REVIEW

Diffusive problem of Stephan and its solution for processes of electrodissolution of semispherical nuclei of the deposit

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Abstract We modeled the processes of growth and dissolution of small amounts of deposit on the solid electrode. Quasi-stationary diffusion method solved the basic problem of growth and dissolution of the semi-spherical nuclei deposit. Equations are obtained for current–voltage curves and chronoamperogram for reversible and irreversible electrode processes of electrodissolution of deposit nuclei. We have derived relations for the peak current and peak potentials of the current–voltage curve.

Keywords The Stephan problem · Theory of electroanalytical stripping methods · The initial stages of electrocrystallization · Nuclei of deposit

Introduction

The method of stripping voltammetry as well as other methods of electroanalytical chemistry is widely used to determine the trace of various substances. On the other hand, voltammetry technique is used to study physical and chemical processes occurring at electroaccumulation and electrodissolution of small quantities of deposit on the solid electrodes, to study the initial stages of electrocrystallization.

Zakharchuk NF is one of the first researchers, who in her works (with co-authors) paid attention to the fact that the method of stripping voltammetry allows the use of metal oxidation polarogram as a source of information about the initial stages of electrocrystallization of metals [1].

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There is large quantity of works (research) on electrochemical analysis at solid electrodes. Their review can be found in works [1–6].

There are much less works on the theory of stripping electrochemical methods. The main ones are the works of Brainina and colleague [3, 4] and Compton RG [5, 6]. In the works of Compton RG, a solution of some diffusion problems for the nuclei of deposit of different forms is given. He points out the importance of consideration of the spherical diffusion.

In work [5] the results of numerical calculations are given. RG Compton's work (with co-authors) on influence of a roughness of an electrode in a method of stripping voltammetry [6] is very interesting. Brainina KhZ obtained basic equations for stripping voltammetry in analytical form.

Voltammograms of dissolution of trace amounts of deposit may contain two current peaks. According to the ideas developed in the works of Brainina and colleague [3, 4], the first peak corresponds to the dissolution of the micro-phase and the second of the micro or macro-phase of the substance of a deposit. To derive the equations of current–voltage curves, Brainina KhZ uses the assumption of variable activity of a substance of the deposit accumulated on the electrode.

In our articles [7, 10], we give a different interpretation of the voltammograms, containing two peaks. The first peak corresponds to electrodissolution of the adsorbed atoms, and the second peak is due to electrodissolution of nucleus of the deposit from the surface of solid electrodes. Activity of the nucleus of the deposit is assumed to be constant.

Electroanalytical stripping methods include two stages: electroaccumulation and deposit electrodissolution on an electrode.

On the assumption of the general physical and chemical representations, it is possible to assume the following

mechanism of electroaccumulation of a deposit on a solid electrode. In the beginning, the adsorbed atoms are collected on an electrode surface, and then three-dimensional nuclei arise and grow. Further, a discontinuous film and then a porous film are formed. At the last stage, the growth of a continuous film of a deposit takes place. Thus, the growth processes (and dissolution) of a deposit on a solid electrode present themselves as complicated processes of a new phase forming. There is no general theory of these processes. Nowadays separate questions of taken problem of the origin and growth of a new phase on the surface of solid bodies [8, 9] are only developed.

The theory

Let us consider the initial stage of growth of separate nuclei of a deposit. Let us admit that the number of nuclei N arisen on an electrode surface does not change eventually (instant nucleation). Nuclei have a semispherical form and are in regular intervals distributed on all the area of an electrode on some distance from each other. Growth of nuclei is caused by diffusion of ions from an electrolyte solution to a nucleus surface. In case of growth and dissolution of noninteracting-diffusion nuclei of a deposit, the problem is to solve the problem of the change of one nucleus size. It is possible to consider that the size of this nucleus corresponds to some average size of a nucleus of a deposit on an electrode surface.

The problem of growth and dissolution of a separate nucleus of a new phase is a known problem of Stephan [9]. It is a difficult diffusive problem. Its resolution causes big mathematical difficulties. Exact resolutions of this problem are only known for some special cases.

For the conditions of stripping voltammetry, it is possible to offer a quasi-stationary method of Stephan problem resolution. The essence of this method is in the following:

1. First, a stationary or nonstationary diffusion problem for the diffusion of ions to a fixed nucleus of radius R is solved. The boundary and initial conditions correspond to the conditions of the stripping voltammetry method.
2. Further, a change of the radius of a nucleus is found proceeding from the condition of balance of mass on the border of the nucleus and the electrolyte solution.
3. The obtained dependence $R(t)$ gives the equation of current–potential curve, as well as the equation for the amount of a deposit on the electrode.

Let us consider the resolution of the problem of growth and dissolution of nuclei deposit on a solid electrode.

Concentration of ions C changes from C_0—in the solution volume, to $C_S = C(R)$—at the nuclei surface.

Anodic electrodissolution of semispherical nucleus is defined with the following system of equations:

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) \tag{1}$$

$$C[t=0, r>R(t)] = C_0 \tag{2}$$

$$C(t, r \to \infty) = C_0 \tag{3}$$

$$-\frac{nFD}{i_0}\frac{\partial C}{\partial r}\bigg|_{r=R(t)} = \exp(\beta f \eta) - \frac{C[t, R(t)]}{C_0}\exp(-\alpha f \eta) \tag{4}$$

$$\{C_T - C[t, R(t)]\}\frac{\partial R}{\partial t} = D\frac{\partial C}{\partial r}\bigg|_{r=R(t)} \tag{5}$$

The essence of the quasi-stationary method is that the formulation of the diffusion problem (1–5) is replaced by the equations:

$$\frac{d^2 C}{dr^2} + \frac{2}{r}\frac{dC}{dr} = 0 \tag{6}$$

$$C(r \to \infty) = C_0 \tag{7}$$

$$-\frac{nFD}{i_0}\frac{\partial C}{\partial r}\bigg|_{r=R} = \exp(\beta f \eta) - \frac{C(R)}{C_0}\exp(-\alpha f \eta) \tag{8}$$

$$C_T\frac{\partial R}{\partial t} = D\frac{\partial C}{\partial r}\bigg|_{r=R} \tag{9}$$

where: t, time of electrolysis; r, distance; D, diffusion coefficient; n, the number of electrons; F, the Faraday constant; i_0, exchange current density; α, β, coefficient of transfer; $f=(nF)/(R_G T)$; R_G, universal gas constant; T, absolute temperature; η, overpotential; and $C_T=1/V_M$, where V_M is the molar volume of the substance of the precipitate.

The quasi-stationary method is applicable, when the inequality below is carried out:

$$k = \frac{C_0 - C_s}{C_T - C_s} << 1$$

This inequality is true for the usual conditions of the stripping voltammetry method, when the ion concentration C_0 is sufficiently low.

The boundary condition (8) corresponds to quasi-reversible electrode processes. For a reversible electrode process, the Eq. 8 is replaced by

$$C(R) = C_0 \exp(f\eta) \qquad (10)$$

and for an irreversible electrode process, is recorded as

$$-\frac{nFD}{i_0} \left.\frac{\partial C}{\partial r}\right|_{r=R} = \exp(\beta f\eta). \qquad (11)$$

Potentiostatic conditions are characterized by the relation η=const. In the case of linear sweep voltammetry with the potential: $\eta = wt$, where w is the velocity of potential sweep. Cathodic process of electroaccumulation is described by the Eq. 6 for the concentration distribution, the boundary condition (7), the condition of mass balance (9) and boundary conditions.

For a quasi-reversible electrode process, the following Eq. 12 is used:

$$\frac{nFD}{i_0} \left.\frac{\partial C}{\partial r}\right|_{r=R} = \frac{C(R)}{C_0} \exp(\alpha f\eta) - \exp(-\beta f\eta) \qquad (12)$$

For a reversible electrode process, the following Eq. 13 is used:

$$C_S = C_0 \exp(-f\eta) \qquad (13)$$

For an irreversible electrode process, the following Eq. 14 is used:

$$\frac{nFD}{i_0} \left.\frac{\partial C}{\partial r}\right|_{r=R} = \frac{C(R)}{C_0} \exp(\alpha f\eta) \qquad (14)$$

The amount of electricity on an electrode for a semi-spherical model is determined from the formula:

$$Q = \frac{2}{3}\pi n F C_T R^3 N. \qquad (15)$$

The equation of current–voltage curve is obtained from the equation:

$$I(t) = \frac{dQ}{dt}; \ I(t) = nFC_T N 2\pi R^2 \left(\frac{dR}{dt}\right). \qquad (16)$$

After receiving the equation of the current–voltage curve, you can find the current peak and the potential in the current peak either in an analytical form or as a result of numerical calculations on a PC.

The results of solving some diffusive problems by quasi-stationary diffusion method are given in Table 1, for a model of diffusion-noninteracting semispherical nuclei of the precipitate [10].

Table 1 shows that the equations describing the electrodissolution stage include the parameters that are determined at the electroaccumulation stage. The main of them is the size of the nucleus radius R_0, which represents either the

Table 1 Electrodissolution stage of separate nuclei of the precipitate

Reversible electrode process	Irreversible electrode process
Voltammetry with linear potential sweep	
1) Nucleus radius	
$R(t) = \sqrt{R_0^2 - \frac{2DC_0}{C_T}\left[\frac{\exp(fwt)-1}{fw} - t\right]}$	$R(t) = R_0\left\{1 - \frac{I_0[\exp(\beta fwt)-1]}{3\beta fwQ}\right\}$
2) The equation of current–voltage curve	
$I(t) = 2\pi nFDC_0[\exp(fwt)-1]R(t)$	$I(t) = I_0\exp(\beta fwt)R(t)$
3) Peak current	
$I_p = \frac{1}{\sqrt{3}}fwQ$	$I_p = \frac{4}{9}\beta fwQ$
4) Peak potential	
$E_p = E_r + \frac{1}{2f}\ln\frac{fwC_TR_0^2}{3DC_0}$	$E_p = E_i + \frac{1}{\beta f}\ln\frac{\beta fwQ}{I_0}$
5) Width of semipeak	
$\Delta E = \frac{0.742}{f}$	$\Delta E = \frac{2.01}{\beta f}$
Chronoamperometry	
1) Nucleus radius	
$R(t) = \sqrt{R_0^2 - \frac{2DC_0t}{C_T}[\exp(f\eta)-1]}$	$R(t) = R_0 - \frac{i_0 t\exp(\beta f\eta)}{nFC_T}$
2) Initial current	
$I(0) = 2\pi nFDNC_0R_0[1 - \exp(f\eta)]$	$I(0) = I_0\exp(\beta f\eta)$

initial value of the radius of the nucleus at the stage of the electrodissolution or the final value of the radius of the nucleus at the stage of electroaccumulation. The solution of diffusion problems for electroaccumulation of residue on the surface of the electrode provides a formula for the radii of the nuclei, which are given in Table 2.

Tables 1 and 2 provide the dependence of the peak current I_p of the voltammograms from the parameters of the stage of electroaccumulation: from the concentration of C_0, and also the time t and the overpotential η. For example, for a reversible electrode process, the following relations can be obtained:

$$I_p = K_1 C_0^{3/2}; \ I_p = K_2 t^{3/2}; \ I_p = K_3[1 - \exp(-f\eta)]^{3/2} \qquad (17)$$

where K_1, K_2 and K_3 are some constants.

Formulas (17) are valid for a reversible electrode process in the case of "instantaneous" nucleation.

In the formation of a continuous film on the electrode, formulation of the corresponding diffusive problem will look as (for a reversible electrode process):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (18)$$

$$C(t, x \to \infty) = C_0 \qquad (19)$$

Table 2 Electroaccumulation stage: radii of nuclei of a deposit

Electrolysis mode	Reversible electrode process	Irreversible electrode process
Potentiostatic conditions (η=const)	$R(t) = \sqrt{\frac{2DC_0 t}{C_T}[1 - \exp(-f\eta)]}$	$R(t) = \frac{i_0 t \exp(\alpha f \eta)}{nFC_T}$
Linear sweep voltammetry (η=wt)	$R(t) = \sqrt{\frac{2DC_0}{C_T}\left[t + \frac{\exp(-fwt)-1}{fw}\right]}$	$R(t) = \frac{i_0[\exp(\alpha fwt)-1]}{nFC_T \alpha fw}$

$$C(t = 0, x) = C_0 \tag{20}$$

$$C(t, x = h) = C_0 \exp(-f\eta) \tag{21}$$

$$C_T \frac{dh}{dt} = D \frac{dC}{dx}, \tag{22}$$

where x, distance from the electrode surface; h, film thickness.

The solution of (18–21) is well known in electrochemistry:

$$\frac{\partial C}{\partial x} = \frac{C_0[1 - \exp(-f\eta)]}{\sqrt{\pi D t}}. \tag{23}$$

Substituting the expression for the derivative of (23) in the equation of mass balance (22), we have

$$h(t) = \frac{2C_0[1 - \exp(-f\eta)]}{C_T}\sqrt{\frac{Dt}{\pi}}. \tag{24}$$

Using (24) for Q we can obtain:

$$Q(t) = 2nFSC_0[1 - \exp(-f\eta)]\sqrt{\frac{Dt}{\pi}}, \tag{25}$$

where S is the electrode surface area.

If we assume that in this case, $I_p \sim Q$, we obtain the relations:

$$I_p = K_4 C_0; \ I_p = K_5 t^{1/2}; \ I_p = K_6[1 - \exp(-f\eta)] \tag{26}$$

where K_4, K_5 and K_6 are constants that can be determined from the relation (25).

Results and discussion

Basic diffusion problems of growth and dissolution of the semi-spherical nuclei of deposit (Stephan's problems) were solved by quasi-stationary method.

We obtained the equations of current–voltage curve and chronoamperograms for reversible and irreversible electrode processes of electrodissolution of nuclei of deposit.

We derived relations for the peak current and potential of the peak current of the current–voltage curve.

It is necessary to notice that most of the formulas for the growth of nuclei of deposit were received earlier; however, they were received by other methods.

The review of appropriate works and known formulas for the growth of nuclei of deposit is provided in monographies on electrocrystallization [11–14] and works [15, 16].

The strict decision of a problem of the Stephan for a case of electrocrystallization is not achieved up to now. The most exact decision of the Stephan's problem for growth of nuclei of deposit, in our opinion, was given by S. Fletcher [15, 16].

As work [16] affirms, "note that we shall not treat the full moving boundary problem (Stephan problem) in the sense of incorporating time-varying crystal radii in the diffusion equation. Instead, we shall use a good approximation".

We obtained equations in analytic form for the growth and dissolution of the hemispherical nuclei of deposit by quasi-stationary method; these equations allow to deduce the parities for cyclic current–voltage curves.

The software which allows to model processes of growth and dissolution of separate nuclei of deposit on solid electrodes was developed on the basis of the equations given in Tables 1 and 2.

The main unknown parameter (adjustable parameter) of the theory is the number of nuclei on the electrode surface. The number of nuclei is not known a priori.
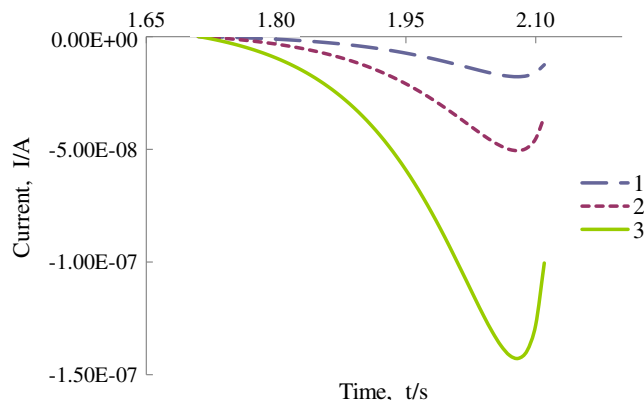

Fig. 1 Schematic dependence of current–voltage curves for different values of the bulk concentration: 1—C_{01}=10^{-7} M; 2—C_{02}=2×10^{-7} M; 3—C_{03}=4×10^{-7} M; w=0.025 V/s
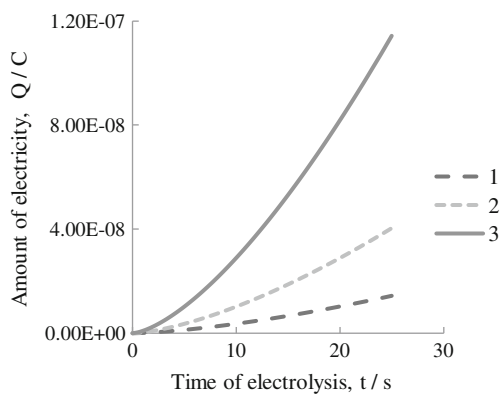
Fig. 2 Schematic dependence amount of electricity of the time of electrolysis for different values of the bulk concentration: $1—C_{01}= 10^{-7}$ M; $2—C_{02}=2\times 10^{-7}$ M; $3—C_{03}=4\times 10^{-7}$ M; $\eta=0.3$ V

Figures 1, 2, 3 and 4 represent the schematic calculated dependences that are most often studied in the study of specific systems. Such experimentally observed dependences for metals and anions are given in the works [3, 4, 7].

To compare theory with experiment, we have studied the electroaccumulation of iodine on the surface of the silver electrode by a method of stripping chronopotentiometry.

As background electrolyte, 1 M K_2SO_4 solution was used. Ions of iodine were entered by addition into background solution KJ. Ion concentration of iodine was 10^{-6} to 10^{-5} M in all experiments. Electroaccumulation process was conducted at potential $E=+0.1$ V (SCE).

Figure 5 shows the dependence of the transitive time from the time of electroaccumulation in the coordinates τ– $t^{3/2}$. Equation for τ was obtained in the work [17]. It is the equation for the electrodissolution of hemispherical nuclei of deposit:

$$\tau = Q/I,$$

where τ, transitive time; Q, amount of an electricity on an electrode; and I, an electrolysis current.

In the case of instantaneous nucleation and a reversible electrode process, it follows from the formulas in Table 2 that Q, and consequently τ, is proportional to the electrolysis time $t^{3/2}$. Thus, in the coordinates Q–$t^{3/2}$ linear dependence should be observed. As seen in Fig. 5 the experimental points are reasonably well described by linear dependence.

Conclusions

In general case, on the assumption of formulas (17) and (26), the dependence of peak current of voltammograms from time can be expressed as $I_p=K\cdot t^n$. The exponent $n>1$ in the case of growth of nuclei of deposit (the initial part of the overall I–t curve) and $n<1$ in the case of film growth (the final section of the total I–t curve).

Thus, by the magnitude of the exponent n in the experimentally observed dependence of the peak current of voltammograms from the concentration of ions of depolarizer, time or capacity pre-electrolysis, we can conclude that on the electrode, electroaccumulation of deposit takes place in the form of nucleus, or as a continuous film.

Fig. 4 Schematic dependence amount of electricity of the overpotential for different values of the time of electrolysis: $t1=15$ s; $t2=20$ s; $t3=25$ s. $C_0=10^{-7}$ M
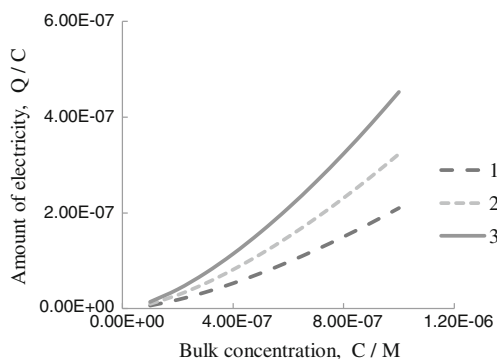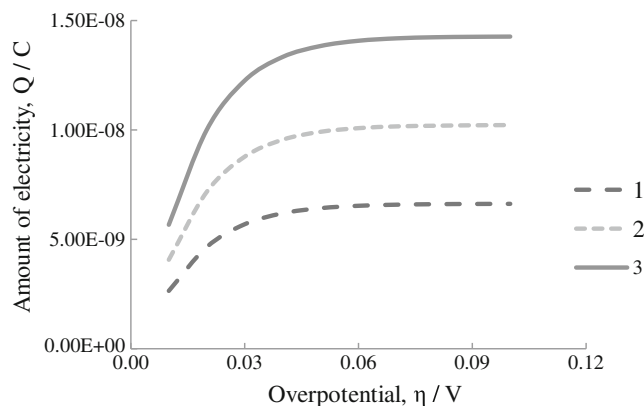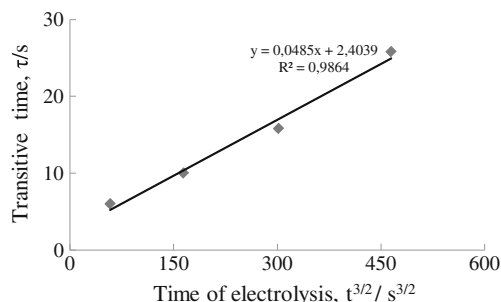

Fig. 3 Schematic dependence amount of electricity of the bulk concentration for different values of the time of electrolysis: $t1=15$ s; $t2= 20$ s; $t3=25$ s; $\eta=0.3$ V

Fig. 5 Dependence transitive time of the bulk concentration for different values of the time of electrolysis

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