

NUMERICAL MODEL OF IONIC MASS TRANSFER DURING ANODIC SOLUTION OF METAL

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Mathematical descriptions of the macrokinetics of anodic solution of metals under the influence of an electric current are usually based on the assumption that the condition of electrical neutrality of the solution is satisfied over the whole of space up to the surface of the dissolving metal [1-4]. However, as shown in [5], migration of ions through the diffuse part of the electric double layer at the anode-solution boundary can sometimes make a marked contribution to the resulting rate of ionic mass transfer and can thus influence the rate of solution. The analytical method of solution used in [5] was based on the smallness of a parameter proportional to the square of the ratio between the effective thicknesses of the diffuse and diffusion anode boundary layers. In this article we use a numerical method to solve the system of equations of ionic mass transfer; it does not require the imposition of any limitations on the external parameters of the electrochemical system.

We shall consider stationary anodic solution of a metal. We assume that the hydrodynamic conditions of solution can be represented by Nernst's diffusion model; we shall take no account of the effect of convective transfer due to the normal component of the velocity of the liquid at the interphase boundary [4]. Moreover, we assume that the solution contains not only metal cations (with charge ez_1) but also cations (ez_2) and anions (ez_3) of the indifferent electrolyte. In these conditions the system of equations of ionic mass transfer is

$$\frac{d}{dx} \left\{ \frac{dc_i}{dx} + \frac{z_i F c_i}{RT} \frac{d\varphi}{dx} \right\} = 0 \quad (i = 1, 2, 3), \quad (1)$$

$$\frac{d^2 \varphi}{dx^2} + \frac{4\pi F}{\epsilon_0} \sum_{i=1}^3 z_i c_i = 0. \quad (2)$$

Here c_i is the local concentration of ions of species i , φ is the local electric potential, ϵ_0 is the dielectric permittivity of the solution, and x is the coordinate reckoned from the electrode toward the solution; the positions of the electrode and the external Helmholtz plane are $x = -x_h$ and $x = 0$, respectively.

The boundary conditions in system (1)-(2) are as follows:

$$\frac{dc_i}{dx} + \frac{z_i F c_i}{RT} \frac{d\varphi}{dx} = - \frac{i \delta_{1i}}{z_i F D_i} \quad \text{at } x = 0, \quad (3)$$

$$\frac{d\varphi}{dx} = \frac{\epsilon_h}{\epsilon_0 x_h} (\varphi_h - \varphi_0) \quad \text{at } x = 0, \quad (4)$$

$$c_i = c_{i0} (1 - \delta_{1i}), \quad \varphi = 0 \quad \text{at } x = -\delta, \quad (5)$$

where δ_{1i} is the Kronecker delta ($\delta_{1i} = 1$ when $i = 1$, $\delta_{1i} = 0$ when $i \neq 1$), i is the anodic current density, the D_i are the ionic diffusion coefficients, ϵ_h is the dielectric permittivity of the compact part of the electric double layer, φ_h and φ_0 are the potentials of the planes $x = 0$ and $x = -x_h$, and the c_{i0} are the volumetric values of the ionic concentrations (we assume that there are processes which keep them constant in the bulk of the solution).

The quantities φ_0 and i are interrelated by the equation of the kinetics of electrochemical solution. For many systems of practical importance this equation can be adequately approximated by the equation of the theory of delayed discharge [6]:

$$i = K \exp \left[\frac{\alpha z_1 F (\psi_0 - \psi_r)}{RT} \right], \quad (6)$$

where K and α are empirical constants.

We shall assume that the charges and diffusion coefficients of all the ions are the same ($|z_i| = z$, $D_i = D$, $c_{i0} = c_0$) and shall introduce the following dimensionless variables:

$$y = \frac{x}{\delta}, \quad C_i = \frac{c_i}{c_0}, \quad Z_i = \frac{z_i}{z}, \quad \psi = \frac{F\phi}{RT}, \quad I = \frac{i\delta}{zF D c_0},$$

$$B = \frac{\epsilon_0 x h}{\epsilon h}, \quad K^* = K \frac{\delta}{D c_0}, \quad \beta^2 = \frac{\epsilon_0 R T}{4 \pi c_0 z^2 F^2 \delta^2}.$$

Then the system of equations and boundary conditions (1)-(5) takes the form

$$\frac{d}{dy} \left(\frac{dC_i}{dy} + Z_i C_i \frac{d\psi}{dy} \right) = 0, \quad (7)$$

$$\beta^2 \frac{d^2 \psi}{dy^2} + \sum_{i=1}^3 Z_i C_i = 0, \quad (8)$$

$$\frac{dC_i}{dy} + Z_i C_i \frac{d\psi}{dy} = -I \delta_{i1} \text{ when } y = 0, \quad (9)$$

$$B \frac{d\psi}{dy} = \frac{1}{\alpha z} \ln(K^*/I) \text{ when } y = 0, \quad (10)$$

$$C_i = 1 - \delta_{i1}, \quad \psi = 0 \text{ when } y = 1. \quad (11)$$

Equations (7)-(8) are very nonlinear. For this reason, the usual iteration procedure either gives divergent results or requires a very good initial approximation, which as a rule is not known. The method in which the derivatives $\partial C_i / \partial t$ and $\partial \psi / \partial t$ are introduced and the desired solution is sought in the form of the asymptotic at $t \rightarrow \infty$ requires a number of time steps of the order of 10^6 , which is also unacceptable. Therefore, in the calculations we used Gummel's iteration method which was developed for semiconducting devices [7]. For this purpose we express the C_i in the form $C_i = \Phi_i \exp(-Z_i \psi)$ and substitute in (8). We then linearize the exponential terms depending on ψ as follows:

$$f(\psi^{(k+1)}) = f(\psi^{(k)}) + \frac{\partial f(\psi^{(k)})}{\partial \psi} (\psi^{(k+1)} - \psi^{(k)}), \quad (12)$$

where k is the number of the iteration. In the variables C_i Eq. (8) becomes

$$\beta^2 \Delta \psi^{(k+1)} - (C_1^{(k)} + C_2^{(k)} + C_3^{(k)}) \psi^{(k+1)} = -(C_1^{(k)} + C_2^{(k)} - C_3^{(k)}) - (C_1^{(k)} + C_2^{(k)} + C_3^{(k)}) \psi^{(k)}. \quad (13)$$

From the $C_i^{(k)}$ found from Eq. (7) we can calculate the $\psi^{(k+1)}$ from (13), and can then use them to calculate the $C_i^{(k+1)}$ from (7), and so on. The difference scheme for Eqs. (7) and (13) was obtained by the method of integral balances and was solved at each iteration step by the method of trial runs [8].

Calculations were made in the following ranges of the parameters: $\beta^2 = 10^{-6} - 10^{-4}$, $I = 1 - 20$, $B = 0.01 - 0.1$, $K^* = 5 \cdot 10^{-3}$, $\alpha z = 1$.

Figure 1 plots $C_1(y)$ for various values of I and B with $\beta^2 = 10^{-6}$, $K^* = 5 \cdot 10^{-3}$. A characteristic of these graphs is the presence of a maximum displaced into the bulk of the solution, in contrast with the quasineutrality approximation [3, 4], giving a monotonic profile of $C_1(y)$ with maximum at the point $y = 0$. The cause of this behavior of $C_1(y)$ is the strong electric field arising from the sudden change of dielectric permittivity at the boundary between the compact and diffuse layers. As seen from Fig. 1, when $B = 10^{-2}$ (curves 2, 4, 6) the values of the cation concentration near the electrode are practically equal to zero. This fact, which implies complete impoverishment of the electrode layer in cations of the dissolving metal and is a direct consequence of the sharp rise in the electric field in the compact layer, may be clearly illustrated in an approach based on the electric boundary layer method [9]. In fact, according to boundary layer theory [9], the expression for the concentration of cations of dissolving metal near the electrode is

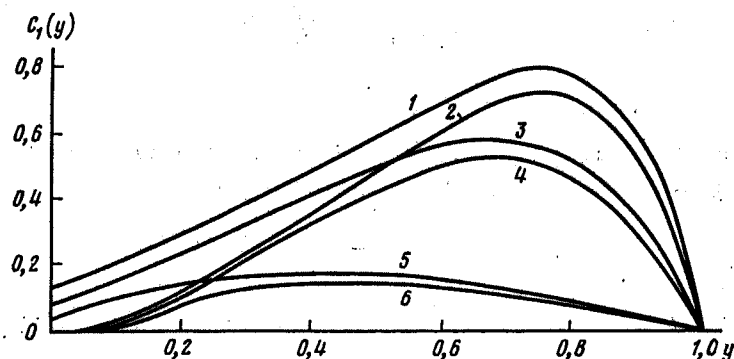


Fig. 1. Concentration profiles of cations of dissolving metal near the anode for three values of dimensionless anode current density I : 1, 2) 20; 3, 4) 8; 5, 6) 1. Graphs are calculated for two values of B equal to 0.1 (1, 3, and 5) and 0.01 (2, 4, and 6).

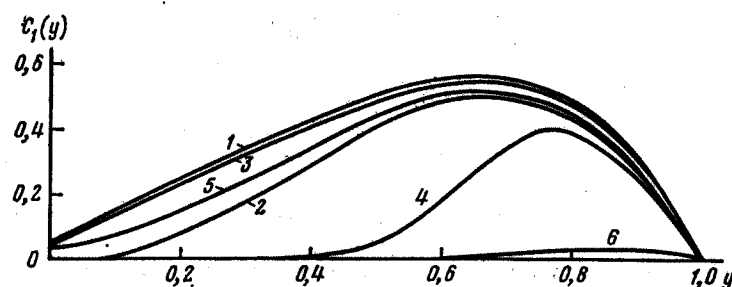


Fig. 2. Influence of parameters β and B on anode concentration profile of $C_1(y)$; 1, 3, and 5 correspond to $B = 0.1$, $\beta^2 = 10^{-6}$, 10^{-5} , and 10^{-4} ; for 2, 4, and 6 the corresponding values of β^2 are the same but $B = 0.01$.

$$C_1(0) = C_1^{(0)}(0) \exp(-z_1 \psi_h^{(1)}), \quad (14)$$

where $C_1^{(0)}(0)$ is the value found by neglecting the influence of the electric double layer, and $\psi_h^{(1)}$ is that part of the concentration polarization which is due to the presence of the diffuse part of the electric double layer. For the potential $\psi_h^{(1)}$, Chernenko [9] derived the following transcendental equation:

$$\psi_0 - \psi_h^{(0)} - \psi_h^{(1)} = \frac{B}{z_\beta} \left\{ 2 \sum_{i=1}^3 C_i^{(0)}(0) [\exp(-z_i \psi_h^{(1)}) - 1] \right\}^{1/2}. \quad (15)$$

Here $\psi_h^{(0)}$ is the concentration polarization in the absence of the influence of the double layer. The solution to Eq. (15) for known values of ψ_0 and $\psi_h^{(0)}$ is very sensitive to the values of B and β . Thus, when $B = 10^{-2}$, numerical solution of Eq. (15) gives the result that $\psi_h^{(1)} = 9.28$ when $\beta = 10^{-2}$ and $\psi_h^{(1)} = 6.81$ when $\beta = 10^{-3}$. Substituting these values into Eq. (14), we get the values of $C_1(0)$, which are, respectively, $1.2 \cdot 10^{-5}$ and $1.7 \cdot 10^{-3}$. On the scale of the graphs in Fig. 1 these values are practically equal to zero. As B decreases, the maximum of $C_1(y)$ becomes sharper and shifts toward increasing y .

Figure 2 gives the calculated graphs of $C_1(y)$ for various values of β and B with $I = 8$. For $B = 0.1$ further decrease of β below 10^{-3} does not lead to any appreciable changes in the behavior of the function $C_1(y)$.

Within the range of I investigated by us, the concentration of electrolyte cations near the electrode is several orders of magnitude lower than the concentration of cations of dissolving metal. Thus solution of the metal occurs effectively in its own salt, irrespective of the electrolyte composition.

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CHARACTERISTICS OF CORROSION-CAVITATIONAL DAMAGE OF STEEL ÉI943 IN H_3PO_4 SOLUTIONS

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Under the conditions of cavitation attack, to which the turbines of pumps are subjected during transfer of extraction phosphoric acid, steel ÉI943 (Kh23N28M3D3T) has an unsatisfactory resistance.

To investigate the electrochemical behavior of steel under cavitation conditions, vibrations induced by a magnetostriction oscillator were transferred to a specimen connected to a potentiostat and serving simultaneously as a waveguide.

The electrochemical factor was estimated from the quantity of electricity passed through the specimen [1].

Under steady conditions an increase in the phosphoric acid concentration from 0.5 to 5 moles/liter at 25°C leads to a positive shift in the passivation potential φ_p (Fig. 1a). The shift increases with the solution temperature.

During cavitation, passivation of the surface is virtually absent. Clearly, the oxides formed are removed from the surface before they have time to form a protective layer. The rate of electrochemical solution of the steel in the passive region increases by a factor of 40-50 under cavitation conditions.

TABLE 1. Dynamic Viscosity of Phosphoric Acid Solutions and Corrosion-Cavitation Losses of Specimens of Steel ÉI943 in These Media at Amplitude of Oscillations of Specimen A = 20 μ m and t = 70°C

H_3PO_4 concn., M	Dynamic viscosity η , P	Total losses Δm_{tot} , mg	Electrochemical losses Δm_{ec} , mg	$\frac{\Delta m_{ec}}{\Delta m_{tot}}$, %
0.5	0.017	7.7	0.44	5.2
5.0	0.030	6.6	1.0	15.2
Commercial soln., 12.7	0.113	5.7	2.4	42.1