

DISTRIBUTION OF IONIC CONCENTRATIONS IN SOLUTION IN THE COURSE OF ANODIC DISSOLUTION OF METALS

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It is necessary to find the distribution of ionic concentration close to the surface of an intensely dissolving anode, for investigation of the pitting corrosion of a metal, for the electrochemical polishing of metals, for electrochemical dimensional treatment, and for precise definition of the conditions for the transfer of metal from the active to the passive state.

The problem was recently solved for the case of complex-formation with the anions of the electrolyte [1-3]. Mathematical expressions were obtained for the distribution of ionic concentration in a system containing three sorts of particle with arbitrary charges, and also for the anodic polarization curve and the limiting anodic currents [3].

The principal interest, from the viewpoint of elucidation of the laws of anodic dissolution of metals, is consideration of the electrochemical reaction:



The rate of this is limited by the stage of diffusion-migration removal of cations of the dissolving metal M^{z_1} , from the electrode surface into the interior of the solution containing the inert electrolyte KA. The solutions of several problems on the distribution of ionic concentration and potential in the pre-electrode region, for systems with three specific types of ion, within the limits of the Nernst pellicular diffusion model, have been published [4-7]. The general method of solving problems of ionic mass transfer, in solutions of arbitrary composition, under conditions such that the effect of mixing of the solution can be described by the Nernst pellicular model, was formulated in [8]. In our paper, this method, which was previously applied to describe processes of electrochemical complex-formation [3], was used to calculate the ionic concentrations in the Nernst diffusion boundary layer $0 \leq x \leq \delta$, adjacent to the anode surface $x = 0$, at which the reaction (1) took place under a stationary regime.

We denoted by c_1 , c_2 , and c_3 the local molar concentrations of the cations of the dissolving metal M^{z_1} , of the anions A^{z_2} , and of the cations K^{z_3} (where z_1 , z_2 , and z_3 were the corresponding valencies), and by D_1 , D_2 , and D_3 — the diffusion coefficients of these ions. With sufficiently concentrated solutions, and if furthermore the anodic current density i was not too large, the diffusion layer was electrically neutral at all points, so that the system of equations for ionic mass transfer could be expressed in the following simplified form:

$$\begin{aligned} \frac{dc_1}{dx} + \frac{z_1 F c_1}{RT} \frac{d\varphi}{dx} &= - \frac{i}{z_1 D_1 E}; \quad \frac{dc_2}{dx} + \frac{z_2 F c_2}{RT} \frac{d\varphi}{dx} = 0; \\ \frac{dc_3}{dx} + \frac{z_3 F c_3}{RT} \frac{d\varphi}{dx} &= 0; \\ z_1 c_1 + z_2 c_2 + z_3 c_3 &= 0. \end{aligned} \quad (2)$$

Here φ denoted the local electrical potential, reckoned from the interior of the solution,

If M^{z_1} cations were originally absent from the interior of the solution, and the anodic dissolution regime was stationary, then the boundary conditions for system (2) were:

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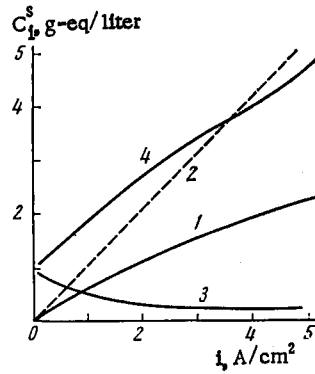


Fig. 1. Dependence of the pre-electrode ionic concentrations: 1) $c_1^{(s)}$, 4) $c_2^{(s)}$, and 3) $c_3^{(s)}$, on the current density; 2) corresponds to the distribution of $c_1^{(s)}$ vs i , calculated without allowance for the migration mechanism of transfer.

$$\begin{aligned} c_1 = 0, \quad c_2 = c_2^{(0)}, \quad c_3 = -\frac{z_2}{z_3} c_2^{(0)}, \\ \varphi = 0 \quad \text{at } x = \delta. \end{aligned} \quad (3)$$

We introduced the dimensionless variables:

$$y = \frac{x}{\delta}, \quad C_k = \frac{c_k}{c_2^{(0)}} \quad (k = 1, 2, 3), \quad \psi = \frac{F\varphi}{RT}, \quad I = \frac{i\delta}{z_1 F D_1 c_2^{(0)}}$$

and rewrote the system of Eqs. (2) as follows:

$$\begin{aligned} \frac{dC_1}{dy} + z_1 C_1 \frac{d\psi}{dy} &= -I; \\ \frac{dC_2}{dy} + z_2 C_2 \frac{d\psi}{dy} &= 0; \\ \frac{dC_3}{dy} + z_3 C_3 \frac{d\psi}{dy} &= 0; \\ z_1 C_1 + z_2 C_2 + z_3 C_3 &= 0. \end{aligned} \quad (4)$$

The boundary conditions (3) then took the form:

$$C_1 = 0, \quad C_2 = 1, \quad C_3 = -\frac{z_2}{z_3}, \quad \psi = 0 \quad \text{at } y = 1. \quad (5)$$

The solutions of system (4), with boundary conditions (5), determined the local profiles of ionic concentration and potential:

$$\begin{aligned} C_1 &= \frac{z_2}{z_1} (e^{-z_1 \psi} - e^{-z_1 \psi_s}); \\ C_2 &= e^{-z_2 \psi}, \quad C_3 = -\frac{z_2}{z_3} e^{-z_2 \psi}; \\ \frac{z_1 - z_2}{z_2} (e^{-z_1 \psi} - 1) - \frac{z_1 - z_3}{z_3} (e^{-z_1 \psi} - 1) &= \frac{z_1}{z_2} I (1 - y). \end{aligned} \quad (6)$$

The pre-electrode (at $x = 0$) value of the concentration of M^{z_1} cations was determined by the equation:

$$C_1^{(s)} = \frac{z_2}{z_1} (e^{-z_1 \psi_s} - e^{-z_1 \psi_s}), \quad (7)$$

where ψ_s represented the root of the following transcendental equation:

$$\frac{z_1 - z_2}{z_2} (e^{-z_1 \psi_s} - 1) - \frac{z_1 - z_3}{z_3} (e^{-z_1 \psi_s} - 1) = \frac{z_1}{z_2} I. \quad (8)$$

For the particular case $z_1 = 2$, $z_2 = -1$, and $z_3 = 1$ (representing, e.g., the dissolution of a metal which forms divalent ions in a solution of sodium chloride), we found, from Eqs. (7) and (8), the pre-electrode concentration of M^{2+} cations, in dimensional units:

$$c_1^{(s)} = \frac{(I+2)\{(I+2) + \sqrt{(I+2)^2 - 3}\} - 6}{3\{(I+2) + \sqrt{(I+2)^2 - 3}\}} c_2^{(0)}. \quad (9)$$

In Fig. 1 we have made a comparison of the dependence of concentration $c_1^{(s)}$ on the current density i , calculated from Eq. (9) with allowance for migration (curve 1), and as calculated by purely diffusive transfer of ions (curve 2), when the pre-electrode concentration of M^{2+} cations could be described by the equation:

$$c_1^{(s)} = I c_2^{(0)} = \frac{i\delta}{2FD_1}.$$

Calculations were carried out for the following values of the parameters: $c_2^{(0)} = 1$ g-eq/liter, $\delta = 10^{-3}$ cm, $D_1 = 0.5 \cdot 10^{-5}$ cm²/sec. It is evident from Fig. 1 that the contribution of the migration mechanism, to the removal of M^{2+} from the electrode surface, became appreciable at current densities of the order 1 A/cm² and above. Figure 1 also shows the variations of $c_k^{(s)}$ with i for the cations K^+ (curve 3), and for the anions A^- (curve 4). These relationships were expressed by the equations:

$$c_2^{(s)} = \frac{1}{3} c_2^{(0)} \{(I+2) + \sqrt{(I+2)^2 - 3}\} \quad (10)$$

$$c_3^{(s)} = 3c_2^{(0)} \{(I+2) + \sqrt{(I+2)^2 - 3}\}^{-1} \quad (11)$$

Equations (7) and (8) made it possible to analyze quantitatively other practically important cases, such as the anodic dissolution of iron in sulfuric acid ($z_1 = 2$, $z_2 = -2$, and $z_3 = 1$). In this case the pre-electrode values of the ionic concentrations were determined by the following relationships:

$$c_1^{(s)} = \left(\xi^2 - \frac{1}{\xi} \right) c_2^{(0)}; \quad (12)$$

$$c_2^{(s)} = \xi^2 c_2^{(0)}; \quad (13)$$

$$c_3^{(s)} = \frac{2}{\xi} c_2^{(0)}, \quad (14)$$

where the dimensionless value ξ depended on the dimensionless current density I , in accordance with the equation:

$$\xi = 2 \sqrt{\frac{I+3}{6}} \cos \left\{ \frac{\pi}{3} - \frac{1}{3} \arccos \left[\frac{1}{4} \left(\frac{6}{I+3} \right)^{1/2} \right] \right\}. \quad (15)$$

The use of the equations, derived in our work, made it possible to determine the pre-electrode ionic concentrations for systems in which a Nernst diffusion model was used (the most favorable cases in this sense were systems with surfaces equally available with respect to diffusion). The quantitative information obtained, on the distribution of ionic concentration close to the anode, was of considerable value, in particular for solving the problem of whether the concentration of anodic dissolution products reached the solubility limit of the electrode material at a critical current density, corresponding to conversion of the electrode from the active to the passive state.

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