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Effect of Hydrodynamic Conditions on the Silver Electrodeposition from Water-Ethanol Solutions of Electrolytes

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Abstract—Effect of hydrodynamic conditions on the silver electrodeposition from the aqueous and water–ethanol solutions of silver nitrate is studied with the purpose of the establishing the process limiting step nature. In the investigated systems of the silver electrodeposition in the potentiodynamic regime the current strength depends on the intensity of stirring and is changed due to the change in the limiting step and the surface morphology. Adding of nonaqueous solvent to the larger extent influences the electrolytic rather than diffusion stage of the process.

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The contemporary materials science assigns the key importance to the nano-dimensional metal powders , which have the functional characteristics different from those of the condensed phases [1–3]. The successes in scientific research and use of nano-particles of a metal to a considerable extent depend on the development of the methods of their synthesis, in particular, on the possibility of the method of preparing the particles satisfying the requirements of specific scientific or practical problem. A promising trend in the contemporary technology is the electrochemical deposition of the nano-dimensional powders of a metal from the solutions of electrolytes [4, 5], resulted in passing the metal and its compounds from the dissolved state to the cathode in the form of a friable sediment. The practical realization of this process assumes the knowledge of the factors influencing the sediment formation and determing eventually the physicochemical properties of the obtained product.

The initial stage of the sediment formation is nucleation on the active centers of the support. Varying the regime of the process and the electrolyte composition one can realize the wide spectrum of the dynamics of the sediment growth: to accelerate, or to sharply decelerate the growth of the primary formations and to form other crystals on their surface. Precipitation at the maximal current density is characterized by the deceleration of the stage of the metal cations diffusion to the electrode surface, which contributes to the formation of friable spongy highly dispersed precipitates.

Electrochemical reduction of metal ions from the water-organic solvents proceeds via the series of sequential processes on the cathode, including reaching the electrode by the hydrated (solvated) ions, deformation of solvate shell discharge of the ions, etc,. The solvent composition should affect the process of the metal electrodeposition [6].

Earlier we obtained the nano-dimensional powders (average size of 50 nm) containing copper in the system water–2-propanol [7, 8]. The spectrum of the practical application of the obtained materials is wide enough and diverse. The copper powder introduction into the lubricating compositions containing allowed to improve the performance of the conjugated working pairs [9]. The nano-dimensional copper powders adding to polymeric matrices admit to the latter the antibacterial properties with respect to many bacterial species [10]. The ultra-dispersed state of metal increases considerably the activity of the copper based

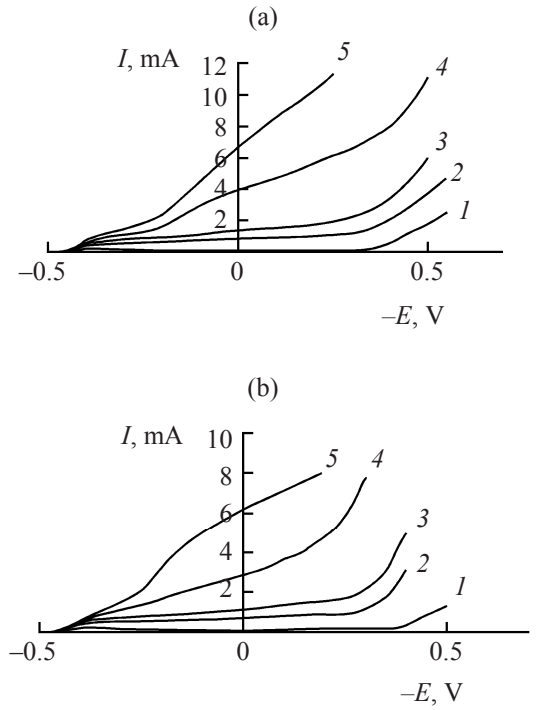

Fig. 1. Polarization curves of cathodic deposition of silver from (a) aqueous and (b) water–ethanol solutions of $AgNO_3$. Rotation rate of disc electrode: (*1*) 0, (*2*) 200, (*3*) 400, (*4*) 900, and (*5*) 1600 rpm.

hybrid catalysts for the different oxidation-reduction reactions [11].

Silver is also promising for the practical use. The new form of nano-silver [12] opens great possibilities for creating the effective preparations with the high biological activity for the use in medicine, environment protection and agriculture. A number of publications is dedicated to the study of the synthesis of nano-silver [12, 13]. The development and the improvement of ideas about the mechanism of processes in the water–organic solutions of electrolytes is necessary for the solution of the appearing new practical problems.

In the present work is studied the influence of hydrodynamic conditions on the silver electrodeposition from aqueous and water–organic solutions of silver nitrate for the purpose of the elucidation of nature of the process limiting step.

The silver ions discharge on the cathode proceeds in correspondence with the reaction (a).

$$Ag^+ + e \rightarrow Ag^0,\ E^0 = 0.799\ V. \qquad (a)$$

Besides is possible simultaneous reduction of nitrate ions (b, c).[1]

$$NO_3^- + 3H^+ + 2e \rightarrow HNO_2 + H_2O,\ E^0 = 0.94\ V, \qquad (b)$$

$$2NO_3^- + 4H^+ + 2e \rightarrow N_2O_4 + 2H_2O,\ E^0 = 0.80\ V. \qquad (c)$$

The rate of the electric reduction of silver from the solutions (at the current strength I, μA) is determined, in particular, by the applied potential (E, V) and by hydrodynamic conditions. The polarograms of the cathodic precipitation of silver are represented in Fig. 1.

When the potential reaches E ~0.3 V (silver chloride electrode) the simultaneous reaction (d) of the hydrogen liberation becomes possible.

$$2H_3O^+ + 2e \rightarrow H_2 + 2H_2O. \qquad (d)$$

As seen from Fig. 1, an increase in the intensity of stirring leads to an increase in the current strength I, that indicates an important role of convective diffusion. For affirming the assumed were built the $I - \sqrt{\omega}$ dependences for a number of the potential values (Fig. 2).

When E = +0.4 V that corresponds to small deviations from the steady-state value, the processes obeys the combined diffusion-kinetic control. This assumption is confirmed by the fact that the obtained experimental results can be well linearized in the I^{-1}–$\omega^{-0.5}$ coordinates. In accordance with equation (1) [14] from the value of the section intercepted on the Y-axis can be calculated the value of kinetic current I_k, and the value of coefficient a_1 defines diffusion current (2).

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{a_1\sqrt{\omega}}, \qquad (1)$$

$$I_d = a_1\sqrt{\omega}. \qquad (2)$$

For the process of electrical reducing of silver ions the I_k values calculated from the experimental data equal to 1.73 μA (for the aqueous solution) and 0.75 μA (for the water–ethanol mixture). This decrease in the rate of electrode process can result from the entering the C_2H_5OH molecules into the dual electrical layer and into the solvation shell of the discharged Ag^+ cations.

Negative shift of cathode potential leads to increase in the rate of the electrode process and, as a result, in

[1] By the data [14], for the solutions used by us the silver yoield on the qurrent is 95–97%. Therefore accounting of concurrent reactions does noc affect the principal conclusions (below) about the nature of lomiting step.

the limiting stage becomes of diffusion nature. Near this potential (+0.3 V) the I–$\sqrt{\omega}$ plots are linear and are extrapolated into the coordinates origin. In accordance with the fundamental equation of diffusion kinetics for revolving disk electrode (3) [15] the angular coefficient of this line a_2 depends on the solution kinematic viscosity (ν), concentration (c_0) and coefficient of diffusion of the discharged cations (D).

$$a_2 = 0.62nFSD^{2/3}\nu^{-1/6}c_0. \quad (3)$$

Here n is the number of electrons in the reaction (a), S is apparent electrode surface area, F = 96487 Q mol^{-1} is Fraraday unit.

For the aqueous solutions the obtained experimental value a_2 is 0.038 A min$^{0.5}$ cm^{-2} cycles$^{-0.5}$, which is close to value a_1 of 0.039 A min$^{0.5}$ cm^{-2} cycles$^{-0.5}$ calculated according to Eq. (1). Taking into account the fact that in our case $c_0 = 0.05\times10^{-3}$ mol cm^{-3}, $S = 7.069\times10^{-2}$ cm^2, n = 1, and $\nu = 0.897\times10^{-2}$ cm^2 s^{-1} [16], for the aqueous solution is obtained $D = 4.018\times10^{-6}$ cm^2 s^{-1}. Analogous calculation carried out for the water – ethanol mixtures, gave the close value of the diffusion coefficient of cations ($D = 3.975\times10^{-6}$ cm^2 s^{-1}). (Value $\nu = 0.996\times10^{-2}$ cm^2 s^{-1} for the solutions containing 0.01 molar fraction of C_2H_5OH was found by the interpolation of reference data for the water – ethanol mixtures [16]). The results obtained are consistent qualitatively with the of Stokes–Einstein law [17], which connects the ion diffusion with the medium viscosity.

Analysis of the data obtained for the more negative cathodic potentials indicates the disturbance of the linearity of I–$\sqrt{\omega}$ plot (Fig. 2). With an increase in the frequency of the revolving disk electrode (RDE) rotation the current grows "faster" than this follows from Eq. (2). This effect is explainable by an increase in the real electrode surface area in the course of the silver deposition. If the electrolysis proceeds sufficiently long, then with an increase in the overall mass the deposit acquires dendritic form and the kinetics of process is complicated by the effects characteristic of the porous electrodes.

As noted in [18], cathodic sediment can display fractal properties. In the case of diffusion to the "fractal" electrode the dependence of the process rate on the intensity of stirring obeys Eq. (4) [19].

$$I \sim \omega^{\alpha}. \quad (4)$$

Exponent α is connected with the fractal dimension of the electrode surface (d_f) by the relation (5).

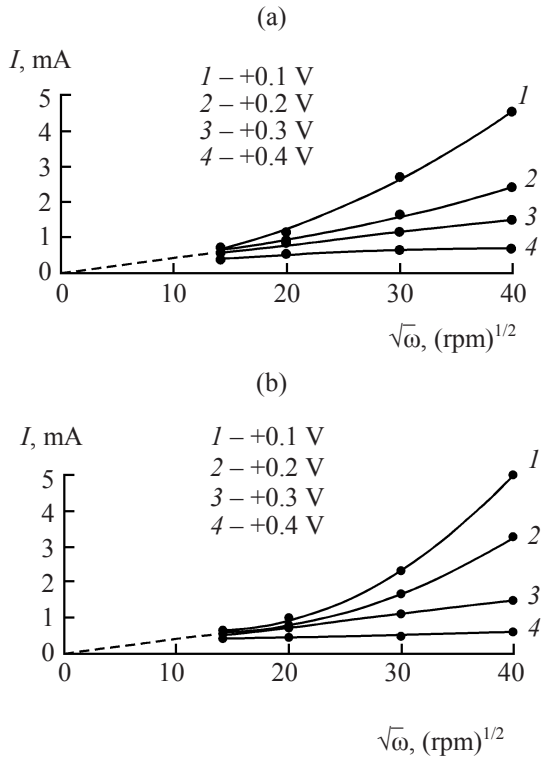

Fig. 2. Plots I–$\sqrt{\omega}$ for a series of potential values in (a) aqueous and (b) water–ethanol solution of silver nitrate.

$$\alpha = (d_f - 1)/2. \quad (5)$$

In the particular case of the ideally flat electrode the fractal dimension equals two and, therefore, the "fractal" dependence (4) is converted into the classical Eq. (2). The analysis of the obtained experimental material on the electrodeposition of silver from the aqueous and water–etanol solutions of $AgNO_3$ showed that the dependence of the process rate on the intensity of stirring do obey equation (4). This is confirmed by the high values of correlation coefficients R^2 (see the table).

Fitting experimental data

E, V (SCE)	$AgNO_3$ aqueous solution		$AgNO_3$ dissolved in water–ethanol system (0.01 mole fraction)	
	α	R^2	α	R^2
0.2	0.635	0.997	0.873	0.987
0.1	0.902	0.997	0.999	0.989
0.0	1.051	0.994	1.041	0.994
–0.1	1.121	0.993	1.092	0.995
–0.2	1.141	0.996	1.203	0.997
–0.3	1.136	0.997		

The table lists the values of the parameter α calculated according to the experimental data in accordance with Eq. (4). At the shift of potential to the cathodic side the value of α grows due probably to the increase in the deposit surface area in the course of electrolysis. However, the fractal dimension d_f in this case connected with value α cannot be used as the quantitative characteristic of the degree of surface development since the calculated with formula (5) values $d_f > 3$, which contradicts physical sense. Apparently, the currently used models connecting the nature of the dependence of the process rate on the RDE rotation frequancy with the fractal dimension of surface are not applicable to describing the evolution of cathodic sediments.

The conducted investigations demonstrated an important role of hydrodynamic conditions at the electrochemical reduction of silver from the aqueous and water–ethanol solutions of $AgNO_3$. With the potentiodynamic regime of conducting the process the concrete form of the dependence of current strength on the intensity of stirring is changed as a result of a change in the limiting stage and morphology of surface. The comparison of the values of kinetic and diffusion currents for the aqueous and water–ethanol solutions allows to conclude that the adding of nonaqueous solvent contributes to the electrochemical rather than to the diffusion stage of process.

EXPERIMENTAL

For the polarization measurements was used a three-electrode cell with the revolving disk electrode, the rotation frequency 200, 400, 900, and 1600 rpm. Cylindrical stainless steel rod 3 mm diameter was used as the working electrode. For insulating the side surface and elimination of edge effects it was pressed into the teflon cup of 8–10 mm outside diameter, so the rod butt surface served as the working surface of the RDE. The RDE surface was cleaned by the treatment with fine-grained emery paper and degrease in acetone. The platinum wire was used as an auxiliary electrode. As the reference electrode served the saturated silver chloride electrode (SCE). The Luggin capillary was used for diminishing the resistive component at the measuring the cathode potential under current. The capillary was placed near the working electrode at a distance equal to the capillary outside diameter (50 μm). Polarization measurements were conducted in the potentiodynamic regime (the potential sweep rate 20 mV s^{-1}). The polarization of working electrode was achieved from a PI-50-1 potentiostat with a PR-8 programmer. Potentiodynamic polarograms were recorded with a two-coordinate recording potentiometer PDA-1.

As the components of working solutions were used silver nitrate of chemically pure grade and ethyl alcohol of analytically pure grade. The salt concentration was 0.05×10^{-3} mol cm^{-3}, ethanol concentrations 0.00 and 0.01 ppm. For increasing the electrical conductivity of the aqueous and water–etanol solutions of silver nitrate, a small quantity of nitric acid (0.5 ml per 500 ml of water) was added.

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