ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 3, pp. 463–469. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © S.M. Kuz'min, S.A. Chulovskaya, A.V. Balmasov, V.I. Parfenyuk, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 3, pp. 367–372.

Electrochemical Processes on the Copper Electrode in Water–Ethanol Solutions of Copper Sulfate

S. M. Kuz'min[a], S. A. Chulovskaya[a], A. V. Balmasov[b], and V. I. Parfenyuk[a,b]

[a] *Institute of Solution Chemistry, Russian Academy of Sciences,*
ul. Akademicheskaya 1, Ivanovo, 153045, Russia
e-mail: vip@isc-ras.ru

[b] *Ivanovo State Chemical Engineering University, Ivanovo, Russia*

Received January 14, 2010

Abstract—The system $Cu/H_2O–C_2H_5OH–CuSO_4$ was studied in a wide range of organic component concentrations by the impedance spectroscopy method. In the studied range of ethanol concentrations the diffusion of ions to an electrode is the limiting stage of the electrode process. An increase in the ethanol concentration results in a decrease in the double electrical layer capacity, which is caused by a change in the double electrical layer structure at the electrode-solution boundary.

DOI: 10.1134/S1070363211030030

The electrode impedance spectroscopy method plays an appreciable role in fundamental and applied studies [1, 2]. It can be used for studying any type of solid and liquid materials: ionic, mixed, semiconducting, and even insulators. The method is especially important for studying charge transfer in heterogeneous systems including phase and electrode boundaries and microstructure elements.

The determination of the influence of the metal and solvent nature on the double electrical layer structure and also on adsorption phenomena at the metal-solution boundary is of principal importance for the creation of the general theory of the structure of charged interphase boundaries and for the understanding of the mechanisms of electrode processes. The increasing interest to nonaqueous solutions is caused by growing application of such systems in chemical current sources and metal-oxide electrolytic capacitors, for the preparation of nanosized copper-containing powders, which found an application in lubricating compositions, for the production of new effective catalysts with extended specific surface areas, and for modification of medical materials with the purpose to impart them with biocidal properties [3, 4]. Furthermore, ethanol attracts more and more attention as a fuel for low-temperature fuel cells [5].

To describe the behavior of electrochemical systems under the action of alternating current, a method of building-up electric equivalent circuits, which possess the same frequency properties as a prototype system, is widely use. In the simplest case the equivalent circuit represents a resistor-condenser two-terminal device. As the impedance theory was developed, the trend to complicating equivalent circuits was observed. It is connected with the fact that at building-up a model one or several elements are assigned to each physicochemical process, which are further united in a common equivalent circuit in view of the sequence of occurring reactions.

To describe electrochemical processes complicated by the electrode surface inhomogeneity and kinetic or diffusion hindrances in a near-electrode layer, it is necessary to introduce special elements in an equivalent circuit, which are usually named in the engineering practice as systems with distributed parameters. Most known of them is Warburg's diffusion impedance [6].

The properties of the interphase boundary in the system $Cu|H_2O–iso\text{-}C_3H_7OH–CuSO_4$ [7] in the frequency range from 600 up to 60000 Hz were studied using an R5021 alternating current bridge, and in wider ranges of frequency and organic component concentration, using a Solartron electrochemical measuring complex. The impedance spectra were interpreted according to the scheme, which we used earlier [7].

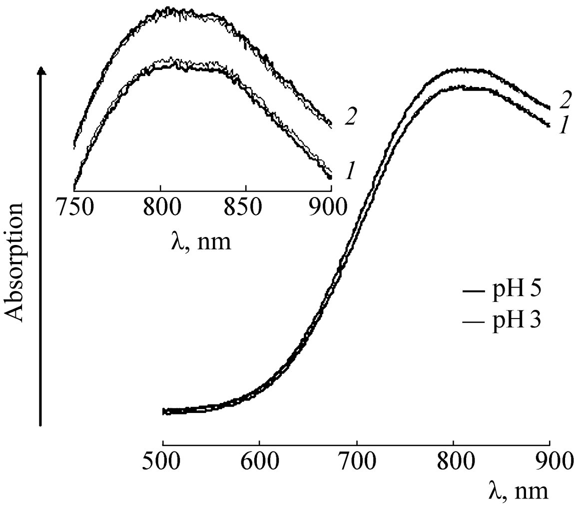

Fig. 1. Electron absorption spectra in sulfate solutions: (*1*) aqueous and (*2*) water–ethanol.

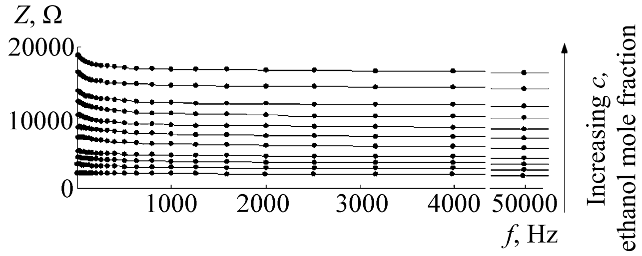

Fig. 2. Dependences of impedance modulus on the signal frequency at various ethanol concentrations.

Reliability of the impedance spectroscopy data considerably depends on model approximations, which cannot be built without additional information on the properties of the medium and the interphase boundary. When $CuSO_4$ is dissolved (0.005 mol kg^{-1}) in aqueous and water–ethanol solvents the medium becomes weakly acidic depending on the alcohol concentration (pH 5.0±0.5), which allows us to assume that copper hydroxo complexes are formed. To determine the state of ions in the solution, the medium was additionally acidified. An examination of the electronic spectra (Fig. 1) has shown that spectral characteristics of solutions under study with various pH values are identical, which points to similar states of ions in the solutions.

Experimental absolute values of impedance in relation to the frequency of applied voltage at various organic component concentrations are presented in Fig. 2. A monotone run of the curves points to the fact that the nature of electrode process remains unchanged in the frequency interval under study.

The data obtained were interpreted by means of a graphical method of the impedance representation. Impedance hodographs for all studied systems have common characteristic features. To a first approximation, the hodograph shape represents elements of circles with centers lying below a real axis (Fig. 3).

Such behavior of an electrochemical system is most often described by means of a constant phase element (*Q*) [Eq. (1)] [8].

$$Q = A^{-1}(j\omega)^{-n}. \qquad (1)$$

Here A is a preexponential factor independent of frequency; n is an exponent defining the frequency dependence character ($-1 < n < 1$), its deviation from 1, in particular, characterizing a degree of the capacitor nonideality; j is imaginary unit; $\omega = 2\pi f$ is a circle frequency.

When simulating experimental impedance using an equivalent circuit including a constant phase element (Fig. 4a) the characteristic n value has appeared close to 0.5, which points to the diffusion character of the process. Furthermore, noticeable discrepancies of experimental and calculated (Fig. 5, dashed line) impedance values in the low-frequency region were observed. Therefore the analysis of the impedance spectra was carried out with the use of element G with distributed diffusion-type parameters (Fig. 4b).

Gerisher's impedance, which was included in the equivalent circuit (Fig. 4), has given the best agreement between the experimental and theoretical impedance spectra (Fig. 5, solid line). Gerisher's impedance value (2) depends on diffusion factor Y_0 and on constant k commonly describing the rate of sequential chemical reactions with an electrochemical stage [6] or electrode porosity [9]. The diffusion factor Y_0 is connected with Warburg's constant by relation (3).

$$G = \frac{1}{Y_0\sqrt{k + j\omega}}, \qquad (2)$$

$$\frac{1}{\sqrt{2}Y_0} = \sigma = \frac{RT}{z^2F^2A\sqrt{2}}\left(\frac{1}{D_o^{1/2}c_o} + \frac{1}{D_r^{1/2}c_r}\right). \qquad (3)$$

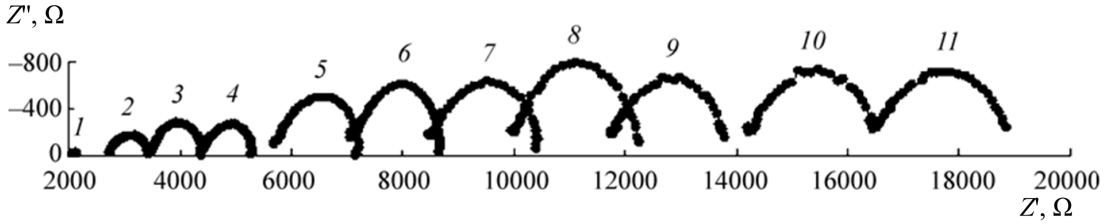

Fig. 3. Frequency impedance spectrum of copper sulfate water-ethanol solutions. Ethanol concentration: (*1*) 0.00, (*2*) 0.02, (*3*) 0.04, (*4*) 0.06, (*5*) 0.08, (*6*) 0.10, (*7*) 0.12, (*8*) 0.14, (*9*) 0.16, (*10*) 0.18, and (*11*) 0.20 mole fraction.

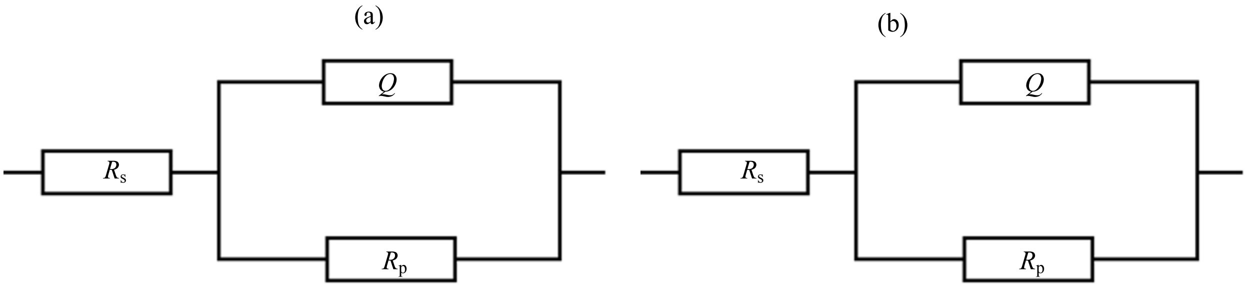

Fig. 4. Equivalent circuits simulating an electrochemical cell impedance using: (a) element of constant phase *Q* and (b) Gerisher's diffusion impedance.

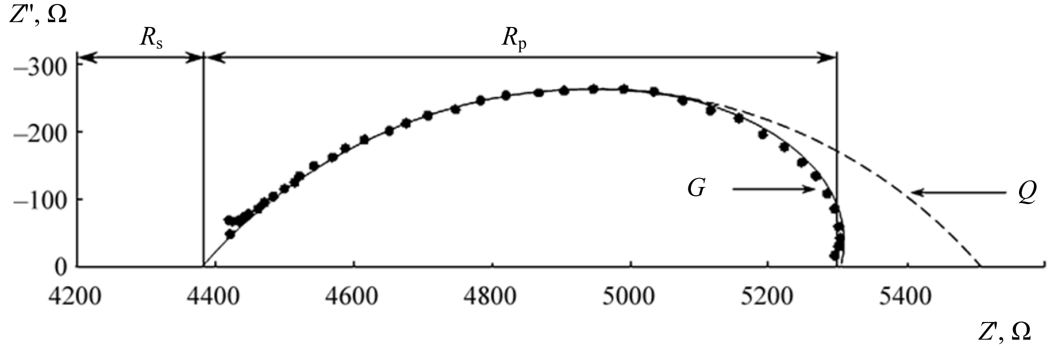

Fig. 5. Graphical interpretation of elements simulating cell impedance.

Here $\omega = 2\pi f$ is cyclic frequency; z is mobile ion charge; F is Faraday constant; c_o and c_r are concentrations of oxidized and reduced substance forms in bulk solution; D_o and D_r are diffusion coefficients of the oxidized and reduced forms.

Statistic parameters of approximating experimental data according to the equivalent circuit (Fig. 4b) are presented in the table.

Quantitative analysis of the impedance dependence on frequency based on the selected equivalent circuit allows us to interpret its elements according to the physicochemical nature of the processes passing on the electrode. Electrolyte resistance (R_s) is equivalent to the length of the segment, which is cut off by the hodograph high-frequency edge on the abscissa axis (Fig. 5). A segment on the real axis between high-frequency and low-frequency hodograph ends was interpreted as the interface polarization resistance (R_p).

According to the obtained results (Fig. 6), the electrolyte resistance monotonously increases as the alcohol mole fraction increases. The resulting dependence agrees well with classical representations of conductance variation resulting from the variation of the medium viscosity [10], according to which relation (4) is satisfied.

$$\lambda\eta^{\alpha} = \text{const.} \qquad (4)$$

Here λ is a specific conductivity; η is a viscosity; α is a constant less than or equal to unit. In the concentration

Statistic parameters of approximating experimental data according to the equivalent circuit (Fig. 4b)

c, mole fraction	χ^2	Σ^2
0.00	5.60E–05	0.0043
0.02	4.46E–05	0.0034
0.04	1.00E–04	0.006
0.06	4.20E–05	0.0028
0.08	9.10E–05	0.0058
0.10	5.00E–04	0.0300
0.12	7.70E–05	0.0040
0.14	2.00E–04	0.1600
0.16	1.00E–04	0.0067
0.18	9.50E–05	0.0057
0.20	3.30E–05	0.0020

interval under study the viscosity of water–ethanol mixtures linearly increases as the mole fraction of alcohol increases [11], therefore the dependence of the logarithm of solution resistance on the alcohol mole fraction should be close to linear (Fig. 6).

To calculate specific capacity of the double electrical layer dense part, we used relation (5).

$$C_{sp} = -1/\omega Z''S. \qquad (5)$$

Here Z'' is the imaginary impedance component and S is the geometrical electrode area. Capacity of the double electrical layer dense part was determined by approximating the $C_{sp}(Z'/\omega)$ dependence to the infinite frequency. For alternating-current frequencies in the range of 2–30 kHz the linear dependence was obtained with a correlation coefficient greater than 0.95, that allows us to estimate the value of the double electrical layer specific capacity.

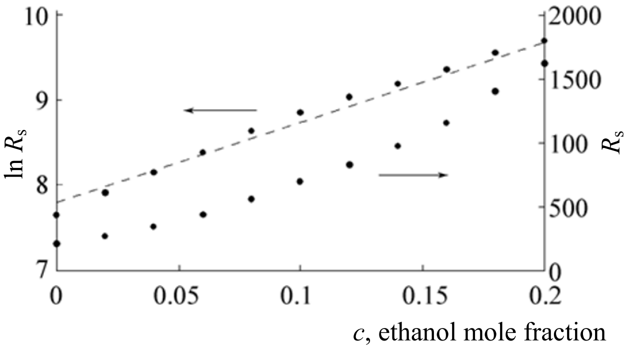

Fig. 6. Effect of ethanol mole fraction on the electrolyte resistance.

It is seen from Fig. 7 that, as the ethanol concentration increases, the specific capacity of the double electrical layer in the systems under study decreases from 1 up to 0.5 μF cm^{-2}, passing through a minimum at the ethanol concentrations of 0.08–0.1 mole fraction. Probably, the double layer has a diffuse structure at so small copper ions concentrations. The decrease in the double electrical layer capacity on adding alcohol in the system is caused by a lower dielectric constant of the organic component as compared with water [11]. Furthermore, the penetration of alcohol molecules results in thickening the double layer dense part (the distance between plates of the parallel-plate capacitor simulating the double layer). The electrode potential in the solution under study is no less important for the formation of a near-electrode layer. At the same time in the case of a zero charge potential [12] the double electrical layer will be minimal.

The value of resistance R_p calculated within the limits of the model characterizes the charge transfer through an interphase boundary. As in this series of experiments impedance was measured at small deviations of a potential from an equilibrium value, the polarization resistance can be presented in the form of Eq. (6).

$$R_p = RT/zFi_{ex}. \qquad (6)$$

Here R is the universal gas constant, T is the thermodynamic temperature, (z = 2) is charge number of the copper ion, F is the Faraday constant, and i_{ex} is a density of the exchange current of the reversible process of copper oxidation passing on the electrode.

$$\mathrm{Cu} \leftrightarrow \mathrm{Cu}^{2+} + 2\bar{e}.$$

Relation (6) allows us to calculate the value of the density of exchange current (7) on the basis of the found values of polarization resistance.

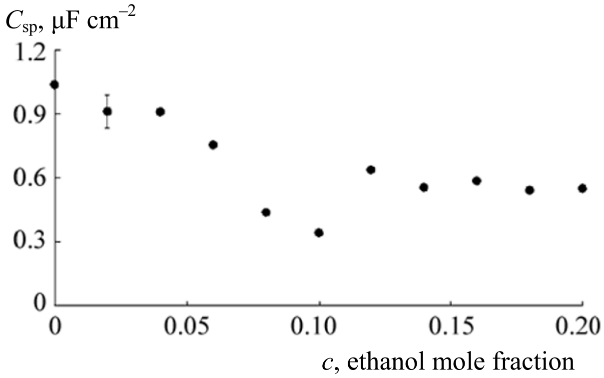

Fig. 7. Effect of the ethanol concentration on the double electrical layer specific capacity.

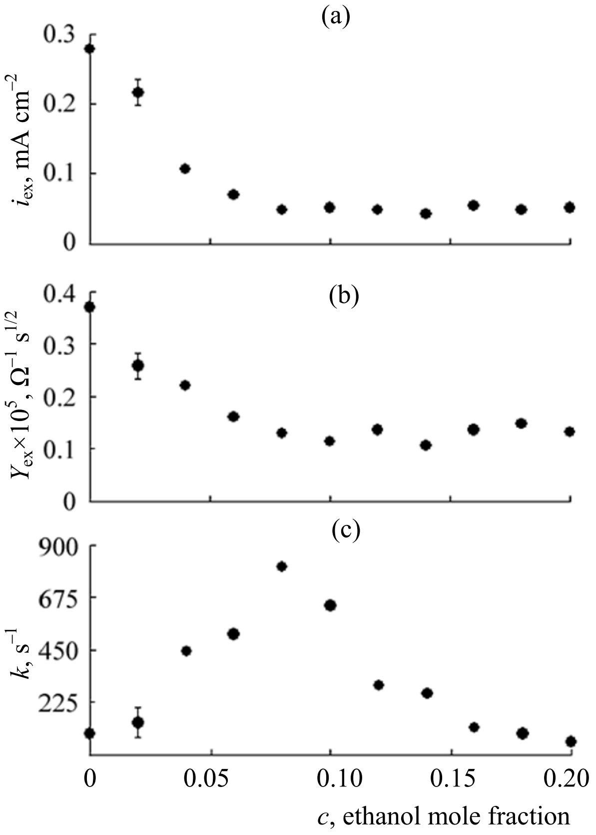

Fig. 8. Effect of ethanol concentration on: (a) exchange current density i_{ex}; (b) diffusion factor Y_{ex}; (c) coefficient k describing the accompanying process rate.

$$i_{ex} = RT/zFR_p. \quad (7)$$

It is seen from Fig. 8a that the exchange current density calculated by relation (6) decreases at small alcohol additions and, since the concentration of ~0.08 mole fraction, remains constant. The values of the exchange current density found in the present work agree with data [13–16] for solutions with close copper ions content.

The fact that the exchange current density decreases with increasing ethanol concentration can be explained by a partial blocking of the electrode surface by ethanol molecules. The variation in the solvent composition in the near-electrode space affects the rate of particles diffusion to the electrode. On this basis we can explain the variation of diffusion factor Y_0 at the increase in the ethanol mole fraction (Fig. 8b) by a decrease in the copper ions diffusion coefficients. We assume that the reaching of a constant exchange current density corresponds to such a state of the interphase boundary when the near-electrode space is filled by alcohol molecules.

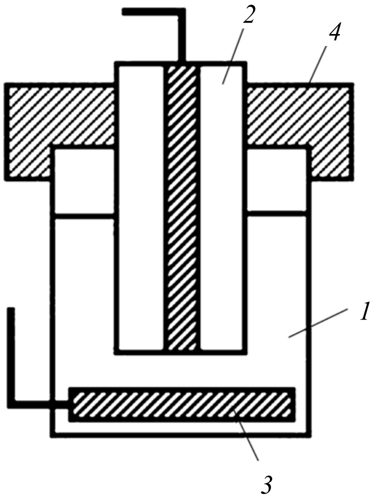

Fig. 9. Scheme of electrochemical cell: (*1*) electrolyte solution; (*2*) working electrode; (*3*) auxiliary electrode; and (*4*) fluoroplastic cover.

In the case under consideration the coefficient k can reflect a concurrence of several processes, which finally define differences between real and its idealized electrochemical cells. These are physicochemical processes (resolvation and desolvation of copper ions), diffusion of electroactive components of the system, and the electrode reaction itself. In particular, the change of solvate shells at the variation of the solvent composition can influence the rate of the copper ions diffusion to an electrode. From the concentration of alcohol of ~0.08 mole fraction the displacement of water molecules from the near-electrode space [7] is completed. It is a probable reason of the presence of a maximum on the dependence of coefficient k on the ethanol concentration (Fig. 8c).

EXPERIMENTAL

The electron absorption spectra of solutions were recorded on a Varian Cary 50 spectrophotometer. The stationary potential of the working electrode in solutions under study was determined with respect to a silver-chloride electrode using a Precision Digital pH OP-208/1 (Hungary) pH-meter. Stabilization of potential values were reached approximately within 10 min after immersing the working electrode.

The measurements of the electrochemical impedance were fulfilled by means of a Solartron 1260A analyzer. The amplitude of the imposed alternating voltage in the experiments was 10 mV. The frequency range was from 0.1 up to 5×10^4 Hz. The electrochemical cell was connected to an impedance-measuring instrument according to a two-electrode four-wire circuit, which allowed us to exclude the impedance of electrically conductive wires from the complete impedance of the system. The resulting impedance spectra of the systems under study were treated by means of the ZViev 2 program, allowing the electrochemical cell impedance to be simulated by equivalent circuits containing up to 20 various elements. Parameters of the model were determined by searching for coefficients of a composite function by a simplex-method. The values of the elements of the equivalent circuits found in several experiments were averaged.

The electrochemical cell (Fig. 9) used for the impedance measurements of a double electrical layer represents a temperature-controlled glass vessel containing solution under study Eq. (1) and equipped by working Eq. (2) and auxiliary Eq. (3) electrodes opposite to each other 5 mm apart. The auxiliary electrode was made of platinized platinum, and the working electrode was a copper rod of 3 mm in diameter pressed in fluoroplastic bush with exterior diameter 10 mm. The rigid fixing of the working electrode in the cell was provided by means of fluoroplastic cover Eq. (4). The application of the auxiliary electrode from the platinized platinum in the form of a disk (25 mm in diameter) allows its capacity to be neglected owing to a large surface area (therewith the current density on the auxiliary electrode is negligibly small).

Reproducibility of the electrode potentials in solution during impedance measurements was provided by the execution of the procedure of the working electrode preparation. A working zone of the electrode was sanded by a fine-grained abrasive paper, degreased by alcohol, and carefully washed out by distilled water. Then the electrode was held for 48 h in air at a humidity of 60% and temperature of 20°C. The electrode was washed by a solution under study and placed in the cell.

To prepare solutions, the salt $CuSO_4\cdot5H_2O$ (analytical grade) and ethanol (chemically-pure grade) were used after additional refining [17]. The solutions were prepared in distilled water by the weight method. Salt samples were weighted on a VLR-200 g-M laboratory balance with a maximal permissible error of weighting ±0.5 mg. Solvents were weighted on a VL-E144 laboratory electron balance with a maximal permissible error of weighting ±30 mg.

Water-organic solutions of copper sulfate were used as the electrolyte (salt concentration 0.005 mol kg^{-1}). Ethanol concentration was varied over the range of 0.00–0.20 mole fraction in steps of 0.02 mole fraction. The range of alcohol concentration was defined using the salt solubility in the mixed solvent as the base.

REFERENCES

1. Grafov, B.M. and Ukshe, E.A., *Elektrokhimicheskie tsepi peremennogo toka* (Electrochemical Circuits of Alternating Current), Moscow: Nauka, 1973.
2. Damaskin, B.B., Petrii, O.A., and Tsirlina, G.A., *Elektrokhimiya* (Electrochemistry), Moscow: Nauka, 2001.
3. Tesakova, M.V., Parfenyuk, V.I., and Godlevskii, V.A., *Elektron. Obrabotka Materialov*, 2008, no. 6, p. 56.
4. Alekseeva, O.V., Chulovskaya, S.A., Bagrovskaya, N.A., Garas'ko, E.V., and Parfenyuk, V.I., *Zhidkie Kristally i ikh Practicheskoe Ispol'zovanie,* 2007, no. 4 (22), p. 84.
5. Tsivadze, A.Yu., Tarasevich, M.R., Andreev, V.N., Bogdanovskaya, V.A., Efremov, B.N., Kapustina, N.A., Titova, V.N., Yavich, A.A., Belova, N.N., and Mazin, P.V., *Alternativnaya Energetika i Ekologiya*, 2007, vol. 48, no.4, p. 57.
6. Damaskin, B.B. and Petrii, O.A., *Vvedenie v elektrokhimicheskuyu kinetiku* (Introduction to Electrochemical Kinetics), Moscow: Vysshaya Shkola, 1983.
7. Kuz'min, S.M., Chulovskaya, S.A., Noskov, A.V., and Parfenyuk, V.I., *Zh. Obshch. Khim*., 2009, vol. 79, no. 11, p. 1766.
8. Stoinov, Z.B., Grafov, B.M., Savvova-Stoinova, B.S., and Elkin, V.V., *Elektrokhimicheskii impedans* (Electrochemical Impedance), Moscow: Nauka, 1991.
9. Gonzalez-Cuenca, M., Zipprich, W., Boukamp, B.A., Pudmich, G., and Tietz, F., *Fuel Cells*, 2001, vol. 1, p. 256.
10. Robinson, R.A. and Stokes, R.H., *Electrolyte Solutions. The Measurement and Interpretation of Conductance, Chemical Potential and Diffusion in Solutions of Simple Electrolytes*, London: Butterworths, 1959, 2nd Ed.
11. Afanas'ev, V.N., Efremova, L.S., and Volkova, T.V., *Fizikokhimicheskie svoistva binarnykh rastvoritelei. Vodosoderzhashchie systemy* (Physicochemical Properties of Binary Solvents. Water-Containing Systems), Ivanovo, 1988, part II.
12. Frumkin, A.N., *Potentsialy nulevogo zaryada* (Zero Charge Potentials), Moscow: Nauka, 1982.

13. Jose Luis Nava-M. de Oca, E. Sosa, Carlos Ponce de Leon, and Oropeza, M.T., *Chem. Engineering Sci.,* 2001, vol. 56, p. 2695.
14. Wan, C.C., Cheh, H.Y., and Linford, H.B., *J. Applied Electrochemistry*, 1979, vol. 9, p. 29.
15. Mishchenko, K.P. and Ravdel', A.A., *Kratkii spravochnik fizikokhimicheskikh velichin* (Brief Handbook of Physicochemical Quantities), Leningrad: Khimiya, 1974.
16. Antropov, L.I., *Teoreticheskaya elektrokhimiya* (Theoretical Electrochemistry), Moscow: Vysshaya Shkola, 1984, p. 459.
17. Karyakin, Yu.V. and Angelov, I.I., *Chistye khimicheskie veshchestva* (Pure Chemicals), Moscow: Khimiya, 1974.