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Corresponding Member of the Academy of Sciences of the USSR V. G. Levich, Yu. A. Chizmadzhev,

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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Corresponding Member of the Academy of Sciences of the USSR V. G. Levich,
Yu. A. Chizmadzhev,
Yu. G. Chirkov

POLARIZATION CURVES FOR ELECTRODES PARTIALLY IMMERSED IN AN ELECTROLYTE SOLUTION

Recently there has been growing interest in questions connected with current formation at electrodes partially immersed in an electrolyte solution. This is due to the fact that in such systems one can study processes occurring in gas porous electrodes. Until now, however, it has been assumed ([1,2]) that current generation is completely determined by diffusion of the reactant through the electrolyte film and meniscus formed on the electrode surface. Nevertheless, simple estimates show that in the majority of practically interesting cases ([3]) considerable regions of the electrodes operate not in the diffusion regime.

Fig. 1

Let us consider a smooth electrode partially immersed in an electrolyte solution, on whose surface there is an electrolyte film* of thickness Δ and length l (Fig. 1). Hydrogen from the gas phase diffuses through the film and is adsorbed on the electrode, where the electrochemical reaction takes place. Let us suppose that adsorption is a rapid process. Then it is sufficient to take into account the following two kinetic stages:

$$i_{\text{diff}} = \frac{2FDHp}{\Delta}(1 - C_0), \tag{1}$$

$$i_{\text{disch}} = \alpha i_0^{(p)} \left[\sqrt{C_0 e^{\bar{\varphi}}} - e^{-\bar{\varphi}}\right], \tag{2}$$

where i_{diff} is the density of the diffusion current of H_2 molecules to the electrode surface, i_{disch} is the current density of electrochemical discharge, F is the Faraday number, D is the diffusion coefficient of H_2 in the electrolyte, H is Henry' s constant, p is the gas pressure, $C_0 = C/Hp$, where C is the concentration of H_2 at the electrode surface, $i_0^{(p)}$ is the exchange current relative to pressure, $\bar{\varphi} = e\varphi/2kT$ is the dimensionless polarization of the electrode, e is the electron charge, φ is the polarization, and α is the roughness factor (the ratio of the true electrode surface to the apparent one).

In the stationary state $i_{\text{diff}} = i_{\text{disch}}$, so that, eliminating the concentration C_0 from (1) and (2), we obtain the equation**

$$\frac{d^2\bar{\varphi}}{dx^2} = \frac{1}{2l_\Delta^2}\left[\sqrt{\frac{e^{4\bar{\varphi}}}{4\nu^2} + \frac{e^{\bar{\varphi}}}{\nu} + e^{2\bar{\varphi}}} - \left(\frac{e^{2\bar{\varphi}}}{2\nu} + e^{-\bar{\varphi}}\right)\right] = \frac{\Phi(\bar{\varphi}, \nu)}{2l_\Delta^2}, \tag{3}$$

with the boundary conditions

$$\bar{\varphi}\Big|_{x=0} = \bar{\varphi}_0, \qquad \frac{d\bar{\varphi}}{dx}\Big|_{x=l} = 0,$$

where

$$l_\Delta = \sqrt{\frac{\lambda \Delta kT}{\alpha e i_0^{(p)}}}$$

is the characteristic length of the problem, λ is the specific electrical conductivity of the electrolyte, and

$$\nu = \frac{2FDHp}{\Delta \alpha i_0^{(p)}}$$

is the characteristic parameter of the problem.

* It will be shown below what changes are introduced into the results by the presence of a meniscus.
** Equation (3) is valid under the condition that there is convection in the system.

It is not possible to obtain an exact solution of equation (3). Therefore let us consider the following special cases.

1. We shall call the **slow-discharge regime** the regime in which the generation of current throughout the film is determined by electrochemical kinetics. The conditions for the onset of such a regime must obviously be determined by the ratio of the limiting diffusion current to the exchange current (i.e., ν) and by the potential $\bar{\varphi}_0$ prescribed at the entrance. From the right-hand side of (3) it follows that the desired criterion has the form: $\bar{\varphi}_0 \ll \bar{\varphi}_{10} = \frac{1}{3}\ln\frac{\nu}{5}$. If the latter condition is fulfilled, then equation (3) takes the simple form

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

$$\frac{d^2\bar{\varphi}}{dx^2} = \frac{1}{l_\Delta^2}\,\mathrm{sh}\,\bar{\varphi} \tag{4}$$

Fig. 2

Fig. 3

and its solution is well known; in particular, if $l \gg l_\Delta$,

$$I = 8\sqrt{\frac{\lambda k T \Delta \alpha i_0^{(p)}}{e}}\,\frac{\mathrm{th}\,\bar{\varphi}_0/4}{1-\mathrm{th}^2\,\bar{\varphi}_0/4}, \tag{5}$$

where I is the current generated in the film. Since electrode polarizations cannot be less than zero, the slow-discharge regime is possible only for $\nu > 5$. Table 1 gives the values of ν and $\bar{\varphi}_{10}$ for nickel, palladium, and platinum at $\Delta = 1\mu$. From the data obtained it follows that this regime is realized on nickel and palladium, but is not realized on platinum. On platinum, at arbitrarily low polarizations, mixed kinetics takes place. The initial portions of the polarization curves (except for the Pt case) in Figs. 2–4 were obtained with the aid of solutions (5), and the range of their applicability with respect to potentials ($\bar{\varphi}_{10}$) is given in Table 1. It can be shown that for platinum at $\bar{\varphi}_0 \ll 1$, equation (3) has the form

Table 1*

	ν	φ_{10}, mV	φ_{20}, V
Nickel	97.5	65	1.2
Palladium	9.75	15	0.85
Platinum	0.975	–	0.8

$$\frac{d^2\bar{\varphi}}{dx^2} = \frac{2\nu}{1+2\nu}\,\bar{\varphi}\,\frac{1}{l_\Delta^2} \tag{6}$$

and

Fig. 4

Figure 4: Fig. 4

$$I = 2\sqrt{\frac{\lambda kT\Delta\alpha i_0^{(p)}}{e}}\sqrt{\frac{2\nu}{1+2\nu}}\,\bar{\varphi}_0. \tag{7}$$

The more electrochemically active the electrode, the more steeply the polarization curve rises at the origin of coordinates and the narrower is the range of potentials.

electrodes, where the entire electrode operates by the electrochemical mechanism. With a further increase in the polarization $\overline{\varphi}_0$, in the region of small x a mixed-kinetics regime sets in, and then the limiting diffusion-current regime. In this case the region in which retarded discharge is realized shifts to the right as $\overline{\varphi}_0$ increases.

2. The **limiting diffusion regime** is realized at finite l. It sets in at a sufficiently high potential at the right-hand end of the film, namely $\overline{\varphi}_l \geq \overline{\varphi}^*$, where $\overline{\varphi}^*$ is equal to the larger of the two quantities: $\overline{\varphi}_1^* = \frac{1}{3}\ln 40\nu$ and $\overline{\varphi}_2^* = \frac{1}{2}\ln 40\nu^2$. Under these conditions $\Phi \equiv \nu = \text{const}$; solving equation (3), we find the initial polarization $\overline{\varphi}_{20}$, beginning with which the limiting diffusion regime is realized:

Fig. 4

$$\overline{\varphi}_{20} = \overline{\varphi}^* + \frac{\nu}{4}\left(\frac{l}{l_\Delta}\right)^2. \tag{8}$$

The total limiting current has the simple form

$$I = I_{\text{lim}} = \frac{2FDHp}{\Delta}\,l. \tag{9}$$

The magnitude I, of course, does not depend on the nature of the electrode, which is reflected, however, in the potential $\overline{\varphi}_{20}$ (Fig. 2 and Table 1). The more active the electrode, the earlier the limiting diffusion-current regime sets in. The character of the curves in Figs. 2–4 is determined by the quantity ν, which depends on the normality of the solution (D and H), the gas pressure, the film thickness, the degree of roughness α, and the nature of the electrode ($i_0^{(p)}$). For example, by increasing α for nickel by a factor of 10, we pass from curve (3) to curve (2) in Fig. 2. Further, by increasing the pressure, we increase both the limiting current and the quantity $\overline{\varphi}_{20}$, as illustrated by Fig. 3 (Table 2).

Table 2*

p, atm	ν	φ_{10}, mV	φ_{20}, V	I_{lim}, μA/cm
1	97.5	65	1.2	875
0.1	9.75	15	0.29	87.5
0.01	0.975	–	0.10	8.75

* In calculating the data of Tables 1 and 2 it was assumed that $\alpha = 3$, $T = 300°\text{K}$, $\lambda = 1\ \Omega^{-1}\cdot\text{cm}^{-1}$, $D = 1.4\cdot10^{-5}\ \text{cm}^2/\text{s}$, $H = 1.1\cdot10^{-7}$ g-at/cm$^3\cdot$atm, $p = 1$ atm, $l = 3$ mm; $i^{(p)}_{0\text{Pt}} = 10^{-3}\ \text{A/cm}^2$; $i^{(p)}_{0\text{Pd}} = 10^{-4}\ \text{A/cm}^2$; $i^{(p)}_{0\text{Ni}} = 10^{-5}\ \text{A/cm}^2$.

3. We shall call a regime **mixed** when at the left-hand end of the film the kinetics is determined by the limiting diffusion current, while at the right-hand end retarded discharge is realized. This regime occurs only in the case of sufficiently long films. In addition, it must be that $\overline{\varphi}_0 \geq \varphi^*$ and $\nu \geq 5$. The solution of the problem in this case is obtained by matching, at a certain point x_0, expressions valid for small (diffusion) and large (retarded discharge) x. The total current has the form*

$$I = I_{\text{diff}} + I_{\text{disch}} = \frac{2FDHp}{\Delta} x_0 + 8\sqrt{\frac{\lambda kT\Delta\alpha i_0^{(p)}}{e}\,\frac{\text{th}\,\overline{\varphi}'/4}{1-\text{th}^2\,\overline{\varphi}'/4}}, \qquad (10)$$

where

$$\overline{\varphi}' = \text{arsh}\,\frac{\nu}{2}.$$

* In the case of platinum, the second term in expression (10) should be replaced according to formula (7); in addition, $\overline{\varphi}'_{\text{platinum}} = (1+2\nu)/4$.

The length of the diffusion region x_0, which is determined by a complicated analytical expression, is shown graphically in Fig. 4 as a function of the potential. The quantity $\overline{\varphi}'$ does not depend on $\overline{\varphi}_0$, so that the second term in (10), corresponding to the region of slow discharge, makes a constant contribution to the total current. The dependence of I on the potential, which is completely determined by the first term, is shown in Fig. 4. The portions of the curves indicated by dashed lines were obtained by interpolating expressions (5), (7), and (10), valid at small and large potentials, respectively (solid portions of the curves). Thus, depending on the activity of the electrode, the polarization curves have qualitatively different forms. In contrast to the curve for platinum, the dependences for palladium, and especially nickel, are characterized by the presence of an inflection point.

For comparison, Fig. 4 also gives the polarization curve obtained theoretically in work [1]. As can be seen from the figure, this curve approximately coincides with (10) for the case of platinum, but differs substantially from the curves for nickel and palladium.

It has already been noted that the mixed regime is realized only for sufficiently long films, namely

$$l \geq l_\Delta \left(1 + \frac{2}{\sqrt{\nu}}\sqrt{\overline{\varphi}_0 - \overline{\varphi}'}\right).$$

Since in this case $x_0 \sim \sqrt{\overline{\varphi}_0}$, the total current does not reach the limiting value that should be observed (see Fig. 2) for films of small length.

In conclusion, let us estimate the contribution made to current formation by the meniscus. It can be shown that, for practically all polarizations of the electrode $\overline{\varphi}_0$, almost the entire meniscus operates in the diffusion regime. Then the current generated in the meniscus is equal to

$$I_{\text{men}} = 2FDHp\int_0^h \frac{dx}{\delta(x)} = 2FDHp\Psi, \tag{11}$$

where h is the length of the meniscus, and $\delta(x)$ is the variable thickness of the meniscus. If $\delta(x)$ has the form of a parabola, then $\Psi \sim 1$ and $I_{\text{men}} \sim 1$ μa/cm. Thus, the current generated in the meniscus is extremely small, and it may be assumed that the entire current I is generated in the electrolyte film. However, the polarization at the beginning of the film is no longer $\overline{\varphi}_0$, but $\overline{\varphi}_h = \overline{\varphi}|_{x=h}$, which can be related to $\overline{\varphi}_0$ by the following relation (having the meaning of ohmic losses in the meniscus):

$$\overline{\varphi}_0 - \overline{\varphi}_h = \frac{el\Psi}{2kT\lambda} \cong 8I \text{ (a/cm)}, \tag{12}$$

where $I = I(\overline{\varphi}_h)$. Thus, knowing the polarization curves for the film, one can easily calculate the polarization curves in the case where there is both a film and a meniscus on the electrode surface. However, as Fig. 4 shows, the current generated in the film does not exceed (for $\overline{\varphi}_0 < 8$) 1 ma/cm. Therefore the ohmic losses in the meniscus are negligibly small, and Fig. 4 gives, with good accuracy, the polarization curves for the case where both film and meniscus are present.

Institute of Electrochemistry
Academy of Sciences of the USSR

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