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Abstract

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ON THE THEORY OF A POROUS GAS ELECTRODE.

CALCULATION OF EFFECTIVE COEFFICIENTS

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1. Until recently, in theoretical works on the porous electrode, due attention was not paid to allowance for the structural factors of the porous body, although the very fact of the influence of structure on the macroscopic characteristics of the system was not in doubt (^{1}). The calculation of the volt-ampere characteristic of a porous electrode with allowance for its structural features has recently been carried out by A. G. Pshenichnikov (^{2}), who used a simplified model of a porous body.

Fig. 1

In the present work we set ourselves the goal of carrying out a more correct allowance for the structure of a porous electrode.

Let us consider a porous electrode filled with electrolyte and gas (Fig. 1). We shall approximate a homogeneous porous body by a set of intersecting tortuous pores. Suppose that each pore has a radius constant along its length. Then it is obvious that the gas and electrolyte fill the porous electrode homogeneously and isotropically. For a given pressure drop p, the gas, displacing the electrolyte, fills all pores whose radius exceeds the critical radius $r^* = 2\sigma\cos\theta/p$, where σ is the surface tension of the electrolyte and θ is the wetting angle. The remaining pores are filled with electrolyte. The process of current passage in the system under study is accompanied by a heterogeneous electrochemical reaction on some part of the internal surface of the porous body. The components necessary for the reaction are present in the gas and the electrolyte, while the porous electrode plays the role of a catalyst. Suppose that the heterogeneous reaction occurs where the three phases meet: gas, electrolyte, and solid body (^{1}). Then, considering the porous electrode macroscopically, it is not difficult to obtain an equation for the polarization φ, averaged over the cross section (see also (^{1,2})),

$$\frac{d^2\varphi}{dx^2} = 2j_0\frac{S}{\lambda}\,\mathrm{sh}\,\frac{e\varphi}{2kT}; \qquad \varphi(0) = \varphi_0; \qquad \left.\frac{d\varphi}{dx}\right|_{x=d} = 0, \tag{1}$$

Fig. 2

Figure 1: Fig. 2

where j_0 is the exchange current, λ the effective electrical conductivity, and S the specific reaction surface. In deriving this equation we assumed the electrical conductivity of the solid component of the porous electrode to be infinitely large and neglected concentration polarization. The solution of equation (1) leads to the following expression for the electrochemical activity I_0:

$$I_0 = -\lambda \left.\frac{d\varphi}{dx}\right|_{x=0} = \sqrt{\frac{8j_0kT}{e}}\sqrt{\lambda S}\sqrt{\operatorname{ch}\frac{e\varphi_0}{2kT} - \operatorname{ch}\frac{e\varphi_d}{2kT}}. \tag{2}$$

The polarization on the gas side of the electrode $\varphi_d = \varphi(d)$ depends on the tol- of the electrode thickness and is determined from the equation:

$$d\Big/\sqrt{\frac{kT}{ej_0}\frac{\lambda}{S}} = 2e^{e\varphi_d/4kT}\left[F\left(e^{-e\varphi_d/2kT}, \frac{\pi}{2}\right) - F\left(e^{-e\varphi_d/2kT}, \arcsin e^{-e(\varphi_0-\varphi_d)/4kT}\right)\right], \tag{3}$$

in which $F(k, \alpha)$ are elliptic integrals of the first kind. As is seen from equations (2) and (3), with increasing electrode thickness ($d \to \infty$) the polarization on the gas side of the electrode $\varphi_d \to 0$, while the electrochemical activity tends to its maximum value. Estimates show that for real systems at $d \sim 1$ mm one may take $\varphi_d \cong 0$. In what follows we shall restrict ourselves to the analysis of this case.

II. From formula (2) it follows that the dependence of I_0 on structure and pressure is determined by the quantities λ and S. Let us establish the relation between these effective parameters and the structure of the electrode. Denote by n the number of pores per 1 cm^2 of the surface of an arbitrary cross section of the electrode, by $f(r)$ the density of the distribution of pores by radii, and by $\beta(r)$ the tortuosity coefficient, defined as the ratio of the total pore length to the electrode thickness d. Then the porosity of the electrode, defined as the volume of pores per 1 cm^3 of electrode, will be equal to

Fig. 2

$$g = \pi n \int_0^\infty r^2 f(r)\beta(r)\,dr. \tag{4}$$

In addition to the total porosity one may also introduce the liquid g_l and gas g_g porosities, defined by the relation:

$$g = \pi n \int_0^{r^*} r^2 f(r)\beta(r)\,dr + \pi n \int_{r^*}^{\infty} r^2 f(r)\beta(r)\,dr = g_\text{l} + g_\text{g}. \tag{5}$$

Proceeding to the calculation of S, let us recall that the electrochemical reaction occurs near three-phase boundaries, i.e., where pores filled with electrolyte intersect pores filled with gas (Fig. 2). Suppose that the electrochemical reaction takes place on the surface of a section of an electrolyte-filled pore of radius r_1, the length of which is δr_1. Considering δ as a parameter independent of the gas pressure, we shall not specify the mechanism by which reactants enter from the gas phase to the reaction site, which determines the magnitude of δ.

In order to demonstrate as simply as possible the method of calculating the effective coefficients and to facilitate the analysis of the general formulas of the theory, let us consider the simplest, but important in applications (3), case of an electrode with two types of pores. Let narrow pores of mean radius r_1 be filled with electrolyte, and wide pores of mean radius r_2 be filled with gas. Then the specific surface S is the product of the total number of intersections of pores of the two types in 1 cm^3 of porous electrode N by the reaction surface S_0 corresponding to one intersection. As is seen from Fig. 2, $S_0 = 2\pi r_1 \delta r_1$. The total number of intersections N is found from probabilistic considerations. The probability that at an arbitrary point of the electrode there is an intersection of gas and liquid pores is equal to the product of the liquid and gas porosities $g_\text{l} g_\text{g}$. At the same time this product is numerically equal to the volume of all intersections of pores of the two types in 1 cm^3 of electrode. Knowing the mean volume of one intersection, equal to $2\pi r_2 r_1^2$, one can find the total number of intersections

and the specific reaction surface area:

$$S = s_0 N = 2\pi r_1 \delta r_1 \frac{g_\text{n} g_\text{g}}{2\pi r_1^2 r_2} = \delta \frac{g_\text{n} g_\text{g}}{r_2}. \tag{6}$$

The effective electrical conductivity is, obviously, proportional to the true electrical conductivity of the electrolyte λ_e and to the volume of pores filled with electrolyte, i.e. $\lambda \sim \lambda_\text{e} g_\text{n}$.

The exact formulas, obtained by an analogous method for the case of an arbitrary microstructure, have the form:

$$S = \delta(\pi n)^2 \int_0^{r^*} r_1^2 f(r_1)\,\beta(r_1)\,dr_1 \int_{r^*}^{\infty} r_2 f(r_2)\,\beta(r_2)\,dr_2; \qquad \lambda = \lambda_\text{e} \pi n \int_0^{r^*} \frac{r^2 f(r)\,dr}{\beta(r)}. \tag{7}$$

III. Since, with increasing pressure, the critical radius decreases, it follows, as is seen from (7), that the effective electrical conductivity decreases monotonically with increasing pressure, while the specific surface area has a maximum, since it is the product of a monotonically decreasing and a monotonically increasing function. (This conclusion does not coincide with the results of work (^{2}).) The electrochemical activity $I_0 \sim \sqrt{\lambda S}$ as a function of pressure has a maximum. The position of this maximum depends substantially on the quantities characterizing the microstructure of the electrode. Applying formulas (7) to the case of an electrode with two types of pores, we obtain

$$I_0 = \sqrt{\frac{\delta}{\beta_\mathrm{n}^2}}\sqrt{\frac{g_\mathrm{n}^2 g_\mathrm{g}}{r_2}}, \tag{8}$$

where β_n is the mean tortuosity coefficient of the narrow pores.

From relation (8) the following conclusions can be drawn:

1) Since $g_\mathrm{g} \sim g$, $g_\mathrm{n} \sim g$, then $I_0 \sim g^{3/2}$, i.e. the electrochemical activity is proportional to the porosity to the power 3/2.
2) At a given porosity and mean radius of the gas pores, the electrochemical activity is maximal if

$$g_\mathrm{n} = {}^2/_3\, g, \qquad g_\mathrm{g} = {}^1/_3\, g.$$

This result differs from that obtained in (^{2}).

Table 1

r_2, μ	$I_0^{\max}$, ma/cm^2	p, mm Hg	d, mm
10	119	60	12,7
1	375	600	4
0,1	1190	7,9 atm.	1,27
0,01	3750	79 atm.	0,4

3) $I_0 \sim r_2^{-1/2}$, i.e. the electrochemical activity is inversely proportional to the square root of the mean radius of the gas pores. It should be noted that r_2 also determines the order of the working gas pressure p, namely $r_2 \sim 1/p$. The dependence of the maximum electrochemical activity $I_0^{\max}$, the working pressure p, and the electrode thickness d on the mean radius of the gas pores is illustrated by Table 1. The figures given in the table were obtained using the data of work (^{3}). Substitution of the experimentally measured values of $g_\mathrm{n}, g_\mathrm{g}, r_2$, and I_0 into formula (8) made it possible to find the coefficient $\sqrt{\delta/\beta_\mathrm{n}^2}$, which proved equal to 2.5. In addition, it was assumed that $\varphi_0 = 180$ mV; $\lambda_\mathrm{e} = 0.67$ $(\Omega^{-1} \cdot \mathrm{cm}^{-1})$; $j_0 = 10^{-5}$ a/cm^2; $t = 95°$; $2\sigma\cos\theta = 600$ μmm Hg; $g = 1$.

For an exact calculation of the effective coefficients, knowledge of the functions $f = f(r)$ and $\beta = \beta(r)$ is necessary. The results obtained in (^{3}) by mercury extrusion methods in fact make it possible to determine the product $f(r)\beta(r)$, and not the distribution function $f(r)$. Experimental determination of the electrical conductivity of a porous body as a function of pres-

$\lambda = \lambda(p)$ would make it possible to determine $f(r)/\beta(r)$. Comparison of the product $f(r)\beta(r)$ with the quotient $f(r)/\beta(r)$ would then make it possible to obtain the pore-size distribution and the tortuosity coefficient.

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