THE NONUNIFORMITY OF THE SURFACE OF THE ELECTRODE AND THE MECHANISM OF THE ELECTRODEPOSITION OF METALS

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The rates of electrochemical reaction on individual sections of the electrode are very diverse since the surface of the electrode is, as a rule, nonuniform and consists of active and passive sections. During the electrodeposition of metals, the surface condition of the electrode changes continuously and, hence, the study of electrode processes is made considerably more difficult. Among the works which contributed to the development of conceptions relating to the effect of the nonuniformity of the electrode surface, one should mention the papers by Erdey-Gruz and Volmer [1], Kohlschutter [2], R. Kaishev [3], K. M. Gorbunova [4], A. G. Semartsev [5], Hoekstra [6], S. V. Gorbachev [7], Fischer [8], and others. Usually, the nonuniformity of the surface of the electrode is not taken into account in the study of the rates of the electrochemical reactions.* Therefore, the results obtained in the study of the polarization of electrodes are not reproducible [9]. Fig. 1 shows polarization curves obtained by various authors during the deposition of copper. It is seen from these data that the cathodic polarization is distinguished not only by the absolute values but also by the mode of variation as a result of current-density variation.

A study of the growth and formation of individual crystals on the cathode made it possible to determine the basic laws for the electrodeposition of metals of low overvoltage, i.e., for the electrocrystallization of metals, as well as for the changes of the active surface of the electrode, and contributed to the elucidation of the causes of the variation of the polarization with time. It was established [9, 10], that during the deposition of metals, on a cathode of the same metal (for instance, the deposition of silver on the silver electrode), the process which takes place is not the formation of new crystals but the continuation of the growth of the active crystals on the cathode surface . The overvoltage encountered in this process is by far greater than the overvoltage necessary for the formation of a three-dimensional nucleus. The initial high polarization at the moment when the current is switched on during the deposition of metals with low overvoltage is due to the presence of a very small active surface of the electrode [9, 11]. It was also shown, that during the deposition of metals on the active sections of the electrode, the polarization is connected not with the retardation of the growth of the crystals but with the change in the concentration of metal ions in the layer adjacent to the electrode [10]. By taking into account the magnitude of the active growing surface of the electrode during the electrolytic growth of monocrystals and by comparing it with the changes in the polarization of the electrode it was shown that the polarization of the electrode is a function of the current density calculated not on the basis of the total surface but only of the active growing portions of the surface [12].

Together with N. T. Vagramyan [13], in a work, in which we took into account the true density of the current, we established that, on the introduction of an organic surface-active substance into the electrolyte, there is no additional electric field connected with the adsorption of organic molecules. In this way, we were able to determine quantitatively, on the basis of the polarization curves, the magnitude of the active as well as of the passive parts of the cathode. Indeed, since the polarization is determined by the current density calculated for the active part of the growing surface, then, knowing the value of the polarization, one can determine the active part of the electrode surface (S_a). If the total surface of the electrode is known then

$$S_{passive} = S_{total} - S_{active}$$

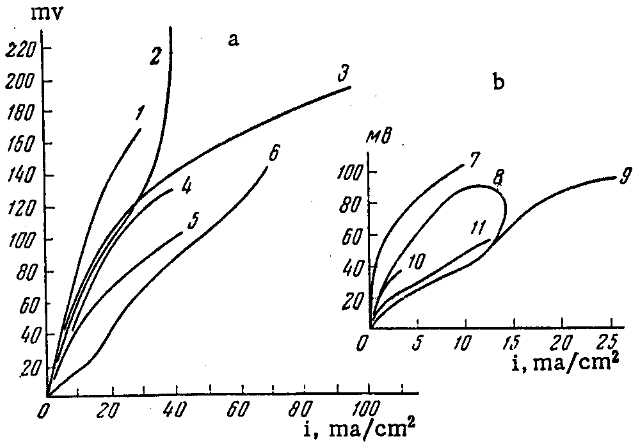


Fig. 1. Polarization curves obtained by various authors during the electrodeposition of copper. a: 1) 1.5 N $CuSO_4$ + 1.5 N H_2SO_4 (Haring, 1920); 2) 1 N $CuSO_4$ + 1 N H_2SO_4 (S. V. Gorbachev and A. V. Izmailov, 1951); 3) 1 N $CuSO_4$ Shreier and Smith, 1952); 4) 1 N $CuSO_4$ + 50 ml alcohol + 1 N H_2SO_4 (rapid method, 1952); 5) 1 N $CuSO_4$ + 0.6 N H_2SO_4 (Reichenstein, 1913); 6) 1 N $CuSO_4$ + 1 N H_2SO_4 (Gradam, 1946). b: 7) 1 N $CuSO_4$ + 1 N H_2SO_4 + 50 ml alcohol Mashchovets, 1950); 8) 0.7 N $CuSO_4$ + 0.4 N H_2SO_4 (Esin and Levin, 1935); 9) 1 N $CuSO_4$ + 2 N H_2SO_4 (Baimakov, 1938); 10) 1 N $CuSO_4$ + + 0.2 N H_2SO_4 (Isizaka, 1951); 11) 1 N $CuSO_4$ + 1 N H_2SO_4 (Fersten and Gerber, 1930).

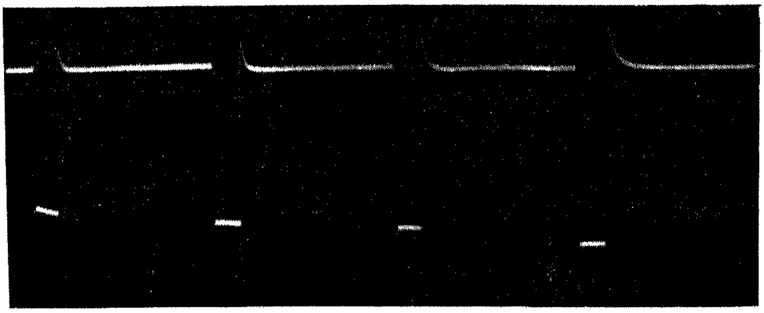


Fig. 2. Passivation curve for zinc cathode obtained in 2 N $ZnSO_4$ with an addition of octyl alcohol (0.0115 M) at i_{cath} = 2 ma/cm² and 18°C.

From the increase in the polarization of the electrode when the current is switched off for various time intervals (Fig. 2), one can determine the rate of passivation of the electrode. By this method, together with Z. A. Solov'eva [14], we studied the rate of the adsorption of additions of surface-active substances. Fig. 3 shows the rate curves of the adsorption of octyl alcohol on a zinc surface, and Fig. 4 shows the adsorption of the octyl alcohol as determined by the electrochemical method described above [9]. It is seen from these results that the polarization-curve method makes it possible to study successfully the adsorption on hard metal surfaces. It should be noted that determining adsorption isotherms for metals with small surface area by means of other methods presents considerable difficulties. By taking into account the nonuniformity of the electrode surface, we were able together with Yu. S. Tsareva [9, 15, 16], to develop in our laboratory an electrochemical method of determining the adhesion of the deposit to the base.

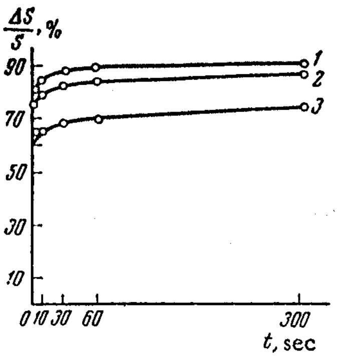


Fig. 3. Adsorption rate curves for octyl alcohol on zinc surface in 2 N $ZnSO_4$. Alcohol concentration: 1) 0.0115 M; 2) 0.0057 M; 3) 0

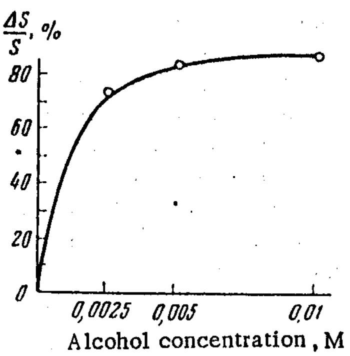


Fig. 4. Adsorption isotherm for octyl alcohol in 2 N $ZnSO_4$.

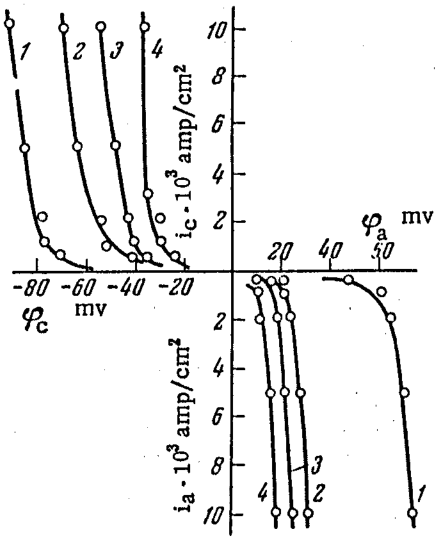


Fig. 5. Effect of various anions on the polarization during electrodeposition of zinc. 1) $Zn(ClO_4)_2$; 2) $ZnSO_4$; 3) $ZnCl_2$; 4) $ZnBr_2$

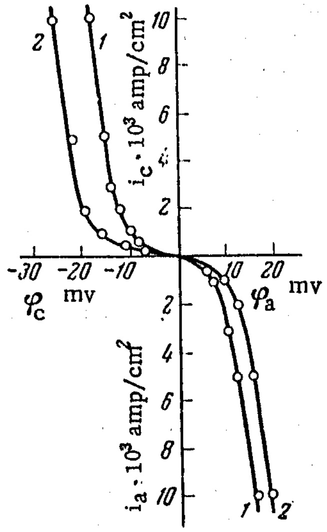


Fig. 6. Effect of surface-active substances on the polarization during the electrodeposition of cadmium. 1) Without additions; 2) with the addition of gelatin.

The study of the changes in the condition of the electrode surface showed that the degree of activity of the electrode can vary widely depending on the conditions of the electrode as well as the nature of the metal deposited. Sometimes, the adsorption proceeds so quickly that it is not possible to determine the adsorption rate by this method. It is seen from the above that the surface condition of the electrode determines the value of the overvoltage of the electrochemical reaction.

According to the value of the overvoltage metals can be divided, in the main, into three groups. The first group comprises the metals of low overvoltage Ag, Cu, Zn, Cd, and others. The second group comprises the metals whose deposition proceeds at a large overvoltage: Fe, Co, Ni, and others. The third group comprises those metals which cannot be obtained pure in the form of compact deposits from aqueous solutions; these metals are: Mo, W, U, V, Td, Ti, and others. The polarization curve for these metals of the first group has the characteristic form shown in Fig. 2. The initial high polarization decreases in the process of electrolysis down to a certain value, the total polarization, however, is relatively small. A number of similar curves for various metals (Zn [17], Cu [18], Ag [19], Cd [20], and others) can be found in literature. These curves indicate that the active surface of the electrode increases during the electrolysis and that the surface of the cathode becomes passivated if the electrode is kept in the electrolyte without any current. Indeed, if the current is interrupted for various time intervals and then switched on again, a jump of potential $\Delta\varphi$; takes place at the moment when the current is switched on [14, 16]. As a result, the polarization at the beginning of the electrolysis has a high value, and, at the same time, the longer the time interval τ during which the electrode is kept in the electrolyte without any current, the larger $\Delta\varphi$ $[\Delta\varphi = zf(\tau)]$. The drop in the polarization after the current is passed shows that the rate of the passivation of the electrode surface is low compared with the rate of metal deposition. For the deposition of metals of the first group, the rate of the discharge of ions should be proportional to that part of the electrode surface which is free of extraneous particles.

The metals of the second group are distinguished by a different form of the polarization curve [21]: the polarization does not decrease during electrolysis and remains constant when current is interrupted for various time intervals. A constant polarization when the current is interrupted for various time intervals is not an indication that the passivation is absent; on the contrary, it indicates that a high rate of passivation since these metals are much more easily passivated than the metals of the first group. Actually, Hoekstra [22] showed that if during the deposition of nickel the passive film is scratched off the cathode surface, the nickel potential is shifted towards negative values. It was also shown in one of our earlier works [23] that, when the polarization curve for nickel is determined by the rapid method, the higher the speed of recording the curve the more negative is the potential without current. The displacement of the potential of freshly deposited nickel towards positive values is connected with the passivation of the metal surface. Apparently, the surface of these metals cannot be kept absolutely clean for any length of time because of the adsorption of foreign particles. As a result, the surface becomes passivated and acquires a more stable state. As pointed out earlier, the velocity of transition into a more stable state varies depending on the conditions of electrolysis and the nature of the metal deposited. In connection with the presence of a strong film of foreign particles on the surface of the cathode (for the metals of the second group), a substantial fraction of the overvoltage is due to foreign particles (adsorbed on the electrode surface) which hamper the discharge of metal ions.

The metals of the third group are characterized by a high reactivity with respect to the medium and the formation of surface compounds. Therefore, it is not possible to obtain compact deposits of these metals in pure form from aqueous media. A number of attempts have been made to obtain metallic deposits of Ta [24], W [25], Ti [26], U [27], Mo [28] and V [29]. They were, however, unsuccessful. Thus, for instance, Clark and Lietzke [30] showed by means of labelled atoms that W can be deposited on a number of metals (Pb, Zn, Cd, Fe, Co, Ni, and others). The product, however, of the electrochemical reduction is not the pure metal but tungsten oxide. It is also shown that these metals of the third group are obtained on the cathode preferentially in the form of oxide and hydroxides. This is quite natural since the heat of formation of oxides of these metals is very high. A great affinity to oxidation is the very cause of the failure to obtain these metals in pure form by means of electrolysis in aqueous solutions: the reduced ion reacts immediately with the medium and forms oxides or hydroxides of the metal.

Hence, it can be assumed that the chemical overvoltage during the deposition of metals is due, to a considerable extent, to the difficultly in the discharge of metal ions owing to the inhibitive action of the extraneous particles which are adsorbed on the surface of the electrode, and to the formation of surface compounds. It is obvious that the extraneous particles which are adsorbed on the surface, and the surface compounds retard not only the rate of the discharge of metal ions but also their ionization. In other words, the extraneous particles interfere with the electrochemical reaction in one, as well as in the reverse, direction. Therefore, it could be expected that not only the cathodic but also the anodic overvoltage will be high. These concepts make it possible to predict some regularities. In particular, when the overvoltage during the dissolution and deposition is high, the exchange current should be very small.

Let us consider some experimental results.

The deposition of cadmium and zinc. The polarization of the cathode and anode during the electrodeposition of cadium and zinc under various conditions of electrolysis was studied in detail by Müller and Barchmann [31]. The most remarkable results of this work is the fact that the change in the conditions of the electrolysis and in the composition of the electrolyte, has the same effect on the cathodic as on the anodic polarization, i.e., when the cathodic polarization increases, the anodic polarization increases too. Thus, for

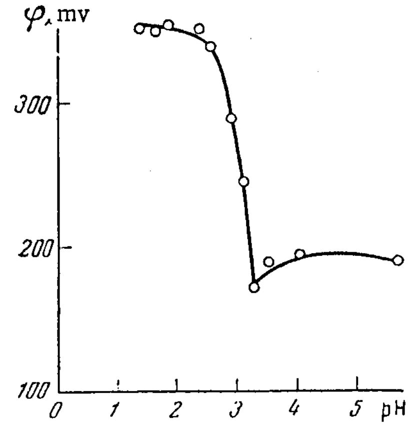
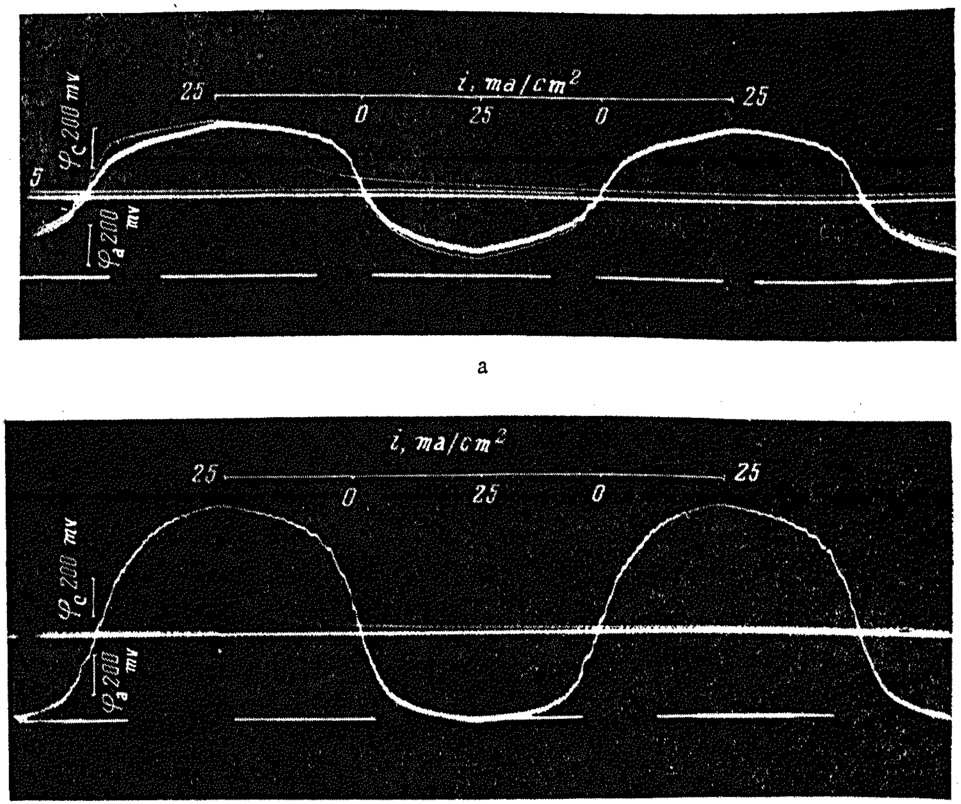


Fig. 7. Effect of the pH of the solution on the polarization during the electrodeposition of cobalt. 1 N $CoCl_2$ at 25°C; i_{cath} = 10 ma/cm^2.

instance, during the deposition of cadium and zinc from various solutions of their salts, the values of the cathodic and anodic polarization increase, depending on the anions, in the following order: $Cl^- < Br^- < SO_4^{2-} < ClO_4^-$ (Fig. 5) Müller and Barchmann showed that with a rise in the temperature of the electrolyte the cathodic as well as the anodic reactions are facilitated. When surface-active substances are introduced, the cathodic and anodic polarizations increase (Fig. 6). Thus, whenever the retardation of the cathodic process is increased, a retardation of the anodic process takes place.

Electrodeposition of cobalt and nickel. It is generally assumed that the metals of the iron group differ substantially from the remaining metals with respect to their electrochemical properties. Therefore, a study of the overvoltage during the deposition and dissolution of these metals is of special interest. Recently, in our laboratory, A. A. Solov'eva and O. A. Abrarov [32] investigated the cathodic and anodic polarization of cobalt and nickel. They showed that with an increasing temperature of the electrolyte, a decrease of the same magnitude in the cathodic as well as in the



a

b

Fig. 8. Cathodic and anodic polarization of cobalt, recorded by the rapid method. a) pH = 2.9; b) pH = 3.1.

anodic polarization takes place. During the study of the polarization of these metals, a new phenomenon was discovered: the rate of the electrochemical reaction increases rapidly within a narrow range of the pH (2.9-3.1) of the solution (Fig. 7). Additional experiments showed that in the pH range in which the deposition becomes easier, the rate of the dissolution of metals increases too (Fig. 8, a). In this way, it was established that the operating conditions which facilitate the discharge of the ions of the metals of the iron group during the electrolysis also accelerate the ionization of metal atoms.

DISCUSSION OF THE RESULTS

There are at present two main theories on the appearance of the overvoltage at electrodes:

The theory of concentration polarization [33], according to which the cause of the polarization is a retardation in the supply and disposal of the materials taking place in the electrochemical reaction. The rate of the anodic process is determined by the equation

$$i_a = nFc_0\left(e^{\frac{\varphi_a nF}{RT}} - 1\right)\sqrt{\frac{D}{kT}};$$

and, correspondingly, the rate of the cathodic process is determined by the equation

$$i_c = nFc_0\left(1 - e^{\frac{\varphi_c nF}{RT}}\right)\sqrt{\frac{D}{kT}}.$$

It is obvious that if the conditions of the electrolysis are conductive to a rapid attainment of the maximum current for the anodic process, the cathodic process under these conditions will proceed at a current far below the maximum current. Thus, at a high anodic polarization the cathodic polarization will be small. Hence, it is seen that the overvoltage of Zn, Cd, Ni, and Co in the experimental results quoted cannot be explained by concentration polarization. It should also be noted that the determination of the nature of the polarization in general presents no difficulties, since, at present, there are methods of separating chemical and concentration polarization [34].

The theory of retarded discharge [35]. According to the most widely accepted views, a retardation in the discharge of metal ions is due to the fact that they are strongly hydrated, and a considerable activation energy is necessary for their reduction. According to the equation of chemical kinetics, the velocity of a chemical reaction is an exponential function of the activation energy, and since the electrode potential affects the activation energy, the relation between the current and the potential will be of the form

$$i_c = kc_{\mathrm{Me}^{n+}}e^{-\frac{\alpha\varphi F}{RT}}.$$

According to the theory of retarded discharge [35], considerable forces of interaction between metal ions and water molecules must be overcome in the discharge of metal ions:

$$\mathrm{Me}^{n+}(\mathrm{H_2O})_m + ne \rightarrow \mathrm{Me} + m\mathrm{H_2O}.$$

At the same time, if the dehydration process of metal ions is less economic from the energy point of view than the adsorption of atoms on the electrode surface, then there should be no retardation of the process when the reaction proceeds in the opposite direction (from right to left) and this is apparent from the potential curves for ions and adsorbed atoms of the same metal. It can be expected that if, during the deposition of metals, the process takes place at a high overvoltage, the anodic process will proceed easily without a special overvoltage It should be noted that it does not follow from the theory of the retarded discharge that a large overvoltage during the ionization of atoms should correspond to a large overvoltage during the discharge of the ions of the same atoms. The results quoted earlier indicate that almost the same difficulties are encountered when the electrochemical reaction proceeds in one or in the reverse direction. This indicates that the overvoltage observed during the deposition of metals cannot be unequivocally explained by the retardation of the dehydration of metal ions.

The theory of the formation and growth of crystals [1, 36]. In a number of papers, the overvoltage during the electrolytic deposition of metals is explained by the retardation in the formation of a two- and three-dimensional nucleus. According to this theory, the relations between the dimensions of the nucleus [9] and the magnitude of the electrode polarization is represented by the following expression:

$$(\varphi_2 - \varphi_1) Fn = \eta Fn = \frac{2M\sigma}{dr}.$$

This relation shows that the smaller the size of the crystal the larger is the overvoltage η during the electrodeposition of metals. If a high supersaturation is necessary for the growth of small crystals, i.e., the process proceeds at a high overvoltage then the reverse process of the dissolution of crystals will proceed very easily without the overvoltage. However, the experimental results quoted above does not agree with the conclusions following from this theory.

There is also a hypothesis that differences in the rate of the reduction of ions are connected with the potential of the zero charge of the metal deposited. It has already been noted in literature [37] that these considerations are not convincing. We shall only point out that, if, according to the concept of the potential of zero charge, the charge on the surface of the cathode facilitates the discharge of metal ions, then this charge should hinder the process of ionization. This, however, is not confirmed experimentally.

We think that the most probable hypothesis is that which assumed that the retardation of the electrochemical process during the electrolytic deposition of metal depends to a great extent on the presence of extraneous particles on the electrode surface. According to this concept, the energy of activation is necessary in the same degree, not only for the discharge of metal ions, but also for the ionization, and this face is actually observed experimentally. It should also be pointed out that the discharge of metal ions is possible after the desorption of extraneous adsorbed particles, or as a result of the penetration of metal ions through the film, or by the deposition of metal on the extraneous particles. Therefore, the value of the overvoltage during the discharge of metal ions also includes, in the first case, the work of the desorption of extraneous particles; in the second case, the work of overcoming the energy barrier through the film; and, in the third case, the work of the formation of a new nucleus [38].

LITERATURE CITED

[1] T. Erdey-Gruz and M. Volmer, Z. Phys. Chem., (1), 157, 165 (1931).

[2] V. Kohlschutter and A. Torricelli, Z. Elektrochem., 38, 213 (1932).

[3] R. Kaishev, E. Budevski and I. Malinovski, Izv. Bolg.AN (Bulletin of Bulgarian Acad. Sci.), Physics series 1, 76 (1950).

[4] K. M. Gorbunova and A. T. Vagramyan, Doklady Akad. Nauk SSSR 4, 443 (1934).

[5] A. G. Samartsev, Doklady Akad. Nauk. SSSR 7, 478 (1935).

[6] H. Hoekstra, Coll. Czech. Chem. Comm., 6, 17 (1934).

[7] S. V. Gorbachev, Zhur. Fiz. Khim., 24, 888 (1950); E. P. Starostenko, Thesis, MKhTI (Moscow Chemical and Technical Institute), 1950; N. N. Balashov, Thesis, MKhTI, 1949.

[8] H. Fischer, Z. Elektrochem., 59, 612 (1955).

[9] A. T. Vagramyan, Electrodeposition of Metals [in Russian] Moscow, AN SSSR Press, 1950; A. T. Vagramyan and Z. A. Solov'eva, Methods of Studying the Processes of the Electrodeposition of Metals [In Russian], Moscow, AN SSSR Press, 1955; A. T. Vagramyan and T. B. Il'ina-Kakueva, The Distribution of the Current on the Electrode Surface During the Electrodeposition of Metals [in Russian], Metallurgizdat, 1955.

[10] A. T. Vagramyan, Acta physicochim. URSS, 19, 148 (1944).

[11] N. N. Balashova, Yu. S. Tsareva and A. T. Vagramyan, Doklady Akad. Nauk SSSR 71, 73 (1950).

[12] A. T. Vagramyan, Doklady Akad. Nauk. SSSR 22, 243 (1939).

[13] N. T. Vagramyan and A. T. Vagramyan, Zhur. Fiz. Khim., 23, 78 (1949).

[14] A. T. Vagramyan and Z. A. Solov'eva, Zhur. Fiz. Khim., 24, 1252 (1950).

[15] A. T. Vagramyan and Yu. S. Tsareva, Doklady Akad. Nauk. SSSR, 74, 303 (1950).

[16] A. T. Vagramyan and Yu. S. Tsareva, Metalloberfläche, 6, A 163 (1952); Bertorelle Eugenio chimica industria, 35, 556 (1953).

[17] P. F. Mikhalev, Izv. AN SSSR, Mathematics and Natural Sciences Series, 789 (1937).

[18] L. L. Shreier and I. W. Smith, J. Electrochem. Soc., 98, 193 (1951); W. H. Gauvin and C. A. Winkler, Can. J. Res., 2, A 37 (1943).

[19] A. G. Samartsev and E. S. Evstrop'ev, Zhur. Fiz. Khim. 5, 854 (1934).

[20] A. T. Vagramyan, Doklady Akad. Nauk. 27, 805 (1940).

[21] Z. A. Solov'eva and A. T. Vagramyan, Izv. AN SSSR, Chemistry Series, 2, 230 (1954).

[22] H. Hoekstra, Coll. Czech. Chem. Comm., 6, 17 (1934).

[23] A. T. Vagramyan and Z. A. Solov'eva, Doklady Akad. Nauk SSSR, 77, 629 (1951).

[24] H. I. Sein and M. Z. Holz, J. Electrochem. Soc., 96, 43 (1949).

[25] S. I. Sklyarenko, O. S. Druzhina and M. M. Mazagal'tseva, Zhur. Fiz. Khim., 13, 1326 (1940).

[26] M. M. Haissinsky, N. N. Gratsianskii and A. P. Vovkrgam, Zap. in-ta'khim. Ukr. AN, 7, 173 (1940).

[27] C. A. Pierle, J. chim. phys., 23, 517 (1919).

[28] R. Kremann and R. Müller, Electromotorische Kräft Elektrolyse und Polarisation, B. 2. Leipzig. Akad. Verlaggesellschaft, 1931.

[29] P. Truchof, Ann. chim., 7, 165 (1952).

[30] W. Clark and M. Lietzke, J. Electrochem. Soc., 99, 245 (1952).

[31] E. Müller and H. Barchmann, Z. Elektrochem., 39, 343 (1933).

[32] Z. A. Solov'eva and O. A. Abrarov, Zhur. Fiz. Khim., 30, 1572 (1956).

[33] S. V. Gorbachev, Zhur. Fiz. Khim., 30, 1484 (1956); V. G. Levich, Acta physicochim. URSS, 17, 257 (1942); 19, 117 (1944); 19, 133 (1944).

[34] N. T. Kudryavtsev, Zuhr. Fiz. Khim., 23, 549 (1949); A. T. Vagramyan, Zhur. Fiz. Khim., 22, 217 (1948).

[35] A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa and B. N. Kabanov. The Kinetics of Electrode Processes [in Russian], Moscow State University Press, 1952.

[36] V. G. Levich, Introduction to Statistical Physics, Moscow, GTTI, 1950; L. D. Landau and E. M. Lifshitz, Statistical Physics [in Russian], Moscow-Leningrad, Goztechizdat, 1940.

[37] A. T. Vagramyan and V. N. Balashova, Trudy Soveshchaniya po elektrokhimii, Moscow, AN SSSR Press, 1953, p. 237.

[38] S. V. Gorbachev and Yu. N. Yurkevich, Zhur. Fiz. Khim., 28, 1120 (1954).