A FORMULATION OF THE PROBLEM OF EVALUATING THE CONCENTRATION POLARIZATION IN TRANSIENT STATE ELECTROLYSIS

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We will consider a solution of the problem of concentration polarization in the absence of convection. The current density, *i*, will be assumed to remain constant during the process. We will adopt a symbolism in which *c* is the electrolyte concentration, *x* is the distance from the electrode, *t* is the time, and D is the diffusion coefficient.

A solution must be obtained for the equation of diffusion with a source

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + f(x, t). \tag{1}$$

The initial condition will be given the general form

$$c(x, t = 0) = \varphi(x). \tag{2}$$

The boundary condition will also be given in general form

$$c(x = 0, t) = \mu(t). \tag{3}$$

The function f(x,t) represents the source density.

The mathematical theory of thermal conductivity shows [1] that Eq. (1) can be solved with the conditions (2) and (3) to give

$$\begin{aligned} c(x, t) = {} & \frac{1}{2\sqrt{\pi}}\int\limits_0^\infty \frac{2}{\sqrt{Dt}}\left[\exp\left(-\frac{(x-\varepsilon)^2}{4Dt}\right) - \exp\left(-\frac{(x+\varepsilon)^2}{4Dt}\right)\right]\varphi(\varepsilon)\,d\varepsilon + \\ & + \int\limits_0^t \frac{x}{2\sqrt{\pi D(t-\theta)}}\exp\left(-\frac{x^2}{4D(t-\theta)}\right)\mu(\theta)\,d\theta + \\ & + \frac{1}{2\sqrt{\pi}}\int\limits_0^t\int\limits_0^\infty [D(t-\theta)]^{-1/2}\left[\exp\left(-\frac{(x-\varepsilon)^2}{4D(t-\theta)}\right) - \right. \\ & \left. - \exp\left(-\frac{(x+\varepsilon)^2}{4D(t-\theta)}\right)\right] f(\varepsilon, \theta)\,d\varepsilon\,d\theta. \end{aligned} \tag{4}$$

This general solution can be linked up with the details of the electrolysis by interpreting the boundary conditions (2) and (3) in terms of electrolysis with concentration polarization.

The initial condition will be assumed to have the form

$$\varphi(\varepsilon) = c_0. \tag{5}$$

Greatest interest attaches to the boundary condition $\mu(\theta)$.

An expression for this boundary condition will be obtained by considering the layer adjacent to the electrode during the electrolysis. The depth of this electrode exchange layer will be designated by δ. The electrolyses of $AgNO_3$ solutions with silver electrodes, or of $CuSO_4$ solutions with copper electrodes, can serve as example of such processes. The concentration of the electrolyte in the cathode zone will change in the time $\underline{dt}$ as the result of several processes. The number of cations in the δ layer will diminish because of a Faraday Law discharge at the cathode

$$dm_{c_1} = -\frac{i}{n_c F}\,dt. \tag{6}$$

At the same time, Hittorf transference will lead to the movement of a certain number of cations into this layer from the body of the solution under the action of the electric current

$$dm_{c_2} = U_c \frac{i}{n_c F}\,dt, \tag{7}$$

(U_c is the transference number of the cation in question). Electrolysis results in a breakdown on the initial uniform concentration in the solution and cations will penetrate into the δ layer through diffusion

$$dm_{c_3} = D_c \frac{\partial c_c}{\partial x}\,dt. \tag{8}$$

Thus

$$dm_c = dm_{c_1} + dm_{c_2} + dm_{c_3} = -U_a \frac{i}{n_c F}\,dt + D_c \frac{\partial c_c}{\partial x}\,dt. \tag{9}$$

In the same way we obtain for the anions

$$dm_a = -U_a \frac{i}{n_a F}\,dt + D_a \frac{\partial c_a}{\partial x}\,dt. \tag{10}$$

The condition for the electrical neutrality of the solution gives

$$c_c n_c = c_a n_a; \quad c = \frac{c_c}{n_a} = \frac{c_a}{n_c}; \tag{11}$$

$$\frac{dm}{v} = \frac{dm}{1^2\delta} = dc. \tag{12}$$

Then

$$\delta \frac{\partial c}{\partial t} = -U_a \frac{i}{n_a n_c F} + \frac{D_c n_a + D_a n_c}{n_a + n_c} \cdot \frac{\partial c}{\partial x} \tag{13}$$

An expression for the anodic δ layer can be obtained in exactly the same manner

$$\delta \frac{\partial c}{\partial t} = \frac{iU_a}{n_a n_c F} - \frac{D_c n_a + D_a n_c}{n_a + n_c} \frac{\partial c}{\partial x} \tag{14}$$

Equations (13) and (14) can be written as

$$\frac{iU_a}{n_a n_c F} = \delta \frac{\partial c}{\partial t} + \frac{D_c n_a + D_a n_c}{n_a + n_c} \frac{\partial c}{\partial x}.$$

Faraday's Law has been combined with the Hittorf expression for transference effects to give the expression for the concentration in the electrode layer which appears as the left-hand member of this equation. If there were no diffusion and the second term were lacking, anodic dissolution of the metal would lead to a mere accumulation of matter in the electrode layer and $\partial c / \partial t$ would have a maximum value. Diffusion actually carries out of the electrode layer a considerable portion of the excess material which accumulates there and transfers it into the body of the solution. There would be no accumulation of excess material in the anodic layer if the diffusion rate were quite high and the derivative $\partial c / \partial t$ would then be approximately zero. The relation of these two processes (i.e., of the two terms in the right-hand side of the equation) changes gradually and continuously in the course of the electrolysis. Approach to the stationary state indicates that the concentration has ceased to change and the derivative $\partial c/\partial t$ is tending toward zero. This means that the concentration gradient in the electrode layer has taken on such a high value that diffusion almost balances the flow of matter resulting from electrolysis. On the other hand, the diffusional flow is weak in the initial stage of the electrolysis when the distribution of matter is nearly uniform and electrolysis then leads to an accumulation of excess matter in the layer surrounding the electrode. The value of $\partial c/\partial t$ is at a maximum in this initial stage and the value of $\partial c/\partial x$, is at a minumum.

An independent evaluation of $\partial c/\partial t$ can be obtained through the statistical diffusion theory of Smoluchowski and Einstein. The mean rate of diffusional movement of matter from the electrode surface into the bulk of the solution is calculated from the Einstein Equation:

$$\bar{x} = \sqrt{2Dt}. \tag{15}$$

Equation (14) then takes the form

$$\frac{\partial c}{\partial t} = \frac{iU_a}{n_a n_c F} \frac{1}{\sqrt{Dt}}. \tag{16}$$

Integration gives for the anodic layer

$$c = c_0 + \frac{iU_a}{n_a n_c F} \frac{2}{\sqrt{D}} \sqrt{t}. \tag{17}$$

For the cathodic layer we have

$$c = c_0 - \frac{iU_a}{n_a n_c F} \frac{2}{\sqrt{D}} \sqrt{t}. \tag{18}$$

This equation makes it clear that the concentration gradient does not remain constant, even in the thinnest of electrode layers, during the electrolysis but rises gradually with approach to the stationary state. This approach is asymptotic, of course, and the stationary state is never reached, strictly speaking. Equations (17) and (18) are solutions for the limiting case.

For constant current density

$$f(\varepsilon, 0) = \frac{iU_{\mathrm{a}}}{n_{\mathrm{a}} n_{\mathrm{c}} F}\,. \tag{19}$$

It only remains to substitute the initial condition (5), the boundary condition (17) or (18), and the source density (19) in the general equation (4) in order to obtain a solution to the problem of concentration polarization. The integrals of the first two members can be evaluated exactly. The integral form is retained only for the third member and this is numerically insignificant. The final expression for the anodic process has the form

$$\begin{gathered} c = c_0 + \frac{2iU_{\mathrm{a}}}{n_{\mathrm{a}} n_{\mathrm{c}} F} \sqrt{\frac{t}{D}} \exp\left(-\frac{x^2}{4Dt}\right) + \\ + \left(2c_0 - \frac{iU_{\mathrm{a}}}{n_{\mathrm{a}} n_{\mathrm{c}} F} \frac{x\sqrt{\pi}}{D}\right)\left[1 - \mathrm{erf}\left(\sqrt{\frac{x^2}{4Dt}}\right)\right] + \frac{iU_{\mathrm{a}}}{n_{\mathrm{c}} n_{\mathrm{a}} F} \frac{x^2}{4D} \int\limits_0^{4Dt/x^2} \mathrm{erf}\left(\frac{1}{\sqrt{\beta}}\right) d\beta. \end{gathered} \tag{20}$$

In the same way we obtain for the cathodic process

$$\begin{gathered} c = c_0 - \frac{2iU_{\mathrm{a}}}{n_{\mathrm{a}} n_{\mathrm{c}} F} \sqrt{\frac{t}{D}} \exp\left(-\frac{x^2}{4Dt}\right) + \frac{iU_{\mathrm{a}}}{n_{\mathrm{a}} n_{\mathrm{c}} F} \frac{x\sqrt{\pi}}{D}\left[1 - \mathrm{erf}\left(\sqrt{\frac{x^2}{4Dt}}\right)\right] - \\ - \frac{iU_{\mathrm{a}}}{n_{\mathrm{a}} n_{\mathrm{c}} F} \frac{{}^{2}x}{4D} \int\limits_0^{4Dt/x^2} \mathrm{erf}\left(\frac{1}{\sqrt{\beta}}\right) d\beta. \end{gathered} \tag{21}$$

Thus a solution is obtained for the simplest case of concentration polarization. The question of accuracy naturally arises. The predictions of these equations can be compared with experimental results (see Table). The experimental data were obtained by E. I. Grabova with a refractographic method.

TABLE

Concentration Polarization in 0.5 M $CuSO_4$ at $i = 2$ ma/cm^2; $t = 3$ hours

Distance from the electrode, mm	Concentration, M		Distance from the electrode, mm	Concentration, M	
	experimental results	equation (20)		experimental results	equation (20)
0	—	1.88	6	0.64	0.54
1	1.25	1.45	7	0.61	0.51
2	0.94	1.10	8	0.57	0.51
3	0.81	0.85	9	0.55	0.50
4	0.74	0.68	10	0.53	0.50
5	0.68	0.58			

This table shows that results obtained from the equations presented in the present report are not in complete agreement with the experimental data. The divergence is due to inaccuracy in the generally assumed condition of constancy of the diffusion coefficient.

LITERATURE CITED

[1] A. N. Tikhonov and A. A. Samarskii, Equations of Mathematical Physics [in Russian] (Moscow, Tekhteoretizdat, 1953).