Physical Chemistry

R. M. Perskaya and I. A. Zaidman

1957

SovietRxiv

Abstract

Full Text

Physical Chemistry

R. M. Perskaya and I. A. Zaidman

On Liquid Diffusion Electrodes

(Presented by Academician A. N. Frumkin, 11 II 1957)

The use of liquid diffusion electrodes is promising for the creation of chemical current sources and for carrying out continuous electrolysis processes ($^{1-3}$). In order to clarify the basic regularities governing the operation of such electrodes, we undertook a theoretical and experimental study of certain questions of their macrokinetics, as determined by the distribution of current density in the pores. In contrast to the problems considered earlier ($^{4-7}$), the problem of current distribution in a liquid diffusion electrode, in all practically applicable cases, requires, first, that the finite thickness of the electrode be taken into account and, second, that changes in the concentrations of the reacting substances over the thickness of the electrode be taken into account. In the present communication only plane metallic diffusion electrodes with uniform porosity are considered (the electrical resistance of the metal is assumed to be zero in comparison with the resistance of the electrolyte in the pores).

The basic equation for the current distribution in such electrodes has the form

$$\frac{d^2\varphi}{dx^2} = pR_\mathrm{e}\, i(\varphi, c), \tag{1}$$

where φ is the polarization of the electrode at points located at a distance x from its boundary (here and below x is measured in the direction of electrolyte flow, from the rear to the polarized side of the electrode); p is the perimeter of the pores, constant in any section $x = \mathrm{const}$; R_e is the linear resistance of the electrolyte in the pores, i.e., the resistance per 1 cm of electrode thickness; i is the true current density on the pore surface at the point x; c is the concentration of the active substance at the point x.

In practically important cases of liquid oxidation–reduction systems on a diffusion electrode, the polarization characteristic of the electrode is determined only by concentration changes over the electrode thickness ξ and by the activation polarization η. Thus, the current density at the point x may be represented in the form

$$i = j_0^0 (c_\mathrm{B}^0)^{1-\alpha} (c_\mathrm{O}^0)^{\alpha} \left[\frac{c_\mathrm{B}^x}{c_\mathrm{B}^0} \exp\left(\frac{\alpha\varphi nF}{RT}\right) - \frac{c_\mathrm{O}^x}{c_\mathrm{O}^0} \exp\left(-\frac{(1-\alpha)\varphi nF}{RT}\right) \right], \tag{2}$$

Fig. 1. Diagram of the measuring cell.

Figure 1: Fig. 1. Diagram of the measuring cell.

where $j_0^0 (c_\mathrm{B}^0)^{1-\alpha} (c_\mathrm{O}^0)^\alpha = j_0$ is the exchange current for the given electrode reaction at the point $x = 0$; $\varphi = \xi + \eta$ is the polarization of the electrode at the point x.

Expressing the concentrations of the reductant and oxidant at the point x (c_B^x and c_O^x) through the concentrations in the initial solution: $c_\mathrm{B}^x = c_\mathrm{B}^0 - I_x c_\mathrm{B}^0 / I_{da}$ and $c_\mathrm{O}^x = c_\mathrm{O}^0 + I_x c_\mathrm{O}^0 / I_{dk}$, where the limiting anodic (I_{da}) and cathodic (I_{dk}) currents depend on the flow rate (“throughput”) Q, the concentration c^0, and the electrochemical equivalent (ε) of the reacting substance: $I_{da} = c_\mathrm{B}^0 Q/\varepsilon$ and $I_{dk} =$

$= c_0^0 Q/\partial$, and from (2), and taking into account that, according to Ohm’ s law, for the electrolyte in the pores

$$I_x = \rho \int_0^x i\, dx = \frac{1}{R_e} \frac{d\varphi}{dx},$$

we obtain the basic equation for the distribution of current in a plane liquid diffusion electrode:

$$\frac{d^2\varphi}{dx^2} = pR_e j_0 \left[\left(1 - \frac{1}{R_e I_{da}} \frac{d\varphi}{dx}\right) \exp\left(\frac{\alpha\varphi nF}{RT}\right) - \left(1 + \frac{1}{R_e I_{dk}} \frac{d\varphi}{dx}\right) \exp\left(-\frac{(1-\alpha)\varphi nF}{RT}\right) \right]. \tag{3}$$

As boundary conditions for an electrode of thickness L, one may take

$$\left.\frac{d\varphi}{dx}\right|_{x=0} = 0; \qquad \left.\frac{d\varphi}{dx}\right|_{x=L} = R_e I, \tag{4}$$

where $I = I_{x=L}$ is the total current flowing through the electrode.

Instead of (4), it is sometimes more convenient to use the conditions

$$\varphi|_{x=0} = \varphi_0; \qquad \varphi|_{x=L} = P, \tag{5}$$

where the polarization values at the two surfaces of the electrode, φ_0 and P, are readily determined experimentally.

Fig. 1. Diagram of the measuring cell.
1—diffusion electrode; 2, 3—capillaries leading to the Hg/Hg_2SO_4 electrodes; 4—Pt electrode of comparison; 5—auxiliary electrode for polarization; 6—electrolyte inlet; 7—electrolyte outlet.

For small I, when one may take $\exp(\alpha\varphi nF/RT) = 1+\alpha\varphi nF/RT$ and $\exp[-(1-\alpha)\varphi nF/RT] = 1-(1-\alpha)\varphi nF/RT$, the solution of equation (3) with boundary conditions (4) makes it possible to calculate the initial polarization resistance of the electrode

$$R_D = \lim_{I\to 0}\left(\frac{d\varphi}{dI}\right)_{x=L} = \lim_{I\to 0}\left(\frac{dP}{dI}\right).$$

We obtain

$$R_D = \frac{RT}{2nF}\left(\frac{1}{I_{da}}+\frac{1}{I_{dk}}\right) + \sqrt{\left(\frac{RT}{2nF}\right)^2\left(\frac{1}{I_{da}}+\frac{1}{I_{dk}}\right)^2 + \frac{R_e RT}{pj_0 nF}}\times$$

$$\times \operatorname{cth}\left(L\sqrt{\frac{p^2 j_0^2}{4}\left(\frac{1}{I_{da}}+\frac{1}{I_{dk}}\right)^2 + \frac{pR_e j_0 nF}{RT}}\right). \tag{6}$$

When $Q \to \infty$, I_{da} and $I_{dk} \to \infty$, and the factor determining the concentration polarization over the electrode thickness,

$$\frac{RT}{nF}\left(\frac{1}{I_{da}}+\frac{1}{I_{dk}}\right) \to 0,$$

then

$$R_D \to \frac{R_e \operatorname{cth}(aL)}{a}, \tag{7}$$

where

$$a = \sqrt{\frac{pR_e j_0 nF}{RT}},$$

i.e., R_D is determined only by activation polarization.

To verify the basic regularities following from equations (3) and (6), the dependences of the current-voltage characteristics on the flow rate and concentration of the active substances were experimentally investigated for the redox systems Fe^{2+}/Fe^{3+} and Ce^{3+}/Ce^{4+} in $1\,N$ H_2SO_4 at 25°.

The diffusion electrode—a porous disk 1 mm thick—was made from platinum powder by a metal-ceramic method. The measuring cell (Fig. 1) was made of Plexiglas. The polarization was measured by a compensation method with an accuracy of $±$0.1 mV.

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

Fig. 4

Figure 3: Fig. 4

Fig. 2. Curves $P = f(I)$ for different Q at $c_B^0 \approx c_O^0 = 0.005\,N$ ($\mathrm{Fe}^{2+}/\mathrm{Fe}^{3+}$ in $1N\,\mathrm{H_2SO_4}$).
1—$Q = 5$, 2—$Q = 8.8$; 3—$Q = 20$; 4—$Q = 30$; 5—$Q = 60$ ml/min; I_d—theoretical values of the limiting current for the corresponding flow rates.

Fig. 3. Dependence of P on Q at $I = \mathrm{const}$ for two different concentrations ($c_2 > c_1$). System $\mathrm{Fe}^{2+}/\mathrm{Fe}^{3+}$ in $1N\,\mathrm{H_2SO_4}$.

The polarization was measured on both sides of the electrode—at the outlet of the electrolyte from the electrode ("frontal polarization" P) and at the inlet of the electrolyte into the electrode ("rear polarization" φ_0). The magnitude P was determined with the aid of two reference electrodes ($\mathrm{Hg/Hg_2SO_4}$ in $1N\,\mathrm{H_2SO_4}$), the capillaries of which were introduced into the cell at points a and b (Fig. 1).

Fig. 4. Dependence of P and φ_0 on I. Pt electrode (1 cm^2) in a $\mathrm{Fe}^{2+}/\mathrm{Fe}^{3+}$ solution (0.005 N each in $1N\,\mathrm{H_2SO_4}$); $Q = 2.3$ ml/min.

The distances l_1 and l_2 were accurately measured, which made it possible to calculate the correction for the ohmic potential drop outside the diffusion electrode,

$$\Delta\varphi_{\text{ohm}} = [(\varphi_2 - \varphi_1) - (\varphi_2^0 - \varphi_1^0)]\ l_1/l_2,$$

where φ_1, φ_2 are the potentials of the polarized diffusion electrode relative to the first and second reference electrodes, respectively; φ_1^0, φ_2^0 are the potentials of the diffusion electrode without current relative to the same reference electrodes. For measuring φ_0, an equilibrium oxidation-reduction electrode—a Pt plate in the initial electrolyte solution—served as the reference electrode.

As a result of the measurements it was established:

1. Oxidation-reduction reactions on the diffusion electrode are accompanied by a sharply expressed limiting current (Fig. 2).
2. The magnitude of the limiting current I_d corresponds to complete (100%) reduction of the oxidized form or oxidation of the reduced form, i.e., it is directly proportional to the flow rate and the concentration of the active substance:

$$I_d = FcQ,$$

where F is the Faraday constant in the corresponding units.

3. The portions of the polarization curves in the region of currents $I < 0.5 I_d$ are rectilinear in character, and the linearity is preserved for polarization values considerably exceeding $2RT/F = 51.2$ mV at 25°.

4. The slope of the linear part of the polarization curve, $R_D = P/I$, depends on the flow rate and on the concentration of the active substance (Figs. 2 and 3). At constant concentration, as Q is increased, the slope of the curves tends to a limiting value, which is reached at a certain— "limiting" —flow rate Q_p. The value Q_p is reached the sooner, the higher the concentration of the active substance.

5. The curve of rear polarization $\varphi_0 = f(I)$ repeats the character of the curve of frontal polarization (Fig. 4), with $\varphi_0 < P$. As c and Q decrease, the difference between φ_0 and P decreases, while the frontal current density i_L, readily calculated from $\eta = \varphi - \xi$, increases; i.e., a redistribution of current density occurs inside the electrode. This may be explained by the formation (as a result of the electrode reaction proceeding inside the pores and the appearance of a concentration gradient) of a short-circuited concentration cell, in which the direction of the discharge current in the pores coincides with the direction of the polarization current. As c and Q decrease, at the frontal surface of the liquid diffusion electrode ($x = L$) an ever-increasing self-discharge current density of this concentration cell is subtracted from the current density of the external polarization, while at the rear surface of the electrode ($x = 0$) it is added. At the same time, of course, the total true current density at all points always satisfies the basic equation for current distribution (3).

6. With a large increase in c and Q, the limiting current becomes smaller than the theoretical value. These regions are not considered in the present communication.

The experimental data obtained for the dependence of the current-voltage characteristics of the electrodes on flow rates and concentrations are in qualitative and quantitative agreement with the conclusions following from formulas (6) and (7).

It follows from the foregoing that measurement of $(R_D)_{\mathrm{lim}}$ for solutions of various substances on one and the same electrode makes it possible to determine the relative values of exchange currents. Owing to the rectilinearity of large portions of the current-voltage characteristics, for this purpose it is sufficient to measure one point of $P = f(I)$ at a sufficiently high flow rate.

In conclusion, we take this opportunity to express our gratitude to A. N. Frumkin and N. S. Lidorenko for their assistance and for a number of suggestions in carrying out this work.

State All-Union Scientific-Research
Element-Electrocarbon Institute

Received
5 II 1957

REFERENCES CITED

1. G. W. Heise, *Trans. Electrochem. Soc.*, **75**, 147 (1939).
2. A. Schmid, *Final Report BJOS*, Item 31 (1945).
3. I. E. Bauslit, G. Z. Kiryakov, V. V. Stender, *Izv. AN KazSSR, ser. khim.*, **20**, No. 2 (1948).
4. V. S. Daniel-Bek, *ZhFKh*, **22**, 697 (1948).
5. A. N. Frumkin, *ZhFKh*, **23**, 1477 (1949).
6. O. S. Ksenjek, V. V. Stender, *DAN*, **107**, No. 2 (1956).
7. J. J. Coleman, *Trans. Electrochem. Soc.*, **90**, 545 (1946).
8. K. Vetter, *Zs. phys. Chem.*, **194**, 284 (1950).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.