

HYDRODYNAMIC MODEL OF ION MASS TRANSFER
COMPLICATED BY INTENSIVE GAS EVOLUTION

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Electrode processes are often accompanied by gas emission. Gas bubbles play a double role in mass and charge transfer in the solution: On the one hand, they cause additional mixing of the solution; on the other, the formation and growth of bubbles on the electrode causes partial blocking of its surface, hindering access of reagents and removal of the products of the electrode reactions; furthermore, the dispersed gas phase in the interelectrode space can reduce the effective electrical conductivity of the solution. The necessity of taking account of gas emission in calculations of the macrokinetics of electrode processes has been demonstrated [1, 2] for the case of dimensional electrochemical treatment with allowance for the dependence of the electrical conductivity of the solution on its hydrogen content evolved at the cathode, and also [3, 4] for the case of blocking of the anode surface by gas bubbles formed by side reactions. The opposite effect of convective motion created in the liquid phase by gas bubbles growing on the anode can alter the concentration profiles at the electrodes; this is important, e.g., in the case of formation of insoluble deposits by anodic solution of metals. In this article we propose a method for such a calculation, based on a model of a convection current induced near the anode surface by evolved gas bubbles.

Consider the solution of a metal M in a solution of a completely dissociated acid H_nA_m , where there are three types of ions, M^{z_1} , A^{z_2} , and H^+ (where z_1 and z_2 are the valences of the corresponding metal cations and acid anions). Suppose that an electrochemical reaction* is taking place at the anode (its spatial position will be identified with the plane $x = 0$):



leading to the formation of oxygen. Intensive evolution of oxygen occurs uniformly over the whole anode surface, and the dimension of the bubbles is greater than the thickness of the boundary diffusion layer. Then as the simplest model of convective motion due to gas emission we can adopt the following: The anode surface is covered with a film of gas, with a thickness which increases continuously with time. This film is homogeneous and contains a dispersed gas phase, which, without influencing the hydrodynamics, causes local contact between the anode and the solution, and this effects transport of electric charge through the surface of the metal.

Let us suppose that at the anode, as well as reaction (1), there is an irreversible reaction of ionization of metal atoms:



We shall assume that the anode surface is uniformly accessible with respect to mass exchange, and shall suppose that at some fixed distance $x = \delta$ from the anode the solution is completely mixed (Nernst's diffusion model).

Let i be the anode current density, and η_1 and η_2 the current yields of metal cations and protons respectively. With this notation, at the anode we get the formation of $\eta_2 i S / F$ gram-ions of hydrogen per unit time (where S is the area of the anode surface). From Eq. (1) it follows that $\eta_2 i S / 4F$ gram-molecules of oxygen are formed simultaneously with this amount of protons. According to the above hydrodynamic film model, all of this oxygen goes to increase the gas film thickness. If we denote the instantaneous film thickness by $h(t)$, then the condition for mass balance of oxygen in the film will take the form

* The existence of such a reaction at certain potentials in processes accompanied by anodic solution of metals is an experimentally established fact [5].

$$\frac{\eta_2 i M_4 S}{4F} = \frac{d}{dt}(\rho_4 S h),$$

where M_4 and ρ_4 are the molecular mass and density of the gaseous oxygen. Hence we can find the rate of movement of the free film surface, v_s :

$$v_s = \frac{dh}{dt} = \frac{\eta_2 M_4 i}{4\rho_4 F}. \quad (3)$$

Since, as a rule, the Schmidt number for the ionic components of aqueous solutions is very large (about 10^3), therefore the rate of convective transport of ions in a direction perpendicular to the anode within the diffusion layer can be identified with the rate of growth of the gas film, i. e., with v_s given by Eq. (3). For this reason, we can write the following system of equations for mass and charge transport in the Nernst diffusion layer:

$$-\frac{dC_1}{dy} + C_1 \left(z_1 \frac{d\psi}{dy} - \xi I \right) + I = 0; \quad (4)$$

$$-\frac{dC_2}{dy} + C_2 \left(z_2 \frac{d\psi}{dy} - \xi I \right) = 0; \quad (5)$$

$$\frac{dC_3}{dy} + C_3 \left(\frac{d\psi}{dy} - \xi I \right) + \frac{\eta_2 z_1}{\eta_1} I = 0; \quad (6)$$

$$z_1 C_1 + z_2 C_2 + C_3 = 0. \quad (7)$$

Here the dimensionless concentrations C_k are expressed in units of bulk concentration of anions $C_2^{(0)}$ and, in addition, we have introduced the following dimensionless quantities:

$$y = \frac{x}{\delta}, \quad I = \frac{\eta_1 i \delta}{z_1 F D C_2^{(0)}}, \quad \xi = \frac{\eta_2 z_1 M_4 C_2^{(0)}}{4\eta_1 \rho_4}.$$

The subscripts 1, 2, and 3 refer, respectively, to the ions M^{z_1} , A^{z_2} , and H^+ ; the diffusion coefficients of all the ions are assumed to be positive and equal to D . The boundary conditions for Eqs. (4)-(7) are as follows:

$$C_1 = 0, \quad C_2 = 1, \quad C_3 = -z_2, \quad \psi = 0 \quad \text{for } y = 1. \quad (8)$$

The analytical form of the solution to system (4)-(7) becomes much simpler if $z_1 = -z_2 = 1$. In this case the solution becomes

$$C_1 = \frac{\eta_1 + \eta_2 + 2(\xi\eta_1 - \eta_1 - \eta_2) \exp[-\xi I(1-y)] - (2\xi\eta_1 - \eta_1 - \eta_2) \exp[-2\xi I(1-y)]}{2\xi\{\eta_1 + \eta_2 + (\xi\eta_1 - \eta_1 - \eta_2) \exp[-\xi I(1-y)]\}}; \quad (9)$$

$$C_2 = \frac{1}{\xi\eta_1} \{\eta_1 + \eta_2 + (\xi\eta_1 - \eta_1 - \eta_2) \exp[-\xi I(1-y)]\}; \quad (10)$$

$$\psi = \xi I(1-y) + \ln C_2. \quad (11)$$

According to Eq. (6), $C_3 = C_2 - C_1$.

In the absence of gas evolution, i. e., when $\eta_2 = 0$, the corresponding distributions take the form

$$C_1 = \frac{1}{2} \left\{ 1 + I(1-y) - \frac{1}{1 + I(1-y)} \right\}; \quad (12)$$

$$C_2 = 1 + I(1-y); \quad (13)$$

$$\psi = \ln[1 + I(1-y)]. \quad (14)$$

By comparing Eqs. (9)-(11) with (12)-(14) we can assess the influence of gas evolution on the laws of anodic solution. As we see from Figs. 1 and 2, convective movements of the solution due to gas emission lead to ion depletion of the diffusion layer (this concerns all the ions present in the solution). Simultaneously there is a rise in the potential difference across the diffusion layer. Gas evolution has a particularly marked effect on the anion distribution: Whereas when $\eta_2 = 0$ the diffusion mechanism of anion transport opposes the migration mechanism (the concentration C_2 increases as we approach the anode), when $\eta_2 \neq 0$ diffusion and migration transport anions in one direction only, toward the anode, and the sum of the diffusion and migration currents is compensated by the convection current.

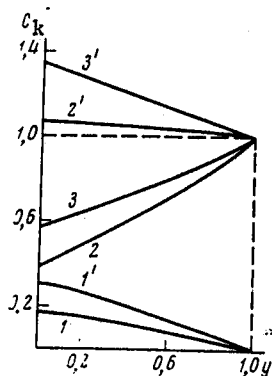


Fig. 1

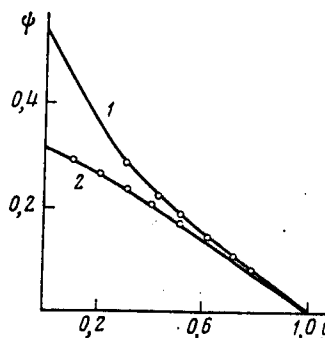


Fig. 2

Fig. 1. Ionic concentration distributions in region near anode with (1-3) and without (1'-3') gas evolution; the figures 1, 2, and 3 refer to the dimensionless concentrations C_1 , C_2 , and C_3 , calculated for the following values of the parameters: $i = 2 \text{ A/cm}^2$; $\eta_1 = 0.9$; $\eta_2 = 0.1$; $C_2^{(0)} = 5 \text{ moles/liter}$; $M_4 = 32$; $\rho_4 = 1.4 \text{ g/liter}$; $\delta = 10^{-3} \text{ cm}$; $D = 10^{-5} \text{ cm}^2/\text{sec}$.

Fig. 2. Distribution of dimensionless potential ψ within Nernst diffusion layer in the presence of the gas evolution effect represented by the film model (1), and in the absence of this effect (2); the curves are calculated for the same values of the diffusion-layer parameters as in Fig. 1.

Our mathematical model shows that, as well as undesirable effects of blocking the anode surface and reducing the conductivity of the solution, anodic oxygen evolution promotes additional stirring of the solution. This conclusion is in qualitative agreement with the available experimental data [6, 7]. Convective ion mass transport, induced by gas evolution, accelerates anodic solution. We can verify this by estimating the ratio of the concentrated driving forces of ionic transfer with and without gas emission:

$$\frac{C_{i*}}{C_{i*}'} = \left(\frac{C_i}{C_i'} \right)_{y=0} = \frac{(1+I) \{ \eta_1 + \eta_2 + 2(\xi \eta_1 - \eta_1 - \eta_2) \exp(-\xi I) - (2\xi \eta_1 - \eta_1 - \eta_2) \exp(-2\xi I) \}}{\xi I (2+I) \{ \eta_1 + \eta_2 + (\xi \eta_1 - \eta_1 - \eta_2) \exp(-\xi I) \}}. \quad (15)$$

It is easy to show that this ratio is less than one for any fixed values of the parameters, in particular for any given current density I . Thus for a given anode current density the true concentration of cations of the dissolving metal in the anode layer is in fact always less than that calculated without taking account of gas evolution. This leads us to another important conclusion: If, for some reason or another (e.g., owing to supersaturation of the solution or to the occurrence of reactions of complex formation and heterogeneous processes accompanying the formation of passivating films), the concentration of cations of the dissolving metal in the anode layer cannot exceed a certain value, then this "critical" value of the concentration, in conformity with Eq. (15), will be reached at a higher anode current density than in the absence of gas evolution.

LITERATURE CITED

1. K. Kawafune, T. Mikoshiba, and K. Noto, *Ann. CIRP*, **16**, 345 (1968); **18**, 305 (1970).
2. J. Kozak, *Arch. Budowy Maszyn*, **19**, 43 (1972).
3. A. D. Davydov and V. D. Kashcheev, *Itogi Nauki Tekh., Elektrokhim., VINITI*, **9**, 154 (1974).
4. V. S. Krylov, A. D. Davydov, and E. Kozak, *Elektrokimiya*, **11**, 1155 (1975).
5. K. J. Vetter, *Electrochemical Kinetics*, Academic Press.
6. L. J. J. Janssen and J. G. Hoogland, *Electrochim. Acta*, **15**, 1013 (1970); **18**, 543 (1973).
7. M. G. Fouad and G. H. Sedahmed, *Electrochim. Acta*, **17**, 665 (1972).