POLARIZATION CURVES FOR ELECTRODES PARTIALLY IMMERSED IN AN ELECTROLYTE

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Problems associated with current generation at an electrode partially immersed in an electrolyte are being viewed with increasing interest at the present time. The reason for this interest is found in the fact that the processes occurring in porous gaseous electrodes can be studied in systems of this type. Current generation here has been assumed to be fully determined by reagent diffusion through the electrolyte film and meniscus carried by the electrode surface [1, 2]. Even simple calculations show, however, that an extensive region of the electrode must operate under nondiffusional conditions, at least in most of those cases which are of practical interest [3].

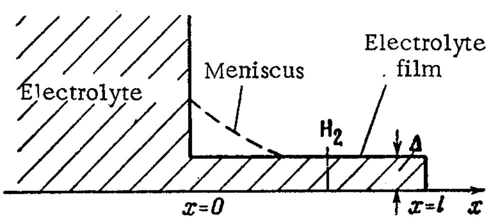

Fig. 1.

We will consider a smooth electrode partially immersed in an electrolyte and carrying a film of this electrolyte on its surface, this film having depth Δ and length l * (Fig. 1). Hydrogen diffuses through the film from the gaseous phase and adsorbs on the electrode where electrochemical reaction takes place. Adsorption will be assumed to be a rapid process. It will then be sufficiently exact to consider just the two following kinetic equations:

$$i_{\mathrm{dif}} = \frac{2FDHp}{\Delta}(1 - C_0), \quad (1)$$

$$i_{\mathrm{dis}} = \alpha i_0^{(p)} [\sqrt{C_0} e^{\bar{\varphi}} - e^{-\bar{\varphi}}], \quad (2)$$

in which i_{dif} is the current density for the diffusion of molecular H_2 to the electrode surface, i_{dis} is the current density for electrochemical discharge, F is the Faraday, D is the diffusion coefficient of H_2 in the electrolyte, H is the Henry 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 equilibrium exchange current corresponding to pressure p, $\bar{\varphi} = e\varphi/2kT$ is the dimensionless electrode polarization, e is the charge on the electron, φ is the polarization, and α is the coefficient of roughness, i.e., the ratio of the true and apparent electrode surface areas.

Since the stationary state is one in which $i_{\mathrm{dif}} = i_{\mathrm{dis}}$, C_0 can be eliminated from (1) and (2) to obtain an equation,†

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

with the boundary conditions $\bar{\varphi}\big|_{x=0} = \bar{\varphi}_0$, $\frac{d\bar{\varphi}}{dx}\Big|_{x=l} = 0$, and $l_\Delta = \sqrt{\lambda \Delta kT/\alpha e i_0^{(p)}}$ being the characteristic length (λ is the specific conductivity of the electrolyte), and $\nu = \frac{2FDHp}{\Delta \alpha i_0^{(p)}}$ the characteristic parameter, of the problem.

* The effect of the meniscus will be brought out below.

† Equation (3) is valid for the condition that convection is established in the system.

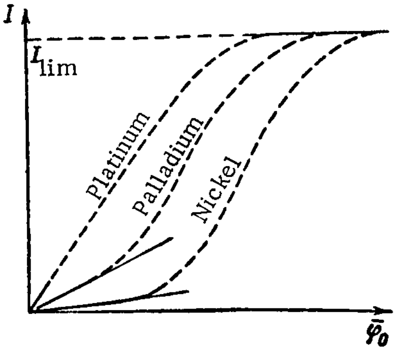

Fig. 2.

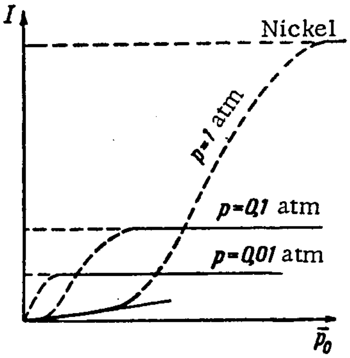

Fig. 3.

The following special cases will be considered since Eq. (3) cannot be solved exactly.

1. Delayed discharge control. This situation arises when the electrochemical kinetics determine the current generation over the entire film. It is clear that the requirements for the onset of such conditions will be expressed in terms of the ratio of diffusional current to exchange current (i.e., by ν) and the potential, $\bar{\varphi}_0$, at the entering edge of the film. A criterion in the form $\bar{\varphi}_0 \leq \bar{\varphi}_{10} = 1/3 \ln \nu/5$ can be developed from Eq. (3). When this requirement is fulfilled, Eq. (3) simplifies to

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

for which a well-known solution is available. In particular, $l \gg l_\Delta$, implies that

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

I being the current generated in the film. Since the electrode polarization cannot be negative, it follows that a condition of delayed discharge control is possible only if $\nu > 5$. Values of ν and $\bar{\varphi}_{10}$ for nickel, palladium, and platinum at $\Delta = 1\ \mu$ are shown in Table 1. The figures of this table make it clear that this condition is established on nickel and palladium, but not on platinum. Only mixed kinetics can be established on platinum, regardless of how far the polarization is reduced. The entering segments of the polarization curves of Figs. 2-4 (except for the case of Pt) were developed through the solution of (5), and are applicable over the ranges shown in Table 1; expression there being in terms of the potential $\bar{\varphi}_{10}$. It can be proven that Eq. (3) takes the following form for platinum at $\bar{\varphi}_0 \ll 1$

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

so that

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

The higher the electrochemical activity of the electrode, the steeper the polarization curve at the origin, and the more narrow the region for electrode operation according to an electrochemical mechanism. Further increase in the polarization, $\bar{\varphi}_0$, brings about the appearance, first of mixed kinetics and then of limiting diffusional current control, in the region of low x values. The region in which delayed discharge control can be realized is, at the same time, displaced toward the right as $\bar{\varphi}_0$ increases.

2. Limiting diffusional control. A situation of this type is met at terminal values of l, arising when the potential on the right end of the film is such that $\bar{\varphi}_l \geq \bar{\varphi}^*$, and $\bar{\varphi}^*$ is the larger of the two values, $\bar{\varphi}_1^* = \frac{1}{3} \ln 40\nu$

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

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

*The values given in Tables 1 and 2 were obtained on the assumption that: $\alpha = 3$, $T = 300°K$, $\lambda = 1\ \Omega^{-1}$, $D = 1.4 \cdot 10^{-5}\ cm^2/sec$, $H = 1.1 \cdot 10^{-7}$ g-at/(cm^3·atm), $p = 1$ atm, $l = 3$ mm, $i_{0Pt}^{(p)} = 10^{-3}\ A/cm^2$, $i_{0Pd}^{(p)} = 10^{-4}\ A/cm^2$, and $i_{0Ni}^{(p)} = 10^{-5}\ A/cm^2$.

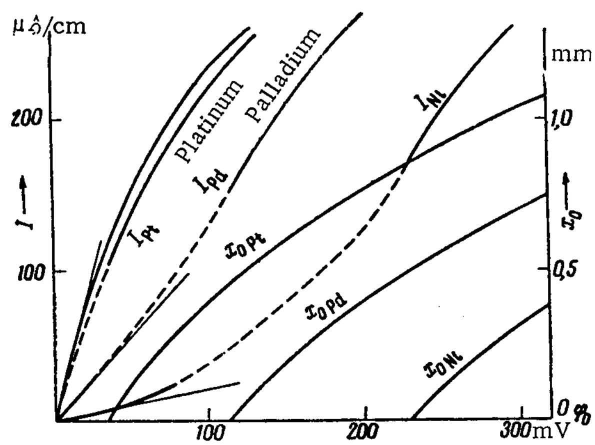

Fig. 4.

and $\bar{\varphi}_2^* = \frac{1}{2} \ln 40\,\nu^2$. One then has $\Phi \equiv \nu =$ const, and solution of Eq. (3) leads to an expression for the polarization, $\bar{\varphi}_{20}$, at which limiting diffusional control can first be established, namely:

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

The expression for the total limiting current then simplifies to

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

The value of I does not depend on the electrode material, but this factor does affect the potential $\bar{\varphi}_{20}$ (Fig. 2 and Table 1). The more active the electrode, the earlier the onset of the limiting diffusional current regime. The character of the curves of Fig. 2-4 is determined by ν; this, in turn, is fixed by the normality of the solution (D and H), the gas pressure, the film depth, the degree of roughness, α, and the nature of the electrode ($i_0^{(p)}$). A ten-fold increase in the value of α for nickel entails passage from curve 3 to curve 2 in Fig. 2. An increase in the pressure also leads to an increase in the limiting current and the value of $\bar{\varphi}_{20}$, as shown by Fig. 3 (Table 2).

3. Mixed kinetics. A situation of this type arises when there is limiting diffusional current control at the left end, and delayed discharge control at the right end, of the film. Cases of this kind are met only in rather long films. In addition, it must be that $\bar{\varphi}_0 \geq \bar{\varphi}^*$ and $\nu \geq 5$. A solution is then obtained by linking the expression valid for low x values (diffusion) with the expression valid for large x values (delayed discharge) at a definite point, x_0. The equation for the total current then takes the form*

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

*It should be noted that the second member of (10) should be replaced by the expression of (7) in the case of platinum; in addition, $\bar{\varphi}'_{\text{platinum}} = (1 + 2\nu)/4$.

where

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

The length of the diffusional region, x_0, is fixed by a complicated analytical expression; its dependence on the potential is shown graphically in Fig. 4. $\bar{\varphi}'$ is independent of $\bar{\varphi}_0$, the region of delayed discharge making a fixed contribution to the total current which is represented by the second member of (10). The dependence of I on the potential is completely determined by the first member of this equation; it is represented in Fig. 4. The dotted portions of these curves were obtained by interpolation of (5), (7), and (10) which are valid for high and low potentials, respectively (full portions of the curves). Thus it follows that the form of the polarization curve will vary with the activity of the electrode. The curve for platinum does not show an inflection point, and thereby differs from the curves for palladium and (especially) nickel.

The theoretical curve obtained in [1] is also included in Fig. 4 for reference; it is seen to be almost identical with the plot of (10) for platinum, but deviates markedly from similar plots for nickel and palladium.

It has already been pointed out that a mixed regime can arise only with long films which satisfy the inequality $l \geqslant l_\Delta \left(1 + \frac{2}{\sqrt{\nu}}\sqrt{\bar{\varphi}_0 - \bar{\varphi}'}\right)$. Since $x_0 \sim \sqrt{\bar{\varphi}_0}$ under these conditions, the total current fails to reach its limiting value, the latter being observed only with short films (see Fig. 2).

We conclude by estimating the contribution of the meniscus to the current generation. It can be shown that essentially the entire meniscus functions under diffusional control at almost all values of the electrode polarization, $\bar{\varphi}_0$. The current generated in the meniscus is therefore given by the expression

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

h being the length, and $\delta(x)$ the variable depth, of the meniscus. When $\delta(x)$ is a parabolic function, $\Psi \sim 1$ and $I_{\text{men}} \sim 1\ \mu\text{A/cm}$. It follows that the current generation in the meniscus is so extremely small that the entire generation I, can be assumed to occur in the electrolyte film. The polarization at the beginning of the film is not $\bar{\varphi}_0$, however, but $\bar{\varphi}_h = \bar{\varphi}|_{x=h}$, the latter being related to $\bar{\varphi}_0$ through the relation (which has the physical sense of a resistance loss):

$$\bar{\varphi}_0 - \bar{\varphi}_h = \frac{eI\Psi}{2kT\lambda} \cong 8I \quad (\text{A/cm}), \tag{12}$$

where $I = I(\bar{\varphi}_h)$. Thus a knowledge of the polarization curves for the film makes it possible to readily develop polarization curves applying to an electrode surface carrying both film and meniscus. Figure 4 shows, however, that the current generated in the film does not exceed 1 μa/cm (at $\bar{\varphi}_0 < 8$). It follows that the ohmic loss in the meniscus is negligibly small, and Fig. 4 therefore gives a highly precise representation of the polarization curves for both film and meniscus.

LITERATURE CITED

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. ***Some or all of this periodical literature may well be available in English translation.*** **A complete list of the cover-to-cover English translations appears at the back of this issue.**
