

THE THEORY OF THE POROUS GAS ELECTRODE THE CALCULATION OF EFFECTIVE COEFFICIENTS

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1. The effect of structural factors has not yet been adequately treated in the theory of the porous electrode, although there can be no doubt that structure is significant in fixing the macroscopic characteristics of the electrode system [1]. A. F. Pshenichnikov [2] has recently calculated volt-ampere relations for the porous electrode, using a simplified model of the solid body and allowing for structural details. It is the aim of the present work to carry out a more exact treatment of the structure of the porous electrode.

Let us consider a porous electrode filled with an electrolyte and a gas (Fig. 1). We will approximate the homogeneous porous body by a collection of intersecting convoluted pores. It will be assumed that the radius of each pore is constant along its entire length. It is clear that the gas and electrolyte will then fill the porous electrode uniformly and isotropically. A fixed pressure drop, p , in the gas will displace the electrolyte from all pores with radii in excess of the critical value $r^* = 2\sigma \cos \theta / p$, with σ being the surface tension of the electrolyte and θ the wetting angle. The remaining pores will be still filled with the electrolyte. Passage of current through this system will be accompanied by a heterogeneous electrochemical reaction on certain parts of the inner surface of the porous body. The gas and the electrolyte furnish the components for this reaction, while the porous electrode functions as a catalyst. It will be assumed that the heterogeneous reaction proceeds at points of contact between the three phases, gas, electrolyte, and solid [1]. Considering the porous electrode as a macroscopic system, one can readily obtain an equation for the cross-sectional average polarization, φ , (see, also, [1, 2]).

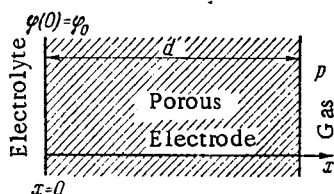


Fig. 1.

$$\frac{d^2\varphi}{dx^2} = 2j_0 \frac{S}{\lambda} \operatorname{sh} \frac{e\varphi}{2kT}; \quad \varphi(0) = \varphi_0; \quad \frac{d\varphi}{dx} \Big|_{x=d} = 0, \quad (1)$$

Here, j_0 is the exchange current, λ is the effective conductivity, and S is the specific reaction surface. The conductivity of the solid component of the porous electrode was assumed to be infinitely large in deriving this equation and concentration polarization was neglected. Solution of Eq. (1) gives the following expression for the electrochemical activity, I_0 :

$$I_0 = -\lambda \frac{d\varphi}{dx} \Big|_{x=0} = \sqrt{\frac{8j_0 kT}{e}} \sqrt{\lambda S} \sqrt{\operatorname{ch} \frac{e\varphi_0}{2kT} - \operatorname{ch} \frac{e\varphi_d}{2kT}}. \quad (2)$$

The polarization at the gas face, $\varphi_d = \varphi(d)$ depends on the thickness of the electrode and is given by the equation:

$$\frac{d}{\sqrt{\frac{kT}{e j_0 S} \lambda}} = 2 \operatorname{arcsin} e^{-e\varphi_d/2kT} \left[F\left(e^{-e\varphi_0/2kT}, \frac{\pi}{2}\right) - F\left(e^{-e\varphi_d/2kT}, \operatorname{arcsin} e^{-e(\varphi_0 - \varphi_d)/4kT}\right) \right], \quad (3)$$

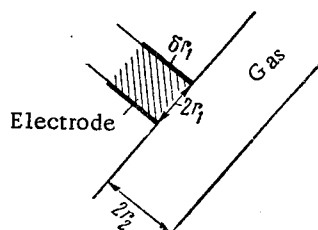


Fig. 2.

TABLE 1

r_2, μ	$j_0^{\max}$ ma/cm ²	$p, \text{ mm Hg}$	$d, \text{ mm}$
10	119	60	12,7
1	375	600	4
0,1	1190	7,9 atm.	1,27
0,01	3750	79 atm.	0,4

in which $F(k, \alpha)$ is an elliptical integral of 1-st order. It follows from Eqs. (2) and (3) that an increase in the thickness of the electrode ($d \rightarrow \infty$) causes the polarization on the gas face to approach zero ($\varphi_d \rightarrow 0$) and the electrochemical activity to tend toward a maximum. Estimates for real systems show that $\varphi_d \approx 0$ when $d \sim 1 \text{ mm}$.

II. It follows from Eq. (2) that the dependence of I_0 on structure and pressure is expressed through the quantities λ and S . We will now set up a relation between the effective values of these parameters and the electrode structure. We will designate the number of pores per 1 cm^2 of arbitrary cross-sectional electrode surface by $\underline{n}$, the density

distribution of pores over radii by $f(r)$, and the coefficient of convolution, defined as the ratio of the total length of the pore to the thickness, d , of the electrode, by $\beta(r)$. The porosity of the electrode, defined as the volume of the pores in 1 cm^3 of electrode, will then be given by

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

In addition to total porosity, one can also introduce a gaseous porosity, g_g , and a liquid porosity, g_l , these defined by the relation:

$$g = \pi n \int_0^{r^*} r^2 f(r) \beta(r) dr + \pi n \int_{r^*}^{\infty} r^2 f(r) \beta(r) dr = g_l + g_g \quad (5)$$

In approaching the calculation of S , it is to be remembered that the electrochemical reaction proceeds in the neighborhood of a three-phase interface, that is, at positions where the electrolyte-filled pores intersect the gas-filled pores (Fig. 2). Let it be supposed that the electrochemical reaction is taking place on a section of an electrolyte-filled pore of radius r_1 and length δr_1 . We will consider the parameter δ to be independent of the gas pressure; moreover, we will make no attempt to specify the mechanism responsible for transfer of reagents from the gaseous phase to the reaction site, though this determines the value of δ .

The simple case of an electrode with two types of pores will be treated both to demonstrate the method of calculating effective coefficients and to simplify analysis of the general equations of the theory. This case is also of importance for applications [3]. Let there be narrow pores of mean radius r_1 filled with electrolyte and wide pores of mean radius r_2 . The specific surface area S is equal to a product of total number of intersections of 2 types of pores in 1 cm^3 of electrode N , by S_0 , reaction surface per intersection. It can be seen from Fig. 2 that $S_0 = 2\pi r_1 \delta r_1$. The total number of intersections, N is found from probability considerations. The probability of finding a liquid-pore - gas-pore intersection at a given point will be determined by the product of the liquid and gas porosities, $g_l g_g$. This product is also numerically equal to the total volume of intersections of pores of the two types in 1 cm^3 of the electrode. Knowing the mean volume of a single intersection to be $2\pi r_1^2 r_2$, the total number of intersections and the specific reaction surface can be found through:

$$S = s_0 N = 2\pi r_1 \delta r_1 \frac{g_l g_g}{2\pi r_1^2 r_2} = \delta \frac{g_l g_g}{r_2}. \quad (6)$$

It is clear that the effective conductivity will be proportional to the true conductivity of the electrolyte, λ_2 , and the volume of the electrolyte-filled pores, i.e., $\lambda \sim \lambda_2 g_l$.

Exact equations are obtained for the case of arbitrary microstructure by analogous methods; these have the form:

$$S = \delta (\pi n)^2 \int_0^{r^*} r_1^2 f(r_1) \beta(r_1) dr_1 \int_{r^*}^{\infty} r_2 f(r_2) \beta(r_2) dr_2; \quad \lambda = \lambda_2 \pi n \int_0^{r^*} \frac{r^2 f(r) dr}{\beta(r)}. \quad (7)$$

III. Since the critical radius diminishes with an increase in pressure, it is clear from Eq. (7) that the effective conductivity must also diminish as the pressure rises. The specific surface area will pass through a maximum since it is the product of a monotonically increasing function and a monotonically decreasing function. (This conclusion does not agree with the results obtained in [2]). The electrochemical activity, $I_0 \sim \sqrt{\lambda S}$, pressure curve passes through a maximum. The position of this maximum is closely dependent on the parameters characterizing the microstructure of the electrode. Application of Eq. (7) to the case of the electrode with two types of pores leads to

$$I_0 = \sqrt{\frac{\delta}{\beta_1^2}} \sqrt{\frac{g_1^2 g_g}{r_2}}, \quad (8)$$

where β_1 is the mean coefficient of convolution of the narrow pores.

The following conclusions can be drawn from (8):

1) Since $g_g \sim g$ and $g_1 \sim g$, it follows that $I_0 \sim g^{3/2}$, i.e., the electrochemical activity is proportional to the 3/2 power of the porosity.

2) For fixed porosity and mean pore radius, the electrochemical activity will be at a maximum when

$$g_1 = {}^{2/3}g, \quad g_g = {}^{1/3}g.$$

This result differs from that obtained in [2].

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-filled pores. It should be noted that r_2 is also determined by the working gas pressure, p , and that through the relation $r_2 \sim 1/p$. The relation between the maximum electrochemical activity, $I_0^{\max}$, the working pressure, p , the electrode thickness, d , and the mean radius of the gas-filled pores is illustrated in Table 1. The figures of this table have been obtained from the data of [3]. Substitution of experimental values for g_1 , g_g , r_2 , and I_0 into Eq. (8) gives an evaluation of the coefficient $\sqrt{\delta/\beta_1^2}$, which proves to be equal to 2.5. It was also assumed that $\varphi_0 = 180$ mV; $\lambda_0 = 0.67$ (ohm⁻¹ · cm⁻¹); $j_0 = 10^{-5}$ amp/cm²; $t = 95^\circ$; $2\sigma \cos \theta = 600$ μ mm Hg; $g = 1$.

An exact calculation of effective coefficients would require a knowledge of the functions $f = f(r)$ and $\beta = \beta(r)$. The results obtained in [3] by mercury extrusion permit a determination of the product $f(r)\beta(r)$, but not the distribution function $f(r)$ itself. An experimental determination of the pressure dependence, $\lambda(p)$, of the conductivity of the porous electrode would make it possible to obtain the value of $f(r)/\beta(r)$. By combining the product $f(r)\beta(r)$ with the quotient $f(r)/\beta(r)$ it would be possible to obtain both the pore radius distribution and the coefficient of convolution.

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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.
