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Abstract

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On the Theory of the Electrodissolution of Films from the Surface of an Indifferent Electrode

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In the works of a number of authors, questions of the electrodissolution of metal films ([1–3]) and of certain compounds containing the electrode material ([3,4]) have been considered, and the possibilities of using these phenomena in polarography have also been discussed.

At the present time we have obtained experimental data on the electrodissolution of films of sparingly soluble compounds formed by the products of the electrode reaction with a special component of the solution. Certain characteristic dependences have been found that make it possible to use the formation of precipitates of insoluble compounds on the electrode as a method for concentrating ions in polarographic analysis ([5]). Since the method can be practically used for analytical purposes and for investigating the kinetics of certain chemical and electrochemical reactions, a theoretical consideration of the electrodissolution of such films is of interest. The present work is devoted to this question. The conclusions obtained are compared with experiment using as an example the system $2\mathrm{Tl}^+ + 6\mathrm{OH}^-/\mathrm{Tl}_2\mathrm{O}_3 \cdot n\mathrm{H}_2\mathrm{O} + 2e$.

In general form, the processes whose result is the formation of a film (first stage) and its dissolution (second stage) may be represented as follows:

$$\left.\begin{array}{r} M^{n+} \to M^{(n+m)+} + me, \\ pM^{(n+m)+} + (n+m)A^{p-} \to M_pA_{n+m} \end{array}\right\} \quad \text{first stage} \qquad (1)$$

(2)

$$\left.\begin{array}{l} M_pA_{n+m} \underset{k_2'}{\overset{k_1}{\rightleftharpoons}} pM^{(n+m)+} + (n+m)A^{p-}, \\ M^{(n+m)+} + me \to M^{n+}. \end{array}\right\} \quad \text{second stage} \qquad (3)$$

(4)

Fig. 1

Figure 1: Fig. 1

Here M^{n+} and $M^{(n+m)+}$ are different valence states of the ions M; A^{p-} is the substance forming a sparingly soluble compound with ions $M^{(n+m)+}$. Equations (1)–(4) describe the anodic process of formation and the cathodic process of electrodissolution of the precipitate. The reverse electrode processes may be represented in an analogous manner.

We shall consider the case where $p = 1$. If there is an excess of the substance A^-, then its concentration may be included in the effective rate constant, which we denote by k_2 ($k_2 = k_2'[A^-]^{(n+m)}$). Then the process of electrodissolution is described by the differential equations

$$D\frac{\partial^2 C_1}{\partial x^2} + k_1 C_2 - k_2 C_1 = 0; \tag{5}$$

$$\frac{\partial C_2}{\partial t} = k_2 C_1 - k_1 C_2 \tag{6}$$

with the following initial and boundary conditions:

$$C_2'(x,0) = C_2^2, \qquad C_1(x,0) = \frac{C_2^0}{\sigma};$$

$$\left(\frac{\partial C_1}{\partial x}\right)_{x=0} = C_1(0,t)\, ke^{Bvt}; \qquad \left(\frac{\partial C_1}{\partial x}\right)_{x=l} = 0. \tag{7}$$

Here C_1 and C_2 are the concentrations of the substances $M^{(n+m)}$ and M_pA_{n+m}; k_1 and k_2 are the rate constants of the forward and reverse chemical reactions; $\sigma = \frac{k_2}{k_1}$; l is the film thickness; $B = -\alpha nF/RT$; $k = \frac{k_s}{D_1}\exp\left[-\frac{\alpha nF}{RT}(\varphi_1 - \varphi^0)\right]$ for the cathodic process; $B = \frac{\beta nF}{RT}$, $k = \frac{k_s}{D_2}\exp\left[\frac{\beta nF}{RT}(\varphi_1 - \varphi^0)\right]$ for the anodic process; φ^0 is the standard potential of the system; v is the rate of potential change in the electrodissolution cycle; t is the electrodissolution time; $\varphi = vt$ is the electrode potential, measured from the initial potential φ_1.

Fig. 1. Dependence of the maximum current of electrodissolution of a $Tl_2O_3 \cdot nH_2O$ film deposited on a graphite electrode ($\varphi_{\text{el}} = +1.0$ relative to the N.C.E.) from a $0.2N\ NH_4OH + 0.2N\ NH_4Cl$ solution (pH 9.5) for 2 min on the concentration of Tl^+ ions in solution, and the corresponding polarization curves. 1 –$3 \cdot 10^{-6} M\ Tl^+$; 2–$5 \cdot 10^{-6} M\ Tl^+$; 3–$8 \cdot 10^{-6} M\ Tl^+$.

In equation (5), the time derivative of the concentration is omitted, since in the case of fast chemical reactions* ($k_1 t, k_2 t \gg 1$) an equilibrium is established between the chemical reactions and the diffusion process (6). Equation (6) contains no term describing the diffusion of the solid substance M_pA_{n+m}, since its diffusion may be neglected.

The boundary conditions reflect the fact that the ions $M^{(n+m)+}$ participating in the electrode process do not enter the film from outside, and the gradient of their concentration at the electrode surface is proportional to the electrodissolution current.

If the film thickness is much greater than the quantity $\mu_2 = \sqrt{D/k_2}$ (μ_2 is the thickness of the reaction layer (7)), then, transforming (5)–(7) by Laplace, it is not difficult to obtain the following expression for the transformed value of the flux of the substance $M^{(n+m)+}$ near the electrode surface:

$$\left.\frac{\partial \overline{C}_1(p)}{\partial x}\right|_{x=0} = \frac{C_2^0}{\sigma\mu_2}\frac{1}{p}\sqrt{\frac{p}{p+k_1}} - \frac{1}{k\mu_2}\sqrt{\frac{p}{p+k_2}}\left.\frac{\partial \overline{C}_1(p+Bv)}{\partial x}\right|_{x=0}, \tag{8}$$

where p is the transformation coefficient.

From (8), with the aid of the convolution theorem, we obtain an integral equation for the electrodissolution current density

$$j(t) = nFD\left.\frac{\partial C_1}{\partial x}\right|_{x=0}:$$

$$j(t) = \frac{nFDC_2^0}{\sigma}\frac{ke^{-k_1t/2}I_0(k_1t/2)}{k\mu_2 + e^{-Bvt}} +$$

$$+\frac{k_1e^{-kt/2}}{2\left(k\mu_2 + e^{-Bvt}\right)}\int_0^t e^{-Bv\tau}e^{k_1\tau/2}j(\tau)\left[I_0\left(\frac{k_1(t-\tau)}{2}\right) - I_1\left(\frac{k_1(t-\tau)}{2}\right)\right]d\tau. \tag{9}$$

For the case $k_1 \gg Bv$*, the approximate solution of this equation can be represented in the form

$$j(t) = \frac{pFDC_2^0}{\sigma}\frac{ke^{-k_1t/2}e^{Bvt}I_0(k_1t/2)}{k\mu_2e^{Bvt} + e^{-k_1t/2}I_0(k_1t/2)}. \tag{10}$$

Direct substitution of relation (10) into equation (9) and numerical integration show that, in the case of sufficiently fast

* It should be noted that only the case of fast chemical reactions is of interest, since a sufficient rate of the reaction forming the precipitate is a necessary condition for concentration.

Fig. 2

Figure 2: Fig. 2

chemical reactions ($k_1 t \gg 1$ and $k\mu_2 \ll 1$), equation (9) is satisfied with good accuracy.

Expanding the Bessel functions in an asymptotic series, we obtain the following simple expression for the electro-dissolution current density:

$$j(t) = \frac{nFDC_2^0}{\sigma} \frac{ke^{Bvt}}{k\mu_2 e^{Bvt}\sqrt{\pi k_1 t} + 1}. \tag{11}$$

Differentiating equation (11) with respect to time, it is easy to find the potential φ_m at which the current reaches its maximum value:

$$\frac{k\mu_2\sqrt{\pi k_1}}{2B\sqrt{v}} = \sqrt{\varphi_m e^{-B\varphi_m}}. \tag{12}$$

Combining equations (11) and (12), we obtain an expression for the maximum electro-dissolution current

$$j_m = \frac{nFDC_2^0}{\sigma\mu_2} \frac{\sqrt{v}}{\sqrt{\pi k_1 \varphi_m}\,(1 + 1/2B\varphi_m)}, \tag{13}$$

which, taking into account the equality $\sigma = \sigma'/f_2$ (σ' is the thermodynamic equilibrium constant of chemical reaction (9)) and assuming $1/2B\varphi_m \ll 1$, is readily represented in the form

$$j_m = \frac{C_2^0 f_2}{\sigma'\mu_2} \frac{\sqrt{v}}{\sqrt{\pi k_1 \varphi_m}}. \tag{14}$$

Equation (14) contains the activity of the precipitate $a_2^0 = C_2^0 f_2$. It is natural to assume that, for a small film thickness, the activity is proportional to the amount of substance in the film, and the latter is proportional to the concentration of ions in the solution and to the duration of electrodeposition. Use of the Nernst equation, taking this proportionality into account, made it possible to obtain a dependence of the equilibrium potential of the system Bi^{III}/Bi^0 on the duration of electrodeposition that agrees well with experiment ([10]).

Fig. 2. Dependence of the potential of the maximum of the polarization curve on the logarithm of the rate of change of the electrode potential; electrodeposition of a thallium film was carried out for 2 min from a solution of $0.2N$ NH_4Cl + $0.2N$ NH_4OH (pH 9.5) at a potential of +1.0 V relative to the S.C.E.

Fig. 3

Figure 3: Fig. 3

Taking into account the considerations set forth above, we obtain an expression for the maximum electro-dissolution current in the form

$$j_m = \frac{k_d' C \tau}{\sigma \mu_2} \frac{\sqrt{v}}{\sqrt{\pi k_1 \varphi_m}}, \tag{15}$$

where C is the concentration of M^{n+} ions in the solution; τ is the duration of electrodeposition; k_d' is a proportionality coefficient.

Figure 1 presents the experimentally obtained dependence of the maximum electro-dissolution current of a $Tl_2O_3 \cdot nH_2O$ film on the concentration of Tl^+ ions in the solution. The dependence is directly proportional, which agrees with equation (15). From this follows an important practical conclusion: concentrating ions in the form of thin films of sparingly soluble compounds, with subsequent recording of the electro-dissolution currents of the precipitates formed, can be used for determining ions of transi-

variable valence, present in the solution in very small concentrations.

Let us now compare the experimentally obtained dependences of φ_m and i_m on the rate of change of the potential v with formulas (12) and (14) or (15). Representing equation (12) in the form

$$\varphi_m =$$

$$= \frac{2.3}{2B} \lg \varphi_m - \frac{2.3}{B} \lg \frac{k\mu_2 \sqrt{\pi k_1}}{2B} + \frac{2.3}{2B} \lg v, \tag{16}$$

it is easy to see that the dependence $\varphi_m = f(\lg v)$ at large values of $B\varphi_m$ should be close to rectilinear.

Fig. 3. Dependence of $i_m\sqrt{\varphi_m}$ on $\sqrt{v}$; for the experimental conditions see the caption to Fig. 2

In Fig. 2 the corresponding experimentally found dependence is presented for the electrodissolution of the film $Tl_2O_3 \cdot nH_2O$. In accordance with equation (12), this dependence is expressed by a practically straight line, the tangent of whose angle of inclination is equal to -0.071, which corresponds to the value $\alpha = 0.2$.

From equation (14) there follows a rectilinear dependence between $i_m\sqrt{\varphi_m}$ and $\sqrt{v}$ at large values of $B\varphi_m$. As is seen from Fig. 3, the experimental data are in good agreement with the conclusions from the theory.

In conclusion I express my sincere gratitude to Academician A. N. Frumkin for valuable comments on the investigation undertaken, and also to B. I. Khaikin for discussion of the results of the calculations.

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Note: Figure translations are in progress. See original paper for figures.