SOME QUESTIONS IN THE THEORY OF POROUS ELECTRODES

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A. G. PSHENICHNIKOV

SOME QUESTIONS IN THE THEORY OF POROUS ELECTRODES

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In connection with the use of porous electrodes for intensifying processes, it is of interest to consider the processes occurring in a porous gas electrode. Yosti et al. (^1) assume that the electrochemical activity of a porous gas electrode is simply the sum of the electrochemical activities of the individual pores. In each pore a three-phase boundary—gas-electrolyte-electrode—is formed, at which the electrochemical reaction proceeds. However, on the basis of this model it is impossible to explain the dependence, essential for a porous gas electrode, of the electrochemical activity of the electrode on the pressure difference between the gas and the electrolyte. As we have shown earlier (^2), this dependence can be explained on the basis of a model of a porous electrode according to which, at each given value of the pressure difference between the gas and the electrolyte, the electrochemical reaction takes place on the surface of broad pores freed from electrolyte, while the current flows in narrow pores filled with electrolyte. A model of a porous electrode convenient for calculation may be represented as a body possessing electronic conductivity and penetrated by parallel cylindrical pores of different radius. We shall assume that neighboring pores are connected with one another by a large number of micropores, or, in other words, that they are separated by walls which are readily permeable to the electrolyte but impermeable to the gas. This condition is realistic because of the large value of the capillary pressure in the micropores.

If the indicated model is adopted, the consideration of the processes occurring in a porous gas electrode can be carried out analogously to the consideration of the operation of a porous non-gas electrode, all pores of which are completely filled with electrolyte. The processes in a non-gas electrode have been considered in detail by V. S. Daniel-Bek (^3), A. N. Frumkin (^4), O. S. Ksenjek (^5), and others. In these works it is shown that the electrochemical activity of a porous non-gas electrode depends, in particular, on the structural parameters of the electrode (the total cross section of electrolyte in the pores and the total surface of the pores). During operation, the structural parameters of a non-gas electrode remain constant. According to the model of a porous gas electrode described above, its structural parameters (the surface of broad pores and the total cross section of narrow pores) are functions of the pressure difference between the gas and the electrolyte. Let us consider the process of hydrogen ionization in a

porous electrode.

For simplification we shall consider a one-dimensional problem, which is permissible under the assumption of a small thickness of the walls between the pores. Let the x-axis be parallel to the axes of the pores and directed from the side of the electrode facing the electrolyte toward the side of the electrode facing the gas. We shall take the intersection of the coordinate axis with the electrode/electrolyte boundary as the origin of coordinates. All quantities will be referred to 1 cm^2 of the apparent surface of the electrode. According to Ohm' s law, for any small element inside the electrode, for a definite pressure difference, one may write (neglecting the change in electrolyte concentration through the thickness of the electrode)

$$Pi\,dx = d\left(\frac{\Phi}{\rho}\frac{d\eta}{dx}\right), \tag{1}$$

where P is the total perimeter of the pores freed from electrolyte; Φ is the total cross section of the pores filled with electrolyte; i is the current density calculated per true surface of the pores freed from electrolyte; ρ is the specific resistance of the electrolyte; η is the deviation of the potential jump between the metal and the electrolyte at the point x from the equilibrium value.

We rewrite equation (1) in the form

$$\frac{d^2\eta}{dx^2} = \frac{P}{\Phi}\rho i. \tag{2}$$

The boundary conditions for an electrode of finite thickness have the form

$$\eta\big|_{x=0} = \eta_0, \qquad \left.\frac{d\eta}{dx}\right|_{x=l} = 0, \tag{3}$$

where η_0 is the measured polarization of the electrode; l is the thickness. Restricting ourselves to the case of small polarizations, we have

$$i = \lambda\eta, \tag{4}$$

where λ is a constant.

The solution of equation (2) with the boundary conditions (3) and taking (4) into account has the form

$$\eta = \eta_0\frac{\operatorname{ch}(l-x)/L}{\operatorname{ch} l/L}, \tag{5}$$

where L is the characteristic length, defined by the expression

$$L = \sqrt{\frac{\Phi}{\rho P \lambda}}. \tag{6}$$

Equation (5) describes the distribution of potential over the thickness of the electrode. The current density I_0, calculated per apparent surface of the electrode, is equal to

$$I_0 = \eta_0 \frac{\Phi}{\rho L} \operatorname{th} \frac{l}{L}. \tag{7}$$

For $l/L < 0.4$, with a sufficient degree of accuracy one may take $\operatorname{th} l/L \approx l/L$, i.e., taking (6) into account,

$$I_0 = Pl\lambda\eta_0. \tag{8}$$

Equation (8) describes the case of a compact metal with a rough surface. Pl is equal to the true surface of the electrode.

The other limiting case, most often encountered in the operation of porous electrodes, corresponds to values $l/L > 1.6$. In this case $\operatorname{th} l/L \approx 1$, and equation (7) takes the form

$$I_0 = \sqrt{\frac{\lambda}{\rho}} \sqrt{P\Phi}\eta_0. \tag{9}$$

When Δp is varied, the quantities P and Φ change according to the pore distribution curve by radii. If the model of a porous electrode described above is adopted, then it is obvious that the total perimeter P of pores freed from electrolyte, referred to a unit of electrode surface, is equal to the surface of these pores S in a unit volume of the electrode, while the total cross section of pores filled with electrolyte, referred to a unit of electrode surface, is equal to the volume of these pores in a unit volume of the specimen. The integral curve of the pore distribution by radii $v(r)$ can be found by the methods described in ([6]). Knowing $v(r)$, one can calculate $S = S(r)$ by graphical integration according to the formula

$$S = 2 \int_0^{v(r)} \frac{1}{r}\, dv, \tag{10}$$

where $v(r)$ is the pore volume in the interval of radii $r_{\max} \div r$.

Under the working conditions of the electrode, each radius corresponds to a pressure difference

Fig. 3

Figure 1: Fig. 3

$$\Delta p = \frac{2\sigma \cos \alpha}{r}, \tag{11}$$

where σ is the surface tension of the electrolyte, and α is the contact angle of wetting.

Starting from the distribution curves $v(r)$, one can express the quantity $\sqrt{P\Phi}$ as a function of the reciprocal radius $1/r$ (a quantity proportional to Δp).

In order to test the theory and the calculation method, 15 structures were investigated. (The electrodes were made from nickel powder, as described in [2].) In Fig. 1, pore-radius distribution curves are shown for 7 structures. The radius is plotted on the abscissa, and the pore volume in the radius interval $r_{\max} \div r$ on the ordinate. For these structures the quantity $\sqrt{P\Phi}$ was calculated; its dependence on $1/r$ is shown in Fig. 2a. Comparison of the calculated curves with the curves expressing the experimental dependence of the current density on Δp at $\eta = 50$ mV in $7N$ KOH at $t = 95^\circ$ (Fig. 2b) leads to the conclusion that there is a definite correspondence between them. This indicates the correctness of the assumptions underlying the model. From Fig. 2 one can determine the quantity I_0 as a function of $\sqrt{P\Phi}$. In doing so, judging from the form of the curves, one may assume that $\Delta p = 600$ mm Hg corresponds to the value $r = 0.5\mu$.

Since

$$\Delta p = A/r, \tag{12}$$

then $A = 80$ dyn/cm. This value is approximately 2 times smaller than twice the value of σ for $7N$ KOH. The discrepancy is apparently connected with the fact that the value of the pore radius can be determined only to within a constant factor, and also with the fact that $\cos \alpha$ in formula (11) is in reality less than unity. In addition, it should be noted that the indicated value of A was obtained from the assumption that the wetting angle between mercury and the sample in studying the pore-size distribution is equal to 128°. If, according to ([7]), the value of the angle is taken to be 154°, then $A = 120$ dyn/cm. This value agrees to within 20% with the value 2σ for $7N$ KOH.

Fig. 3. a—$\frac{1}{r} = 1\frac{1}{\mu}$, $\Delta p = 600$ mm Hg;
b—$\frac{1}{r} = 0.5\frac{1}{\mu}$, $\Delta p = 300$ mm Hg.

The data for 13 structures are given for two values of Δp and r. As is seen from Fig. 3, the dependence of I_0 on $\sqrt{P\Phi}$ is described approximately by a

straight line. This indicates that the theory considered in the present work has at least a semiquantitative character. From the slope of the straight line according to equation (9) one can determine λ and then the exchange current. After substituting the corresponding values we obtain $i_0 =\sim 2 \cdot 10^{-6}$ A/cm^2, which agrees in order of magnitude with the value of i_0 for smooth nickel.

It is interesting to note that, with an increase in λ (which characterizes the electrochemical activity of the electrode material), L decreases (see equation (6)), i.e., the active electrode operates to a smaller depth than the inactive one.

If the curve of the pore-size distribution has the form shown in Fig. 1*a*, then for the maximum of the electrochemical activity one can easily find the ratio of the volumes of pores free of electrolyte and filled with electrolyte. In this case the maximum of the function $\sqrt{P\Phi}$ (and, consequently, the maximum of I_0) occurs when the volumes of pores freed from electrolyte and filled with electrolyte are equal ($v_1 = v_2$).

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Institute of Electrochemistry
Academy of Sciences of the USSR

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