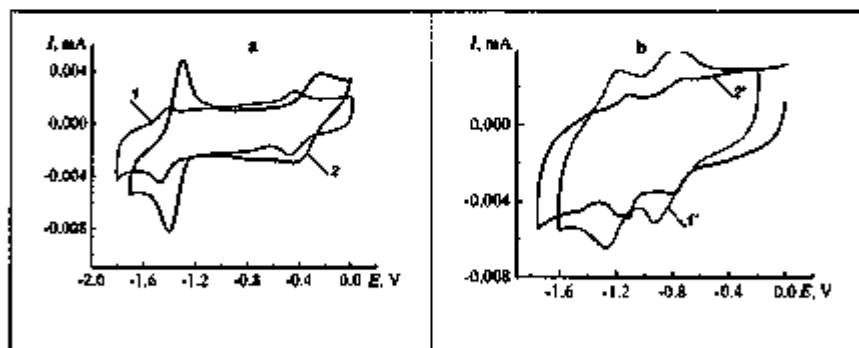
# REDOX PROPERTIES OF COBALT(II) AND NICKEL(II) OCTA-(BENZO-15-CROWN-5) PHthalOCYANINES IN APROTIC SOLVENTS

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Cathodic redox transitions of films based on cobalt and nickel phthalocyanine (CoPc, NiPc) and their octa-[(4-benzo-15-crown-5)-oxy] derivatives (CoCrPc, NiCrPc) [1] were studied by using cyclic voltammetry in the 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> solutions in dimethylformamide (DMF), dimethylsulfoxide, and propylenecarbonate. The films were applied onto a glassy carbon (GC) electrode using a technique of electrostatic rubbing. The merit of this procedure is its simplicity and possibility of applying minor amounts of substance, the weakness is the complexity of determining precise amounts of substance rubbed onto the GC due to conversion of initial solid-phase thick films to ultrathin ones as a result of gradual dissolution. The latter films can be characterized thermodynamically by estimating the formal potentials of redox reactions.

Cyclic voltammograms both for unsubstituted and substituted compounds display two quasireversible redox transitions (Figure). A comparison of formal potentials ( $E_1^f$ ,  $E_2^f$ ) for CoPc – CoCrPc and NiPc – NiCrPc couples shows that  $E_1^f$  and  $E_2^f$  are shifted towards less negative values with the introduction of ethereal substituents in the metal phthalocyanines. Although the shifts of  $E_f$  are no more than 80–100 mV, they point to the facilitation of the redox reactions involving crown-substituted phthalocyanines. This may be explained by the interaction between unpaired electrons in crowns' oxygens with Bu<sub>4</sub>N<sup>+</sup> cations that can facilitate the electron transfer to the CoCrPc and NiCrPc compounds.



Cyclic voltammograms for: (1) CoPc, (2) CoCrPc (a) and (1) NiPc, (2) NiCrPc (b) films rubbed onto GC for 0.1 M Bu<sub>4</sub>NBF<sub>4</sub>/DMF solution measured at  $\nu = 0.1 \text{ V s}^{-1}$ . Formal potentials, V (SCE):  $E_1 = -0.45$ ,  $E_2 = -1.44$  (CoPc) (a);  $E_1 = -0.32$ ,  $E_2 = -1.35$  (CoCrPc);  $E_1 = -0.85$ ,  $E_2 = -1.22$  (NiPc);  $E_1 = -0.75$ ,  $E_2 = -1.12$  (NiCrPc) (b).

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# CHEMICAL AND ELECTROCHEMICAL SYNTHESIS OF POLY-O-PHENYLENEDIAMINE

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Poly o-phenylenediamine (PPD) is a characteristic "ladder" redox polymer. It is usually synthesized anodically from o-phenylenediamine (OPD) in aqueous acid solution on various electrodes (Pt, Au, ITO). Thus synthesized polymeric film, as we demonstrated by mass spectrometry with matrix-assisted laser desorption/ionization (MALDI), contains a mixture of oligomers from dimers to hexamers with prevalence of the former. The quantitative ratio of these oligomers slightly depends upon the type of substrate.

The practical application often requires chemical synthesis. Here it is very important to produce OPD polymerization products in water-soluble form. Earlier, we chemically synthesized modified PPD using silicododecamolybdenic acid (SiMo) [1, 2] as the oxidizer and modifier.

In this work, we studied the conditions for synthesis of water-soluble OPD oligomers as precursors of electrosynthesis. We showed [3] that chemical oxidation of OPD with air oxygen in aqueous acid solution to oligomers in the presence of the oxygen complex of iron phthalocyanine tetrasulfate ( $O_2PcFe(III)$ ) as the catalyst results in acceleration of further electropolymerization, Fig. 1.

We also studied electrosynthesis of PPD on carbonized cloth and showed that synthesis of OPD oligomers starts by some 600 mV earlier than on other electrodes. When the cloth was impregnated with SiMo solution, the latter was strongly fixed on the surface, acting as the catalyst of PPD synthesis, Fig. 2.

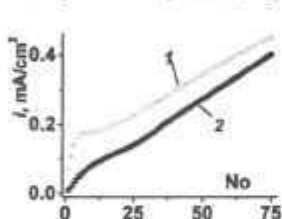


Fig. 1. PPD redox activity vs. number of cycles in its anodic synthesis: 1 – OPD +  $O_2PcFe(III)$  + OPD oligomers after 2.5 hour air bubbling, 2 – OPD without additives.

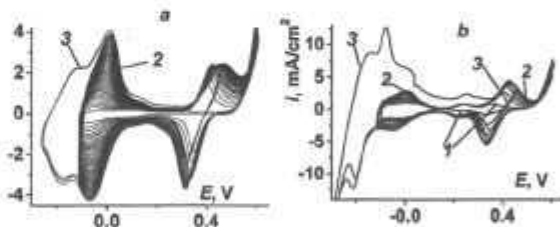


Fig. 2.  $I$  (b) – CVA of cloth treated with SiMo, 2 (a, b) PPD synthesis from  $5 \times 10^{-2} M$  OPD solution in 1 M  $H_2SO_4$  on pure (a) carbonized cloth (synthesis of 60 cycles) and treated with SiMo (10 cycles, b); 3 (a, b) – CVA after completion of synthesis.

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**APPLICATION OF HYBRID ORGANIC-INORGANIC MEMBRANES  
IN THE PROCESS OF ELECTRODIALYSIS CONCENTRATION  
OF LITHIUM CHLORIDE FROM THE ORGANIC SOLUTION  
ON THE BASIS OF N,N-DIMETHYLACETAMIDE**

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Currently existing regeneration processes of organic electrolyte solutions are often energy-intensive and low efficient. In this regard, you need search for new technological processes of separation of solutions on the components of organic and inorganic nature while its concentration. One of the most perspectives is the process of electrodialysis concentration.

Use of electrodialysis in organic electrolyte solutions is a relatively new area of ion exchange membranes application. The aim of this work is to study theoretically and experimentally the electrodialysis concentration of lithium chloride from the organic solution on the basis of n,n-dimethylacetamide.

The task of the work is to study the behavior in the electrodialysis concentration process of perfluorinated membranes MF-4SC, and hybrid organic-inorganic membranes based on them. Concentration was carried out in electrodialyzer-concentrator (EDC) using the laboratory-scale method described in [1]. Analysis of experimental data shows that in the concentration chamber of EDC formed with hybrid organic-inorganic membranes MF-4SC + SiO<sub>2</sub>, salinity of concentrate higher on 13–17 % in comparison with the original membrane MF-4SC.

Calculation of the transport characteristics of membranes was carried out using the model of electrodialysis concentration process [2] and showed that the electroosmotic permeability of the membrane pairs containing hybrid membrane is lower by 2 mol DMAA/F, than the membrane pair included the original MF-4SC.

Thus, the modification of a homogeneous membrane MF-4SC by silica can decrease the electroosmotic permeability of N,N-dimethylacetamide and, consequently, increase the concentration of brine in the process of electrodialysis concentration.

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## OPTICAL PROPERTIES OF POLYMERS AND COMPOSITES ON THE BASE OF METALLIC NANOPARTICLES

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Spectrophotometric investigation of the metallic and bimetallic nanoparticles interactions with light-sensitive polymer, poly-2-methoxy-5-(2-ethylhexyloxy)-1,4-phenyltervinylene (MEH-PPV) in the organic solutions were performed. In order to learn the influence of different additives on the solar energy absorption and the energy transformation by photoactive polymer layers. Prior to it, optical absorption and luminescence spectra of metallic (Ag, Pd, Pt), bimetallic nanoparticles (Pd-Ni, Pd-Co) and spectra of the MEH-PPV in the organic solutions were studied.

Stable metal nanoparticles in liquid phase were produced in reverse H<sub>2</sub>O/AOT/isooctane micelles as microreactors using radiation-chemical method at Lanacom Ltd laboratory [1]. UV-VIS Specord (Shimadzu) was used for optical absorption spectra measurements. Fluorescence spectra registration was performed with Hitachi F-7000 spectrometer. The nanoparticle size effect on the optical characteristics of electron absorption spectra and luminescence were investigated.

To determine reciprocal influence of Pt, Pd nanoparticles and selected porphyrinates, various volumes of reverse micellar solutions with  $\alpha = 5.0$  ([H<sub>2</sub>O]/[AOT]) containing metal nanoparticles, with initial metal ion concentration of  $\sim 4.0 \times 10^{-4}$  M were added to optically sensitive light porphyrinates [2]. In case of Ag nanoparticles, the study was done using solutions with metal concentration increased by order of magnitude, while  $\alpha$  values varied from 1.5 to 8.0. There is a known dependency between fluorescence emission quenching capabilities and photovoltaic parameters of energy converters. Our study has proved that admixture of Pt(II) ions to the porphyrines (H<sub>2</sub>TCP) does not make impact on its luminescence characteristics, while addition of Pt nanoparticles (NP) to porphyrine (PdTCP) solution causes quenching of luminescence in the range of  $\sim 660$  nm. Along with porphyrine's luminescence quenching the buildup of intense Pt NP's luminescence was observed.

Similar effect was determined during examination of Pt NP and Pt porphyrinates (PtTCP) interaction. In case of Pd NP related study, the intensity of the main porphyrine luminescence band ( $\lambda_{max} = 660$  nm) increased by 15 %. Addition of Ag NP to PdTCP has shown only decrease of luminescence band ( $\lambda_{max} = 660$  nm). Our study of reciprocal influence of PtTCP and Ag NP reveled NP size effect on decrease of fluorescence intensity. Volatic data measured for photosensitive MEH-PPV layers prove that the addition of Ag NP, synthesized in reverse micelles with  $\alpha_0 = 5$  causes luminescence quenching, and most efficiently increase the photovoltaic parameters of the light-sensitive polymer layers.

The concept of synergetic effects of bimetallic particles (Pd-Co and Pd-Ni) observed on luminescence quenching should be developed because of these co-catalysts may improve the efficiencies of the solar energy absorption and convergence.

*This work is supported by Russian Foundation for Basic Research (project # 08-03-00796, 09-08-00758).*

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**ORGANIC ELECTRONICS - SILICON DEVICE DESIGN WITHOUT SEMICONDUCTOR BAND THEORY****Schein L.R.***Independent Consultant, San Jose, California, USA*

Before the invention of the transistor in the 1940s, semiconductors were used as detectors in radios in a device called a "cat's whisker." At that time their operation was completely mysterious. Only after the introduction semiconductor band theory did it become clear that the "cat's whisker" is a primitive example of a Schottky diode. Today organic materials are being investigated for their electronic properties. Such materials are especially attractive for lightweight, flexible, and low-cost solar cells and light emitting devices, as well as transistors and electrophotographic photoreceptors. Yet, even after 40 years of work and a large database, the physics and chemistry that determines the electronic properties of organic materials are not well understood. Practicing organic electronics is like attempting to do silicon device design without semiconductor band theory. It is the purpose of this paper to briefly summarize what is known about the electronic properties of organic materials from charge transport data. It will be shown that our understanding of the charge transport mechanism and the electronic structure of organic materials is at a rudimentary phase, very similar to the "cat's whisker" phase of inorganic semiconductor research.

**ELECTROCHEMICALLY CONTROLLED MULTISTABILITY  
OF DOUBLE-DECKER CERIUM PHTHALOCYANINATE ULTRATHIN FILMS**

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Lanthanide-crownphthalocyanine sandwich-type complexes are of great interest from the viewpoint of supramolecular device development. In the present work the optical and electrochemical investigations of Langmuir-Blodgett films (LBF) of novel double-decker cerium tetra-15-crown-5-phthalocyanine complex ( $Ce(R_4Pc)_2$ ) were carried out. The ability of metal center to exist not only in oxidation state +3 typical for Ln series, but also in the oxidation state +4, allows one to expand functional abilities of supramolecular devices based on cerium phthalocyaninates.

The analysis of absorption spectra (AS) of  $Ce(R_4Pc)_2$  in chloroform in consideration of  $Ce^{3+}$  (1.143 Å) and  $Ce^{4+}$  (0.970 Å) ionic radius difference and earlier established linear correlation between lanthanide bis-tetra-15-crown-5-phthalocyaninate band position and ionic radius allows us to reveal that the valence state of cerium in complex solutions is IV. The spectral measurements showed that the absorption spectrum of such complex Langmuir monolayer after spreading onto water subphase appeared as a spectrum of neutral complex with trivalent metal center  $[(R_4Pc)^- Ce^{3+} (R_4Pc)^-]_0$ . Monolayer compression up to surface pressure 23–25 mN/m (phase transition of monolayer) is accompanied by increasing of the all absorption band intensity. The monolayer AS starts to change gradually upon further compression and becomes similar to the spectrum of tetravalent metal complex in solution. Comparison of these data with AS of monolayers of analogous trivalent praseodymium and lutetium crownphthalocyaninates allows us to suppose that intramolecular electron transfer from phthalocyanine macrocycle electronic system to  $4f$  orbital of cerium occurs upon complex solution spreading onto the subphase surface, and the reverse process of electron delocalization starts at high surface pressures. Possible mechanisms of intramolecular redox-transformations in Langmuir monolayers initiated by lateral pressure and found out in the present study for the first time are discussed.

Cyclic voltammograms of both  $Ce(R_4Pc)_2$  LBF obtained at 20 and 25 mN/m and unorderd thin film formed from solution show that within the potential region  $-0.5+1.0$  B ( $Ag/AgCl$ ) each of these systems reveals three redox-processes which potentials depend on molecular order of the film and its initial state. Electrochemical measurements of analogous double-decker trivalent lanthanide (Lu, Tb, Pr) crownphthalocyaninate Langmuir-Blodgett films were carried out to study mechanisms of the observed redox-transformations of the films. LBF multistability upon redox-triggering was demonstrated also using surface plasmon resonance spectroscopy. Fast response and reversibility of switching between stable states can serve as a basis for developing switchable optoelectronic systems.

*This work is supported by Russian Academy of Sciences (program # 18) and Russian Foundation for Basic Research (project # 08-03-00635).*

# STUDY OF THE WATER MOLECULES DISSOCIATION PROCESS AT THE ANION EXCHANGE MEMBRANES USING THE ROTATING MEMBRANE DISK METHOD

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Modification of ion-exchange membranes to change its catalytic activity against to water dissociation reaction is one of the most perspective ways to increase electrodiolysis process efficiency. This can be achieved by replacing ionogenic groups to equipolar with reduced catalytic activity in thin surface layer.

The aim of this work is to study electromass-transfer and water molecules dissociation processes using the rotating membrane disk (RMD) [1] method in the systems with industrial MA-40 membrane and chemically modified by strong polyelectrolyte complex (PEC) anionexchange MA-40M membrane. its surface layer mainly consists of quaternary ammonium bases.

It was determined that membrane treatment by PEC leads to total suppression of water dissociation reaction while conductivity, compared to initial membrane, slightly decreases (up to 20 %). Thus,  $\text{OH}^-$  transport numbers in modified MA-40M membrane drops to 0.1 against 0.2–0.3 for initial MA-40 under overlimiting currents.

It was shown for the first time that for initial and modified anion-exchange membranes (MA-40 and MA-40M) dependence of the limiting current density versus the square root of the membrane disk angular velocity ceases to be linear and goes to plateau when rotation speed higher than 200 rpm. It may indicate of a new kinetics type where the ions transport across the membrane does not correspond to the regulations of classical external-diffusion kinetics.

Mass transport coefficients of studied membranes were calculated using the partial current-voltage characteristics (Fig 1).

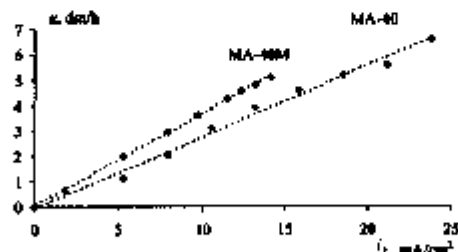


Fig. 1. The dependence of mass transfer coefficients on the current density for membranes MA-40 and MA-40M at the membrane disk rotation speed of 100 rpm.

It was shown that salt ions mass transport efficiency is higher on modified MA-40M membrane compared to initial MA-40 membrane by 20–30 % under overlimiting currents.

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# STUDY OF WATER DISSOCIATION ON THE INTERFACE OF SEMIBIPOLAR MEMBRANES

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Bipolar membranes (BPM) is a bilayer composites, in which cation exchange and anion-exchange layers possess ion-selective properties. Such membranes allows production of protons and hydroxide ions from water molecules under the influence of an electric current. Thus, BPM can be viewed as miniature chemical reactors, having a function of reaction products separation. These properties allows the design of unique electromembrane processes, such as acidification or alkalization of technological solutions without addition of chemicals and by-products or waste. In cases where the required change in solution pH lay within narrow limits, this problem can be solved by the so-called semibipolar membranes [1]. Introduction of various additives to the membrane interface, such as nano- or micro-sized particles of inorganic compounds [2], or ionopolymers [3], can catalyze the water dissociation reaction and reduce bipolar region overvoltage, thereby improving their performance.

The main aim of this work was creation of semibipolar membranes, in which cation-exchange layer is a thin film of MF-4SC with catalytic additive, comparable to the industrial bipolar membranes.

Based on a set of experimental data with model proposed in [4], the effective water dissociation in reaction layer of semibipolar membrane rate constants ( $k_d$ ) and coefficients  $\beta$  were calculated.

Comparing the values of the  $\beta$  for  $k_d$  parameters for semibipolar and bipolar membranes shows that the obtained membranes with catalyst have a high catalytic activity with respect to the water dissociation and can be effectively applied in electro-acidification and alkalinizing of dilute electrolytes solutions.

Table. Obtained semibipolar(\*) and industrial bipolar membranes characteristics

	AM-30*	AM-30+catalyst*	MB-1	MB-2	MB-3
$k_d$ , l/s	3.84	16.8	8.95	0.401	248
$\beta \times 10^9$ , m/V	5.21	6.26	3.65	7.17	6.41

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**PROTON PERMSELECTIVITY AND WATER ELECTROTRANSPORT  
IN COMPOSITE MEMBRANES MF-4SC / POLYANILINE**

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Proton conductivity and water transport with proton in the perfluorinated sulfonic membranes and composites are investigated to use in the fuel cells as polymer solid electrolyte

Transport properties and morphology of the bulk- and surface - modified, nanocomposite membranes MF-4SC/polyaniline are investigated and the interrelationships with the matrix synthesis conditions are revealed. The role of the morphological factors in the nanosystem formation inside of polymer matrix, which presents the interpolymer complex between sulfogroups, nitrogen centers on the aromatic chains of polyaniline and structured water is discussed. Water electrotransport with protons in the bulk- modified composites MF-4SC/polyaniline does not depend on the composite morphology and changes from 3,5 up to 2 mol H<sub>2</sub>O/molH<sup>+</sup> (with the concentration HCl increase from 0 M up to 3M) [1]. It is shown that composites MF-4SC/polyaniline are the materials with high value of proton permselectivity for both emeraldine and pernigraniline forms of polyaniline inside of template matrix (0.98–0.96) [2]. The dynamic hydration numbers of protons and chloride co-ions were estimated using the "true" transport numbers of protons and the electroosmotic coefficients of composites. The gradient distribution of polyaniline in the basic membranes in the synthesis of the surface-modified composites MF-4SC/polyaniline leads to the morphology transitions from microsize coatings (1–2 μm) to the nanosize inclusions of polyaniline fibrils (30–80 nm) [3]. The asymmetry effect of diffusion permeability and current-voltage characteristics were discovered for the anisotropic composites and the model for the estimation of the polyaniline layer thickness was proposed [4]. The possibility of transport and morphology regulations with help of the parameters synthesis variations is demonstrated. The materials obtained are applied in the electrodialysis concentrating of salt solutions and in the fuel cells [5].

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# THE CATALYTIC ACTIVITY OF Ni,P-COATINGS MODIFIED BY CARBON NANOPARTICLES IN HYDROGEN EVOLUTION REACTION

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One of the promising methods for modification of metallic coatings is the inclusion of solid particles of different nature. Such materials are characterized by significantly improved mechanical and unique magnetic properties. Despite the fact that mentioned in the literature study focused primarily on the investigation of physical and mechanical properties of such composites, it should be emphasized that the size effect is also determined by the electronic structure of nanomaterials. These properties, in turn, determine the specific reactivity and may be useful for electrode materials, which enhance the rate of electrochemical processes. Therefore, it is expected that nanostructured nickel coatings will have a high catalytic activity in reactions with the participation of the adsorbed intermediates, for example, in the hydrogen evolution reaction. So, this work was aimed at modification of electrodeposited Ni,P-coatings by particles of multi-walled nanotubes (MWNT), supordispersed diamonds (SDD) and graphite and study of their catalytic activity in the hydrogen evolution reaction in acid medium.

It was found that doping of Ni,P-coatings, even by small amounts of carbon particles leads to a change in their composition, structure and morphology. Thus, usage of the SDD led to an increase in the phosphorus content, while MWNT and graphite decrease this parameter. Despite the insignificant change in the composition, surface morphology changes sufficiently during the transition from the original Ni-P coatings to composites. Inclusion in the coating of solid carbon particles causes a refinement of spherulites and the appearance of a grid of cracks. The most pronounced of these effects are in the case of coatings Ni,P-graphitic. Simultaneously, these coatings are the most amorphous of all the studied materials.

The catalytic properties of synthesized coatings in the hydrogen evolution reaction were investigated. It was found that doped alloys, obtained from the electrolyte with low concentration of nanomaterials, increase the reaction rate of hydrogen evolution almost twice as compared with cast nickel and the original Ni-P alloy. The graphite particles only slightly reduce the activity of the coatings in the investigated reaction. Normalizing the rate of hydrogen evolution to the corresponding values of relative roughness factors of the coatings showed that the high catalytic activity of alloys Ni,P-MWNT caused only by the development of the surface, while all the other studied coatings increase the rate of the process not only by geometric factor, but also because of their electronic structure. The direct relation between the reaction rate and fraction of the grains with (111) orientation was found.

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**STUDY OF pH CORRECTION OF SODIUM CHLORIDE AND SODIUM  
BICARBONATE DILUTED SOLUTIONS IN ELECTRODIALYSIS  
WITH BIPOLAR MEMBRANES**

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With conventional application of electrodialysis for desalination and concentration recently process of acidification and alkalization using electrodialysis with bipolar membranes demands widely. This problem appears during production of acids and bases [1]. pH correction of electrolyte solutions in chemical [2] and food industry [3].

In this work for investigation of pH correction of sodium chloride and bicarbonate chloride diluted solutions (concentration is 0.01 M) two-compartment electrodialysis cell was used as elementary unit and consisted of two bipolar membrane MB-3 and anion-exchange membrane MA-40 between them. Current efficiency of pH correction process of sodium chloride depends on intensity of water dissociation both on bipolar membrane and anion-exchange membrane. It is discovered that when pH values of solution near membrane are more 10 it is observed decreasing of water dissociation rate (decreasing of  $H^+$  and  $OH^-$  transport numbers) caused by deprotonation of tertiary aminogroups of membrane MA-40 [4].

During the investigation of electrodialysis with bipolar membranes for pH correction of bicarbonate solution is necessary to take into consideration chemical reactions between bicarbonate-ion and products of water dissociation, occurring in solution and in ion-exchange material.

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**ELECTROACTIVE POLYMER COMPOSITES BASED ON RUTHENIUM(II) COMPLEX HAVING PHOTOREFRACTIVE SENSITIVITY IN OPTICAL COMMUNICATION RANGE****A.Y. Yagulkov, Ya.G. Gorbunova, A.D. Grishina, A.Yu. Talvadze***A.N. Franklin Institute of Physical Chemistry and Electrochemistry,  
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Composites from PVK and supramolecular ensembles of Ru(II) tetra-15-crown-5-phthalocyanate molecules axially coordinated with ethylisocitronate,  $(R_4Pc)Ru(EIN)_2$ , have the charge transport properties, also photoelectric and photorefractive (PR) sensitivity at the optical communication wavelength 1550 nm. The PR effect is used for correction and amplification informative laser beam and appears in a photosensitive polymer composite upon interference of two laser beams. Under these conditions electrons and holes, generated in bright interference fringes, drift in conducting polymer matrix in opposite directions in an applied dc electric field  $E_0$  until their capture in deep traps. The trapped unlikely charges form a periodic space-charge electric field  $E_{sc}$ , which poles nonlinear optical chromophores, thereby causing periodic modulation of the refractive index  $\Delta n$ , i.e., creating a phase diffraction grating in the polymer layer. At different drift mobility of unlike charges, the grating becomes spatially shifted by a distance  $x$  or a phase  $\psi = 2\pi x/\Lambda$ , where  $\Lambda$  is the grating spacing) relative to the interference pattern. Under these conditions, one of beam (the probe beam) is in phase with the grating-diffracted part of the second pump beam, and their constructive interference results in amplification of the probe beam. The two-beam amplification coefficient equals  $\Gamma = 4\kappa\Delta n \cos 2\theta \sin \psi / \lambda$  ( $\theta$  is a angle between beams,  $\lambda = 1550$  nm). The pump beam is out of phase to the diffracted part of the probe beam and their destructive interference leads to attenuation of the pump beam.

Principal direction of our work is the elaboration of the PR composites based on the hole-conduction polymers having high glass transition temperature  $T_g$ . The high  $T_g$  polymers improve the stability of composite characteristics but requires the use of the third-order nonlinearity optical chromophores as only third-order dielectric susceptibility has nonzero value at chaotic distribution nonlinear optical chromophores which are frozen at casting of the polymers with high  $T_g$ . The third-order nonlinearity was estimated with method ELFISH – the electric-field-induced second-harmonic generation. The third-order susceptibility of 1 M molecular  $(R_4Pc)Ru(EIN)_2$  is estimated as  $\chi^{(3)} = 0.9 \times 10^{-4}$  esu and individual molecule polarizability is about  $\gamma = 4 \times 10^{-32}$  esu.

It was established that at 1550 nm the basic PR characteristics: two-beam coupling gain coefficient  $\Gamma$ , the net coefficient  $\Gamma - \alpha$  ( $\alpha$  is absorption coefficient) and the time constant of the diffraction grating formation,  $\tau$ , equal correspondingly to 25 cm<sup>-1</sup>, 19 cm<sup>-1</sup> and 0.8 s. The additional introduction of C<sub>60</sub> fullerene into the composite and preillumination (preliminary illumination of the whole layer in an optical absorption range of C<sub>60</sub> in the absence of  $E_0$  field) provides partial filling of the deep trap and increase a phase  $\psi$ . As result the two-beam coupling gain increase to  $\Gamma = 48.3$  cm<sup>-1</sup> and in the net gain coefficient to  $\Gamma - \alpha = 42.3$  cm<sup>-1</sup>.

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# ELECTROCHEMICAL CHARACTERISTICS OF NAFION MEMBRANE WITH CNT MODIFIED SURFACE

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The surface of Nafion-117 ion-exchange commercially promembrane was modified by thin composite polymer film of sulfonate polytetrafluoroethylene (SPTFE) doped by carbonic nanotubes (CNT). Complex of experimental data were obtains including electrochemical characteristics (current-voltage curves, chronopotentiograms), transport characteristics (concentration dependences of electroconductivity and diffusion penetrability), structural characteristics (topography and morphology of volume and surface) and contact angles of the initial and the modified membrane surfaces.

It is shown that CNT, which introduced into the volume of the modifying film, "stitch" SPTFE. As a result, the diffusion permeability of membranes with modified surface decreases in comparison with commercially produced membrane. For example, in the system  $H_2O$ /membrane/0.5 M NaCl diffusion constant ( $cm^2/c$ ) is equal to  $5.6 \times 10^{-9}$  and  $13.2 \times 10^{-9}$  consequently.

External wall of nanotubes is "wrapped" by hydrophobic chains of SPTFE, and hydrophobic fragments are concentrated apparently at the surface of nanotubes and hydrophilic side chains are repelled from them and are found on the surface of the modified membranes. Hydrofilylation of the modified membrane surface reduces the development of electroosmosis of the second kind, which noticeably change the electrochemical behavior of ion-exchange membranes under intensive current regimes.

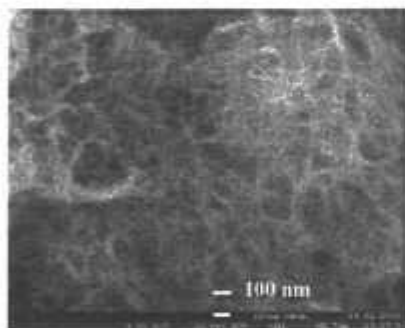


Fig.1. Carbonic nanotubes wrapped in sulfonated polytetrafluoroethylene on the surface of the modified Nafion membrane

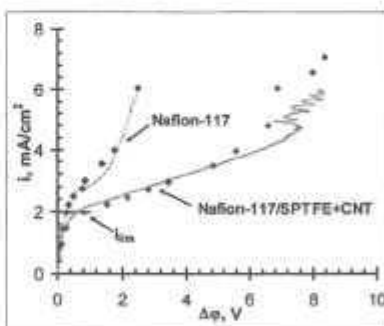


Fig. 2. Current-voltage curves of the origin Nafion-117 membrane and a similar membrane, modified by the film of sulfonated polytetrafluoroethylene doped with carbonic nanotubes

*This work is supported by Russian Foundation for Basic Research (project # 09-08-96529).*

## POLYPORPHINES: A NEW FAMILY OF CONDUCTING POLYMERS

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Porphyrin molecules contain a conjugated macrocycle of 4 pyrrole rings linked via CH bridges, to which various substituent groups can be attached. Such substituted porphyrins demonstrated interesting properties in the areas of catalysis and electrocatalysis, sensors, non-linear optics, luminescence etc.

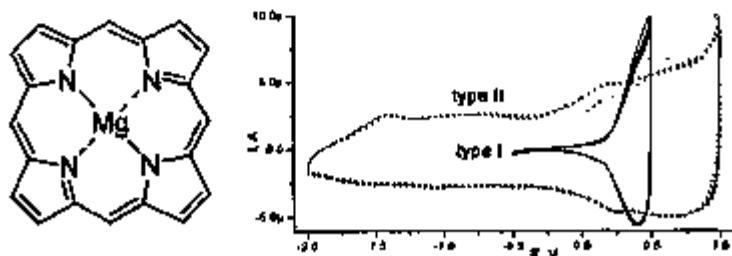
Numerous studies were devoted to incorporation of substituted porphyrins into a conducting-polymer matrix as counter-ions (porphyrins with attached negatively charged groups) or owing to the polymer chain formation by a substituent (e.g. aniline). In 2008 the first examples of conducting copolymers with porphyrins and aromatic rings inside the principal chain were reported.

In our study we have synthesized for the first time representatives of a new family: conducting polymers based on an unsubstituted porphyrin ("porphine") as monomer unit. The deposition can be realized electrochemically with a stable growth of the conducting film. The properties of the resulting polymer depend crucially on the deposition potential, as demonstrated with the use of a set of experimental techniques (CV and chronoamperometry, *in situ* conductivity, optical microscopy, XPS, XRD, UV-visible spectroelectrochemistry, FTIR spectroscopy, MALDI-TOF).

If the porphine oxidation is realized at a low potential the deposited polymer ("film of type I") consists of chains, with neighboring monomer units linked by a single bond in meso-positions. Its redox properties are conventional for conducting polymers, with potential intervals for p- and n-doping (in which the polymer is electronically conducting) separated by an electro-inactivity range (in which the polymer is an insulator).

Electrochemical treatment of this polymer (or the oxidation of solute monomer) under a higher positive potential results in formation of quite a different material with very unusual properties ("film of type II"). In particular, it demonstrates an electroactivity uniformly distributed within an extremely broad potential interval (above 3 V), and the material retains its electronic conductivity within this whole potential range. It implies that the electronic delocalization occurs for a broad range of the polymer oxidation levels including its neutral state (for which conventional conducting polymers become insulating). The spectral properties of the polymer in the UV, visible and IR ranges also change radically. This material with a zero width of the electrochemical band gap and particular optical properties is promising for various applications.

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# CONDUCTING POLYMER AND VANADIUM OXIDE BASED HYBRID NANOCOMPOSITES FOR LITHIUM BATTERIES

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Hybrid nanocomposites based on conducting conjugated polymers (CCP) and different compounds of transition metals attract attention of many researchers engaged in creation of promising cathode materials for lithium batteries. In the present report, using vanadium oxide and polypyrrole based composites as an example, the results of the comparative study of the functional electrochemical characteristics of the host-guest hybrid nanocomposites ( $\text{HNC}_{\text{hy}}$ ), in which the predominant part of the CCP is inserted inside the interlayer galleries of the inorganic matrix, and the core-shell hybrid nanocomposites ( $\text{HNC}_{\text{cs}}$ ), in which the polymer forms the film on the surface of the oxide nanoparticles, are presented.

The data of X-ray diffraction showed the incorporation of polypyrrole macromolecules inside the interlayer space of the inorganic component of  $\text{HNC}_{\text{hy}}$  and also the disordered state of the crystalline lattice of  $\text{V}_2\text{O}_5$  in  $\text{HNC}_{\text{cs}}$ . It was established using TEM that  $\text{HNC}_{\text{hy}}$  consisted of aggregates of polycrystalline particles of 20–50 nm and the size of the particles in  $\text{HNC}_{\text{cs}}$  is 100 nm.

Cycling voltammogram and differential capacity curve of  $\text{HNC}_{\text{hy}}$  contained two cathode peaks at potentials about 2.8 and 2.4 V vs  $\text{Li/Li}^+$  which correspond to intercalation of lithium ions in  $\alpha$ - and  $\beta$ -centers of  $\text{V}_2\text{O}_5$  xerogel, while only one peak about 2.2 V which probably corresponds to the transition of the oxide in  $\gamma$ -phase was observed for  $\text{HNC}_{\text{cs}}$ . At prolonged charge-discharge cycling  $\text{HNC}_{\text{hy}}$ , in comparison with  $\text{HNC}_{\text{cs}}$ , possessed higher specific capacity and improved cycling ability.

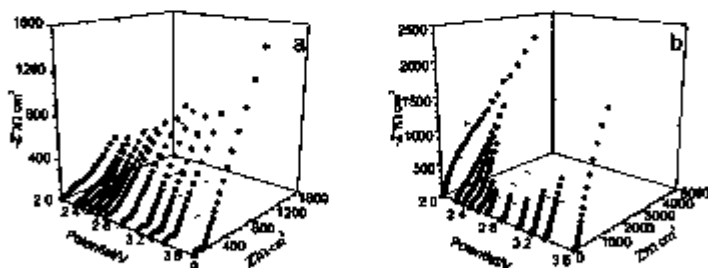


Fig. 1 Nyquist plots for  $\text{HNC}_{\text{cs}}$  (a) and  $\text{HNC}_{\text{sh}}$  (b) at different potentials.

Frequency dependence of impedance was measured in the range between 100 kHz and 0.75 mHz. The different behavior of the impedance of the nanocomposites was established. Equivalent circuits for interpretation the Nyquist plots were proposed; they showed the absence of the passive film on the surface of the nanocomposites of both types. The values of lithium ion diffusion coefficients, which in  $\text{HNC}_{\text{hy}}$  appeared to be one order greater than in  $\text{HNC}_{\text{cs}}$ , were calculated. It was shown that high discharge capacity, stability on prolonged charge-discharge cycling and improved diffusion of lithium ions in  $\text{HNC}_{\text{hy}}$  are the consequence of pillaring action of the CCP macromolecules on the layers of the inorganic matrix.

**EFFECT OF DITHIOTHREITOL ON  $H^+$  TRANSPORT IN FUNCTIONALLY DIFFERENT CELL REGIONS OF CHARACEAN ALGAE****Dodonova S.O., Krupenina N.A., Balychev A.A.***Lomonosov Moscow State University, Faculty of Biology, Biophysics Dep., Moscow, Russia*

Illuminated cells of characean algae produce spatially heterogeneous apoplastic pH profile with alternating regions of high  $H^+$  pump activity and high membrane conductance for  $H^+$ . Action potential (AP) leads to the temporal cessation of counter-directed  $H^+$  flows and opposite pH shifts in different cell areas, which allows the assessment of  $H^+$ -pumps and leak activities. It was shown with the help of pH microelectrodes that, in the cell treated with dithiothreitol (DTT, disulfide reducing agent), the AP-induced pH changes decreased in the alkaline zones and increased significantly in acid zones. Measurements of membrane conductance in alkaline zones showed that DTT lowered the light-dependent membrane conductance of the resting cell and weakened the AP-induced conductance inactivation. The results of this work suggest that S-S bonds reduction decreased the membrane conductance, while the activity of  $H^+$ -pump remained intact or even intensified. The  $H^+$  flows in alkaline and acidic zones are disrupted in such a way that the charge carried by  $H^+$  pump is compensated by fluxes of other ion species. These fluxes, in contrast to  $H^+$  flows, are distributed uniformly and are insensitive to the electric excitation of cell membranes.

**ELECTROSTATIC AND MECHANOCHEMICAL EFFECTS OF POLYVALENT IONS ON PHOSPHATIDYL SERINE MEMBRANES: RELEVANCE TO MECHANOSENSITIVE CHANNEL FUNCTION****Ermakov Yu.A.<sup>1</sup>, Kamaraju K.<sup>2</sup>, and Sukharev S.<sup>2</sup>**<sup>1</sup>*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry  
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Membrane protein function often involves large-scale conformational dynamics which makes it sensitive to the composition and physical properties of the surrounding lipid matrix. The mechanosensitive channel (MscL), a common osmolyte release valve in bacteria, is one the well studied model systems. At membrane tensions of  $\sim 10$  mN/m, MscL complex opens a 3 nm conductive pore undergoing a  $20 \text{ nm}^2$  in-plane expansion.

$\text{Gd}^{3+}$  ions were reported to block many types of mechanosensitive channels, but MscL opening was inhibited only when the channel was reconstituted with anionic lipids, e.g. phosphatidylserine (PS). Taking this lead, we performed a detailed study of PS interactions with  $\text{Gd}^{3+}$  using the lipid monolayer technique, intramembrane field compensation (IFC) on planar lipid bilayers and electrokinetic and isothermal titration calorimetry techniques on liposomes. All techniques suggested an effective  $\text{Gd}^{3+}$ -PS binding constant of  $\sim 10^6 \text{ M}^{-1}$ . Electrokinetic measurements show complete neutralization of phosphatidylserine headgroup charges by  $\text{Gd}^{3+}$ , whereas IFC detects large (100–140 mV) changes of the interfacial dipole potential associated with ion binding. Monolayer data in conjunction with IFC indicated that the strong dipole effect is a result of mechano-chemical compaction of lipid molecules apparently due to coordination of multiple phosphatidylserine headgroups by  $\text{Gd}^{3+}$  ions. The degree of phosphatidylserine compaction depends on the saturation of the acyl chains with the maximum effect observed in dimyristoyl phosphatidylserine, which undergoes a liquid-gel phase transition in the presence of  $\text{Gd}^{3+}$ . The electrostatically-driven mechanochemical compaction of phosphatidylserine by  $\text{Gd}^{3+}$  is predicted to change the lateral pressure profile considered an important physical property of the lipid bilayer altering the function of membrane proteins.

**INACTIVATION OF  $H^+$ -CONDUCTANCE IN THE *CHARA* CELL INDUCED BY ACTION POTENTIAL GENERATION****Krapchenina N.A., Bulychev A.A.***Lomonosov Moscow State University, Faculty of Biology, Biophysics Dep., Moscow, Russia*

The action potential of excitable plant cells is a multifunctional physiological signal. Its generation in characean algae suppresses the pH banding for 15–30 min and enhances the heterogeneity of spatial distribution of photosynthetic activity. This suppression is largely due to the cessation of  $H^+$  influx ( $OH^-$  efflux) in the alkaline cell regions. Measurements of local pH and membrane conductance in individual space-clamped alkaline zones showed that the action potential generation is followed by the transient disappearance of alkaline zone in parallel with a large decrease in membrane conductance. These changes, specific to alkaline zones, were only observed under continuous illumination following a relaxation period of at least 15 min after previous excitation. The excitation of dark-adapted cells produced no conductance changes in the post-excitation period. The results indicate that the origin of alkaline zones in characean cells is not due to operation of electroneutral  $H^+/HCO_3^-$  symport or  $OH^-/HCO_3^-$  antiport. It is concluded that the membrane excitation is associated with inactivation of plasmalemma high conductance in the alkaline cell regions.

## REGULATION OF UCP- MEDIATED PROTON TRANSPORT

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Uncoupling proteins UCP1 and UCP2 are mitochondrial inner membrane proteins, which contribute to the dissipation of the proton gradient in mitochondria. The tight regulation of proton conductance may be important in mitochondrial respiration and metabolism. Meanwhile it is accepted that UCP1 and UCP2 are activated by free fatty acids (FA) and inhibited by purine nucleotides. Neither the mechanism of activation, nor of inhibition are understood. In our recent work (1–3) we investigated the ability of several small molecules and different physical parameters to activate UCP. The well-defined model of planar lipid membranes reconstituted with recombinant UCPS was used. Our data indicate that both unsaturated FAs and the high transmembrane potential  $\Delta\psi_m$  contribute significantly to the increase of the UCP-mediated membrane conductance. In contrast, aldehydic product of lipid peroxidation 4-hydroxy-2-nonenal, which was proposed to be a putative UCP activator, has no direct effect on the protein. We discuss the results in terms of the "fatty acid cycling" hypothesis.

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## PROTON MIGRATION ALONG THE MEMBRANE WATER INTERFACE

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Proton diffusion along membrane surfaces is thought to provide an efficient link between sites of protein release and sites of protein consumption. The two-dimensional confinement may only work if there is an energy barrier which prevents the protons from reacting with mobile buffer molecules from the bulk, or from diffusing into the bulk solution. The origin of this barrier is not clear. Most often, it is attributed to immobile buffer molecules embedded into the membrane. Alternatively, protons may be retained close to the membrane because proton uptake by interfacial water molecules which have sacrificed one hydrogen bond may be energetically less costly than uptake by bulk molecules. We have tested the hypothesis by measuring the  $H^+$  flux along the surface of planar bilayer lipid membranes (1). Therefore, the protons were released in a small rectangular area by flash photolysis of a hydrophobic caged compound (DMPC) (2).  $H^+$  migration to a region of interest was visualized as a change in fluorescence intensity of a lipid bound pH-sensitive dye (PE-fluorescein). Membrane formation without (i) phosphatidylethanolamine headgroups or (ii) phosphate moieties decreased the amount of protons migrating along the surface and increased the proton flux via bulk diffusion. However, if the concentration of mobile buffers was also decreased, proton surface diffusion was observable even in the absence (i) of immobile membrane buffers or (ii) of charged moieties indicating that there has to be a third component contributing to the energetic barrier. Most likely that third component is represented by the first water layer close to the membrane surface since the structural differences from bulk water renders it susceptible to excess protons.

*Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.*

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**CROSS-LINKING OF PHOSPHATIDYLSELINE BY LANTHANIDE IONS:  
MACROSCOPIC PARAMETERS OF BINDING AND ATOMIC DETAILS  
OF ION COORDINATION**

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Interactions of polyvalent ions with charged phospholipids have multiple biological consequences and have been studied for decades, but the atomic details are being clarified only now. Gadolinium ( $Gd^{3+}$ ), a small lanthanide, is widely used as a diagnostic MRI contrasting agent in chelated forms, but free  $Gd^{3+}$  is a potent inhibitor of platelet and macrophage function as well as a non-specific blocker of mechanosensitive channels. Recently we found that  $Gd^{3+}$  blocks bacterial mechanosensitive channel MscL through interactions with negatively charged lipids surrounding the protein, especially with phosphatidylserine (PS). Here we study the thermodynamics and mechanochemical effects of  $Gd^{3+}$  binding to PS and envision these interactions through Molecular Dynamics (MD). Isothermal titration calorimetry of dioleoyl phosphatidylserine (DOPS) liposomes with  $Gd^{3+}$  ( $K_b \sim 10^6 M^{-1}$ ) indicated that the character of reaction changes from endothermic to exothermic, suggesting that initial binding has a large entropic contribution apparently from desolvation of ions and charged headgroups. DOPS monolayers with  $10 \mu M$   $Gd^{3+}$  in the subphase exhibited a 8–10% compaction (at 35 mN/m).

We have performed extensive MD simulations of DOPS bilayers with  $Na^+$  and  $Gd^{3+}$  and found complete neutralization of the surface charge through direct coordination of  $Gd^{3+}$  by both carboxyls and phosphates of PS groups. The most probable coordination patterns were formed by one carboxyl (two oxygens) and one phosphate oxygen from two PS molecules (with 5 additional waters), or by two carboxyls and one phosphate from three different PS headgroups and 3 waters. The coordination produced an ~8% area decrease of the simulated bilayer leading to a strong distortion of the lateral pressure profile with additional peaks of pressure in the peripheral regions of hydrocarbon. The simulations illustrate the nature of cross-linking of multiple PS headgroups by  $Gd^{3+}$  and associated changes of surface electrostatics and lateral pressure distribution, which appear to be the major factors blocking surface recognition of PS by macrophage receptors and opening of membrane-embedded mechanosensitive channels.

# INFLUENCE OF PHYSICAL FIELDS WITH LOW AMPLITUDE ON PROCESSES OF IONIC - MOLECULAR TRANSPORT OF ANTIBIOTICS THROUGH BIOLOGICAL MEMBRANES

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The models of ionic-molecular transport of antibiotics in lipid-albuminous membranes and muscular biological fabrics are presented in the given work. Models are constructed on the basis of generalisation of the experimental material received at research of kinetics of antibiotics' transport in placental and muscular membranes under the influence of electric, constant and variable magnetic, acoustic, laser, microwave and other fields and their combinations. Models can be used for working out of theoretical bases of medicinal phoretic physiotherapy, modern techniques of treatment and physiotherapeutic devices.

The mathematical models of stimulative osmotic migration are constructed on the basis of model of «a friable quasicrystal» and the analysis of experimental laws of migration of anions of Chloramphenicol, Benzylpenicillinium and Oxacillin through lipid-albuminous and muscular membranes *in vitro*.

The structure of a muscular fabric means specific adsorption of ions from an intercellular liquid on the electrostatic or spatially-waterproof mechanism and fixing on the corresponding active centres. The adsorbed ions form a plane of Helmholtz. The charge of these ions is compensated by surplus of ions with opposite charge in an intercellular liquid. Depending on their concentration of ions with opposite charge are distributed more or less diffusively in an electrolyte blanket. Ions with opposite charge are separated from a surface of a capillary by an external plane of Helmholtz, and the volume charge which is settling down between this plane and deep layers of a solution, can move concerning a surface together with a liquid. As a result the electrokinetic phenomena, in particular, osmosis can be observed.

The mathematical models of carrying over of macroions are based on interpretation of the classical equations of electromigratory diffusion of Helmholtz-Smoluhovsky, Goldman and Goldman-Hodzhkin-Katz. It is shown that the mechanism of carrying over of ions in lipid-albuminous and muscular membranes is distinguished. In lipid-albuminous membranes there is an electromigratory diffusion on the lipid-albuminous channels formed for the account of conformational deformations of molecules of phospholipids and fibers with factors of diffusion  $D = (2.6-3.6) \times 10^{-8} \text{ cm}^2/\text{s}$ . Carrying over in muscular fabrics is caused by migration through charged channels between fibers with factors of diffusion  $D = (6.0-10.0) \times 10^{-8} \text{ cm}^2/\text{s}$ . Negative energy of activation of diffusion is caused by the change of structure of muscular fibers and expenses of thermal energy for replacement of CF out of channels' walls.

**PROPERTIES OF VESICULAR SUSPENSIONS PREPARED BY DIFFERENT METHODS**

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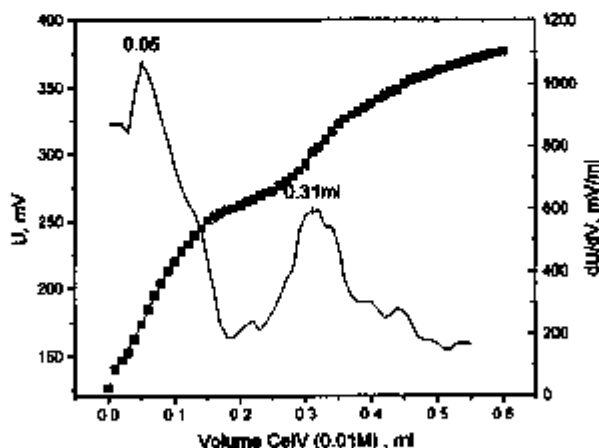
Giant lipid vesicles are obtained mainly by two methods of their formation: (i) electroformation and (ii) gentle hydration (spontaneous swelling). Very often the electroformation is carried out using indium-tin oxide (ITO) coated plates as electrodes. The aim of the present work is to study the influence of the formation method, and more specifically the ITO coatings, on some physicochemical properties of the vesicle suspensions. Electrochemical impedance spectroscopy (EIS) technique will be applied to check the conductivity of identical giant vesicle suspensions (same lipids and suspending media), prepared by the two methods. Our study is intended to point out possible implications of the electroformation method, especially in cases when phenomena, related to the electric properties of the vesicle membranes, are investigated.

**DETERMINATION OF REDUCED HEME IRON OF CYTOCHROME C BY THE TECHNIQUE OF POTENTIOMETRIC REDOX TITRATION**

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Cytochromes are known as important redox proteins involved in the movement of reducing equivalents, coupled with oxidative and photophosphorilation. Due to the transition states of their heme iron atoms, they are able to carry electrons between several parts of electron transfer chains. Among this family of proteins, cytochrome c especially, is unique with two features: 1) it is the only water-soluble protein and 2) in addition to its electron transfer capabilities, it plays a significant role in signaling for apoptosis. In the present work, an attempt is made to evaluate the quantity of reduced heme iron of cytochrome c in the solution. The method is based on the redox titration of Fe(II) with Ce(IV) as titrant. Potentiometry is used to determine the point of equivalence. These and previous results suggest, that the technique of potentiometric redox titration could be a reliable tool for assessment of Fe(II) contents of some proteins. However, precautions are necessary regarding the presence of interferences in the solution under examination.



Titration of 35 mg cytochrome c (0.43% iron) in distilled water with 0.01M Ce(IV). The obtained total Fe(II) content in the solution is 3.1  $\mu$ moles.