

# Hydrophobized Oxygen Cathode of a Fuel Cell with a Liquid Electrolyte: Calculating Overall Currents and Thicknesses

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**Abstract**—The mechanism governing operation of hydrophobized cathodes is discussed. A model is proposed for the active-layer structure. The model consists of equidimensional hydrophobic (agglomerates of polytetrafluoroethylene particles) and hydrophilic (agglomerates of carbon black particles with the catalyst on them) grains. The percolation characteristics of the model are calculated: the presence of a gas cluster and an ionic cluster is established, the specific area of contact between these clusters is determined, the magnitude of ionic conductivity is assayed, and so forth. The “model of cylindrical gas pores” is selected for calculating the overall current. Formulas for the bulk current density are determined. The overall characteristics of a cathode with a platinum catalyst on a carbonaceous carrier (on carbon black) in 7 M KOH at a temperature of 60°C are calculated with allowance made for the fact that the Tafel plots for the process of reduction of oxygen on platinum have two segments with different slopes.

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## MECHANISM GOVERNING OPERATION OF HYDROPHOBIZED CATHODES

In the 1960s to 1970s there was established similarity and difference between hydrophobized electrodes and electrodes functioning in the presence of a pressure drop in fuel cells [1]. The mechanism of action of the latter electrodes may be characterized with the aid of the so-called “biporous model” [2]. According to the biporous model, wide gas-filled and small electrolyte-filled pores are present in such an electrode. The gas reactant first penetrates into the electrode through gas pores and then diffuses into the solution of an electrolyte that fills small pores. It is precisely on the walls of these pores that the electrochemical process goes on. Gas diffusion coefficients in a liquid are a few orders of magnitude as small as those in a gas phase. Correspondingly, to a first approximation we can assume that no restrictions on the gas transport are present in gas pores.

Hydrophobized electrodes are usually pressed out of a mixture of a catalyst and a hydrophobizing agent, polytetrafluoroethylene (PTFE). In the hydrophobized electrodes, as in the electrodes with a pressure drop, one also should take into account only two processes limiting generation of the current, specifically, the gas diffusion into layers of the catalyst wetted by electro-

lyte and ohmic losses caused by the current passage. The difference between the two types of electrodes that requires theoretical interpretation consists of the following. Firstly, hydrophobized systems are capable of generating current even at a zero pressure drop. Secondly, the currents that are obtained on an electrode with a hydrophobizing agent (a few amperes per cm<sup>2</sup>) are an order of magnitude as large and the thicknesses of the active layer (a few hundreds of micrometers) are an order of magnitude as small as those in electrodes hydrophilic. Thirdly, the mechanism of transport of the gas reactant in electrodes with a hydrophobizing agent is far from being obvious.

Answers to these questions had been obtained in [3]. The presence of pores with hydrophilically hydrophobic walls in an electrode is incapable of explaining the fact that hydrophobized electrodes are capable of functioning even at a zero pressure drop. It was shown that the determining role in the gas supply into an electrode is played by small, purely hydrophobic, pores that are present in agglomerates (in porous grains) of particles of the hydrophobizing agent. In fact, the role of gas pores in a hydrophobized electrode is played by a network of chains of porous hydrophobic grains connected with one another.

However, the mechanism of action of hydrophobized electrodes had not been figured out to satisfaction even in [3]. The point is that the structure and charac-

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teristics of hydrophobized electrodes to a considerable extent depend on the mass content of the hydrophobizing agent  $c_{\text{PTFE}}$  in the active layer of the electrode. It is obvious that the dependence of the electrode's electrochemical activity  $I$  on this parameter must have a maximum, because at  $c_{\text{PTFE}} = 0$  the electrode contains no gas reactant and at  $c_{\text{PTFE}} = 1$ , no electrolyte. That is why the major problem of theoretical calculations consists of obtaining the dependence of electrochemical activity on the concentration of the hydrophobizing agent and establishing the value of this concentration at which conditions for the current generation are optimal.

However, there arise difficulties that do not allow us to realize the said calculations: it is not obvious which model would allow us to calculate overall characteristics of an electrode. Strictly speaking, the notion about gas pores as chains comprising grains of the hydrophobizing agent ("model of cylindrical gas pores" [4, 5]) and about that there is an electrolyte-wetted catalyst outside these pores is valid only in the region of small values of the concentration of the hydrophobizing agent. Such a concentration happens to be insufficient to explain processes that go on at optimum and larger concentrations of the hydrophobizing agent. Calculation of the  $I, c_{\text{PTFE}}$  curves cannot be realized with the aid of the "agglomerate model" proposed in [6], either. The agglomerate model is obviously applicable only in the region of high concentrations of the hydrophobizing agent. Thus, the region of concentrations most interesting for practice, where electrochemical activity reaches a maximum, even now does not have an adequate theoretical description.

The grave shortcoming of former theoretical investigations consists of that, in these, values of many parameters entering equations and formulas were taken from experiments. But a full-fledged theoretical work must be constructed without any substantial dependence on the data of experiments. And only thereafter one should conduct calculation of overall characteristics of electrodes and compare theoretical and experimental data. Moving along this path it is possible to reach, in the long run, true insight into the mechanism of operation of a porous electrode. It is precisely this approach that was adopted in this particular investigation.

#### MODEL FOR THE ACTIVE LAYER OF A CATHODE

We will examine properties of a model for the active layer of an electrode that has dimensions 100 by 100 by 100 conditional units [7]. The model contains two sorts of porous grains—cubes of identical dimensions, with the length of their ribs being equal to  $d$ .

**Hydrophobic grains** (agglomerates of polytetrafluoroethylene particles). Their pores are free of moisture—gas arrives in the active layer via these pores. The fraction of volume filled by hydrophobic grains is equal

to  $g$ . The latter is the principal parameter of the model (in fact, this parameter is analogous to concentration  $c_{\text{PTFE}}$ ). At  $g = 0$  the electrode contains no hydrophobizing agent and at  $g = 1$  the electrode contains no catalyst. In the former case, the electrochemical activity is vanishingly small and in the latter case, it vanishes altogether.

A considerable current may emerge in an electrode only upon reaching a percolation threshold, i.e. at  $g \geq g_{\text{cr}}$  [8]. That is the case where a gas cluster forms in the electrode, which is an agglomerate of hydrophobic grains connected with one another that is capable of ensuring the supply of gas to the entire macroscopic (as compared with microscopic dimensions of grains) thickness of the electrode. For a cubic lattice of points under investigation in this work,  $g_{\text{cr}}$  is a root of the characteristic equation [9]

$$4g^3 + 3g - 1 = 0. \quad (1)$$

Its only real root is

$$g = g_{\text{cr}} = [(1 + 2^{1/2})^{1/3} + (1 - 2^{1/2})^{1/3}]/2 = 0.298. \quad (2)$$

Later on we will also be interested in the fraction of hydrophobic grains  $g^*$  entering a gas cluster and the fraction of hydrophobic grains not entering a gas cluster,  $g - g^*$ .

**Hydrophilic grains** (agglomerates of particles of carbon black with particles of the catalyst on them). These can be either filled or not filled by a solution of an electrolyte. The role of hydrophilic grains is to realize the supply of ions (to guarantee this, an ionic cluster must form in the electrode) and electrons (electronic cluster) into the generation zone. It is obvious that ionic and electronic clusters are identical. Consequently, in what follows we will speak solely of an ionic cluster. The fraction of hydrophilic grains will be denoted by the symbol  $g_s$ . An ionic cluster forms at  $g_s \geq 0.298$ . Later on we will also be interested in the fraction of hydrophilic grains entering an ionic cluster  $g_s^*$  and the fraction of hydrophilic grains not entering an ionic cluster  $g_s - g_s^*$ .

Voids in the active layer, pores with hydrophilically hydrophobic walls are irrelevant for the operation of a hydrophobized electrode. They rob the functionally significant elements: grains of polytetrafluoroethylene and catalyst of volume. One must consider electrodes without voids as optimal. That is why the entire space in the model electrode under investigation in this work is filled solely by hydrophobic and hydrophilic grains, i.e.

$$g + g_s = 1. \quad (3)$$

For the working values of parameter  $g$  one must take values in the limit 0.298–0.702. At  $g < 0.298$  no gas cluster is present in the electrode and at  $g > 0.702$  no ionic cluster may form in the electrode. If parameter  $g$  is fixed, the value of parameter  $g_s$  is defined by formula (3).

**Table 1.** Basic quantities that characterize the distribution of gas and electrolyte in the active layer of a hydrophobized electrode

$g$	$g^*$	$g - g^*$	$g_s$	$g_s^*$	$g_s - g_s^*$	$\lambda$
0.298	0.000	0.298	0.702	–	–	0.702
0.320	0.109	0.212	0.680	0.679	0.0009	0.762
0.330	0.175	0.155	0.670	0.669	0.0011	0.810
0.358	0.255	0.103	0.642	0.639	0.0025	0.858
0.406	0.344	0.063	0.594	0.589	0.0050	0.897
0.456	0.430	0.027	0.544	0.534	0.0096	0.937
0.556	0.549	0.007	0.444	0.406	0.0380	0.899
0.606	0.6011	0.005	0.394	0.321	0.0734	0.804
0.656	0.653	0.003	0.345	0.174	0.1709	0.500
0.702	–	–	0.298	0.000	0.2980	0.000

The hydrophilic grains entering the composition of an ionic cluster, which are wetted by a solution of an alkali (the electrochemical process proceeds in them), are “diluted” by hydrophobic grains not entering the composition of the ionic cluster (they are electrolyte-free). Consequently, we must introduce parameter  $\lambda$ ,

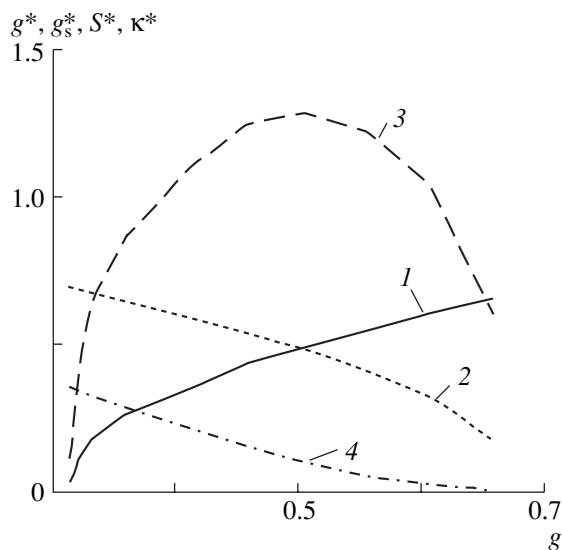
which is the fraction of the volume of the electrode that is located outside a gas cluster where the electrochemical process may really proceed. It is obvious that

$$\lambda = g_s^*/(1 - g^*). \quad (4)$$

#### STRUCTURAL CHARACTERISTICS OF A CATHODE

When performing investigation of characteristics pertaining to the active layer of an electrode of any type after a discussion of distinguishing features characterizing a proposed computer model it is necessary to conduct percolation calculations (solve the problem of connectedness between elements of one type or another [8]) and calculate, on the basis of such calculations, values of effective parameters (coefficients of gas diffusion, ionic conductivity, and so on). This would allow one to subsequently embark on a calculation of the overall current of an electrode and its other characteristics. The results of a percolation calculation for the model hydrophobized electrode under investigation in this work are presented in Table 1. Also presented in Fig. 1 are dependences of parameters  $g^*$  (curve 1) and  $g_s^*$  (curve 2) on the bulk concentration of hydrophobic grains  $g$ .

The data we presented in Table 1 indicate that the number of hydrophobic grains that make up a gas cluster (parameter  $g^*$ ) in the vicinity of the percolation threshold with respect to gas (at  $g = 0.298$ ) substantially differs from the overall number of hydrophobic grains  $g$ . However this difference levels out with increasing parameter  $g$  and disappears altogether at  $g \geq 0.5$ . The number of hydrophilic grains that make up an ionic



**Fig. 1.** Dependence of structural characteristics of a model for the active layer of a hydrophobized electrode on the bulk concentration of grains of the hydrophobizing agent: (1) concentration of hydrophobic grains that enter a gas cluster ( $g^*$ ), (2) concentration of hydrophilic grains that enter an ionic cluster ( $g_s^*$ ), (3) reduced specific surface area of contact of a gas cluster with an ionic cluster ( $S^*$ ), and (4) reduced specific effective ionic conductance of electrode ( $\kappa^*$ ).

cluster  $g_s^*$  behaves itself in a diametrically opposite fashion. Prior to  $g \sim 0.5$  practically all hydrophilic grains enter the composition of an ionic cluster, and the difference  $g_s - g_s^*$  is small. At  $g > 0.5$ , however, quantities  $g_s$  and  $g_s^*$  start moving away from one another. This leads to that the dependence of parameter  $\lambda$  on parameter  $g$  has a maximum at  $g \sim 0.5$ .

The gas cluster that forms in an electrode is distributed over volume in a complicated manner. In the region of concentrations of hydrophobic grains in the vicinity of the percolation threshold, this nontrivial picture may be replaced by a system of gas pores regularly deployed in the active layer of the electrode, which is equivalent to this picture. We will presume that these pores have a square cross-section with the area  $d^2$ . From symmetry considerations we will demand that these gas pores should be three mutually perpendicular collections of identical straight rods that intersect one another. These rods are arranged in space in such a fashion that the centers of exits out of gas pores form a perfect square lattice on a face of a model for the active layer of an electrode. We will denote the distance between neighboring gas pores as  $2L$ . Should  $N$  be the number of gas pores at  $1 \text{ cm}^2$  of the external surface of a model for the active layer of an electrode, then one could show that

$$g^* = 3d^2N - 2d^3N^{3/2}. \quad (5)$$

By definition,

$$N = (1/4)L^2. \quad (6)$$

Because of this, instead of (5) ultimately we have the relationship

$$g^* = (3/4)(d/L)^2 - (1/4)(d/L)^3. \quad (7)$$

The condition (7) makes it possible to establish link between  $L/d$  and  $g^*$ . The data presented in Table 2 and Fig. 2 demonstrate that the distance between gas pores increases upon nearing the percolation threshold with respect to gas (here  $g^*$  tends to zero). Let us note that at  $g^* = 0.5$  (when every other grain of the hydrophobizing agent in a model active layer of a cathode is accessible to gas)  $L = d$ .

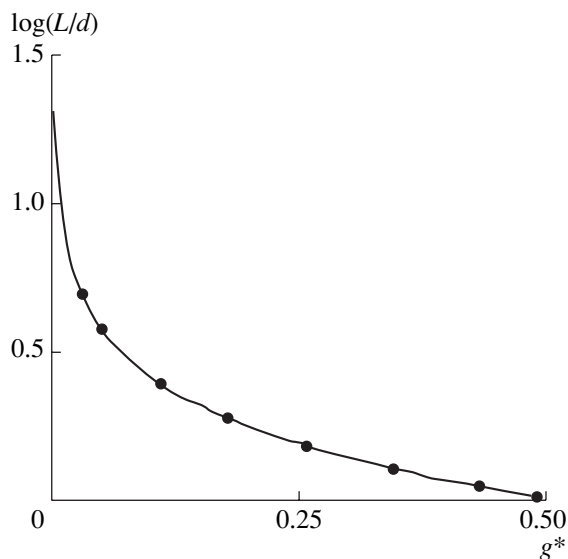
Later on we will need the reduced (divided by the true conductance of electrolyte) effective ionic conductivity  $\kappa^*$  and the reduced specific surface area of contact between an ionic cluster and a gas cluster  $S^*$ . The results of calculations of values of  $\kappa^*$  and  $S^*$  are presented in Table 3 and Fig. 1, together with their dependence on the bulk concentration of hydrophobic grains  $g$ . The surface  $S^*$  has an extremum at  $g = 0.5$  (Fig. 1, curve 3) and the conductivity  $\kappa^*$  monotonically ebbs with increasing parameter  $g$  (Fig. 1, curve 4). Let us note that the true specific surface area of contact between an ionic cluster and a gas cluster  $S$  in a unit volume is defined by the formula

$$S = S^*/d. \quad (8)$$

**Table 2.** Dependence of the distance between neighboring gas pores on the bulk concentration of hydrophobic grains that enter the composition of a gas cluster

$g^*$	$L/d$
0.0000	$\infty$
0.0018	20.4
0.0032	15.2
0.0056	11.4
0.0280	5.0
0.0980	2.6
0.2580	1.5
0.5000	1.0

According to the data we presented in Table 3 and Fig. 1, the conditions for the generation of current are optimum at  $g = 0.5$ , here the surface area of contact between an ionic cluster and a gas cluster  $S^*$  is maximum. It could seem that a dependence of the overall current on parameter  $g$  would also have a maximum at  $g = 0.5$ . However, conductivity  $\kappa^*$  ebbs with growing  $g$ . Consequently, optimum conditions should correspond to a compromise between the growing surface area of contact between hydrophobic and hydrophilic grains



**Fig. 2.** Dependence of the reduced distance between neighboring gas pores in the active layer of a hydrophobized electrode on the bulk concentration of hydrophobic grains that enter a gas cluster.

**Table 3.** Dependence of the reduced effective specific ionic conductance and the reduced specific surface area of contact of ionic and gas clusters in the active layer of a cathode on the bulk concentration of hydrophobic grains

$g$	$\kappa^*$	$S^*$
0.298	–	0.000
0.312	0.352	0.103
0.315	0.347	0.175
0.320	0.339	0.395
0.330	0.323	0.631
0.358	0.287	0.854
0.406	0.214	1.082
0.456	0.152	1.244
0.504	0.095	1.279
0.606	0.023	1.024
0.656	0.005	0.592
0.702	0.000	0.000

and the tendency to diminish  $\kappa^*$ . In this particular investigation we will conduct calculation of overall characteristics only in the region of concentrations of the hydrophobizing agent  $0.3 \leq g \leq 0.5$ : only in this region, strictly speaking, one may use the “model of cylindrical gas pores.”

#### FORMULAS FOR BULK CURRENT DENSITIES

The data we presented in Table 2 and Fig. 2 show that the distance between neighboring gas pores  $L/d$  in the region of concentrations of the hydrophobizing agent  $0.298 \leq g \leq 0.5$  rapidly shrinks from infinity to unity, whereas the density of gas pores  $N$  at first very rapidly grows and then slows down. The notion about a diffusion regime outside gas pores, which for the sake of simplicity are now approximated by cylinders with diameter  $d$  (“model of cylindrical gas pores” [4, 5]) is pertinent in this region of concentrations of the hydrophobizing agent.

Equations and formulas for calculation of currents figure the value of the effective bulk current density  $i$  ( $A\ cm^{-3}$ ), which is the characteristic effective bulk current density  $i^*$  times a factor that depends on the magnitude of the electrode potential. It is on calculation of values of  $i$  and  $i^*$  that we are now going to embark.

It is known that a Tafel plot for an oxygen electrode with platinum has two segments with slopes  $b_m$  and

characteristic bulk current densities  $j_{0m}$ , where  $m = 1, 2$ . At this juncture it is necessary to underline a fundamental difference between bulk current densities denoted here as  $j$  and  $i$ . The  $j$  quantity characterizes grains of a carbonaceous carrier with a catalyst on it that are wetted by a solution of an electrolyte (in so doing, the characteristic bulk current density  $j_0 = i_0 S_c$ , where  $i_0$  is an exchange current and  $S_c$  is the specific surface area of the catalyst) and  $i$  characterizes a hydrophobized electrode as a whole. When determining  $i$ , account should be taken of both the “dilution” of the carbonaceous carrier with a catalyst on it by the hydrophobizing agent and the influence exerted on the current generation process by intradiffusion restrictions concerning the gas supply toward the catalyst wetted by electrolyte and all the other distinguishing features of complicated internal structure of the active layer of a hydrophobized cathode.

We will presume that in the region of high potentials (small polarizations), at  $E^{st} \geq E \geq E^*$ , where  $E$  is the electrode potential (all potentials here and in what follows are presented relative to a reversible hydrogen electrode),  $E^{st}$  is a steady-state potential, and  $E^*$  is the potential at the point of inflection in a Tafel plot,

$$j_{0m=1} = j_1, \quad b_{m=1} = b_1, \quad (9)$$

in the potential region  $E \leq E^*$

$$j_{0m=2} = j_2, \quad b_{m=2} = b_2. \quad (10)$$

Let us introduce the reduced electrode polarization

$$\eta = (E^{st} - E)/b_1. \quad (11)$$

Then the density of current generated in grains of a carrier with a catalyst on it at  $E^{st} \geq E \geq E^*$  will assume the form

$$j = j_1[\acute{c} \exp \eta - \exp(-\eta)], \quad (12)$$

where  $\acute{c} = c/c_0$  is the oversaturation of electrolyte with gas and  $c_0$  is the gas solubility. In the potential region  $E \leq E^*$

$$j = j_2[\acute{c} \exp(\alpha\eta) - \exp(-\alpha\eta)], \quad (13)$$

where

$$\alpha = b_1/b_2. \quad (14)$$

Then from the condition of equality of current densities at the point of inflection in a Tafel plot we have

$$j_2 = j_1 \exp\{(E^{st} - E^*)(b_2 - b_1)/b_2 b_1\}. \quad (15)$$

When written in a generalized form, expressions (12) and (13) assume the following form:

$$j = j_m[\acute{c} \exp \tau_m - \exp(-\tau_m)], \quad (16)$$

where the generalized reduced polarization

$$\tau_m = \eta \quad \text{at} \quad m = 1, \quad (17)$$

$$\tau_m = \alpha\eta \quad \text{at} \quad m = 2. \quad (18)$$

And now we are coming to the question of quantitative description of processes that proceed at the interface between the gas-filled grains of the hydrophobizing agent and the hydrophilic grains that are wetted by a solution of an electrolyte. The equation in polar coordinates

$$(1/\rho^*)d\rho^*(d\acute{c}/d\rho^*)/d\rho^* = \acute{c} - \exp(-2\tau_m), \quad (19)$$

describes the gas diffusion into the electrolyte with a subsequent electrochemical discharge that occurs in the vicinity of a cylindrical gas pore. In designations in expression (19) are as follows:  $\rho^* = \rho/L_{d,m}$  is a reduced polar radius and  $L_{d,m}$  is a characteristic diffusion length

$$\begin{aligned} L_{d,m} &= (nFD\nu c_0/j_m\lambda)^{1/2} \exp(-\tau_m/2) \\ &= L_{d,m}^0 \exp(-\tau_m/2), \end{aligned} \quad (20)$$

where  $n$  is the number of electrons that take part in an elementary act,  $D$  is the diffusion coefficient for oxygen in a solution of an electrolyte, and  $\nu$  is the porosity of hydrophilic grains. Relationship (19) must be complemented with boundary conditions

$$\acute{c}|_{\rho=d/2} = 1 \quad d\acute{c}/d\rho|_{\rho=L} = 0. \quad (21)$$

Upon solving equation (19) with boundary conditions (21) we will obtain the following expression for the density of current  $J_m$  that passes through a unit surface area of a gas pore:

$$\begin{aligned} J_m &= (nFD\nu c_0 j_m \lambda)^{1/2} \exp(\tau_m/2) \\ &\times [1 - \exp(-2\tau_m)]\psi, \end{aligned} \quad (22)$$

where the function

$$\begin{aligned} \psi &= [I_1(L/L_{d,m})K_1(d/2L_{d,m}) \\ &- I_1(d/2L_{d,m})K_1(L/L_{d,m})]/[I_1(L/L_{d,m})K_0(d/2L_{d,m}) \\ &+ I_0(d/2L_{d,m})K_1(L/L_{d,m})], \end{aligned} \quad (23)$$

while  $I_0$ ,  $I_1$ ,  $K_0$ , and  $K_1$  are Besselian functions of a purely imaginary variable.

Lets us now turn our attention to the determination of an expression for the effective bulk current density  $i_m$ . The quantity  $i_m$  in the model of cylindrical gas pores that we adopted is equal to the product of the current generated in a threesome of mutually perpendicular gas pores of length  $2L$ , the quantity  $6\pi dLJ_m$ , and the number of such threesomes in a unit volume of an electrode, the factor  $1/(2L)^3$ . Ultimately, with allowance made for (6) and (22), we have

$$\begin{aligned} i_m &= 3\pi dJ_m N = 3\pi dN(nFD\nu c_0 j_m \lambda)^{1/2} \\ &\times \exp(\tau_m/2)[1 - \exp(-2\tau_m)]\psi = \xi_m \varphi_m(\tau_m), \end{aligned} \quad (24)$$

where the characteristic effective bulk current density of a hydrophobized electrode is described by the relationship

$$i_m^* = \xi_m = 3\pi dN(nFD\nu c_0 j_m \lambda)^{1/2}, \quad (25)$$

**Table 4.** Dependence of the characteristic effective bulk current densities ( $\xi_m$ ), characteristic ohmic lengths ( $L_{\text{ohm},m}$ ), and characteristic ohmic currents ( $I_{\text{ohm},m}$ ) for assorted regions of potentials on the bulk concentration of hydrophobic grains

$g$	$\xi_{m=1}$ , A cm <sup>-3</sup>	$\xi_{m=2}$ , A cm <sup>-3</sup>	$L_{\text{ohm},m=1}$ , cm	$I_{\text{ohm},m=1}$ , A cm <sup>-2</sup>
0.312	0.089	0.232	0.209	0.019
0.315	0.155	0.406	0.157	0.024
0.320	0.383	1.002	0.099	0.038
0.330	0.668	1.747	0.073	0.049
0.358	1.056	2.762	0.054	0.057
0.406	1.539	4.026	0.039	0.059
0.456	2.077	5.434	0.028	0.058
0.499	2.534	6.629	0.021	0.053

and the factor in (24) that depends on the magnitude of potential and specific features of the electrode structure has the form

$$\varphi_m = \exp(\tau_m/2)[1 - \exp(-2\tau_m)]\psi. \quad (26)$$

The results of calculations of the values of  $\xi_m$  are presented in Table 4. Values of the characteristic effective bulk current density  $\xi_m$  at  $g = 0.5$  reach a few amperes per cm<sup>2</sup>. Specifically, in this particular investigation, considered was the cathode of a fuel cell with an alkali electrolyte (7 M KOH) at a temperature of 60°C. The catalyst was platinum that was deployed on a carbonaceous catalyst carrier (carbon black). Let  $E^{\text{st}} = 1.07$  V,  $E^* = 0.97$  V,  $b_1 = 2.6 \times 10^{-2}$  V,  $b_2 = 5.2 \times 10^{-2}$  V,  $n = 4$ ,  $F = 9.6 \times 10^4$  C mol<sup>-1</sup>,  $D = 6 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>,  $\nu = 0.5$ ,  $c_0 = 1.2 \times 10^{-7}$  mol cm<sup>-3</sup>, and electrolyte electroconductivity  $\kappa = 0.42$  S cm<sup>-1</sup>.

We are now passing to the selection of principal parameters of the model under investigation, which are the characteristic bulk current density  $j_1$  (quantity  $j_2$  is defined by relationship (15)) and the dimension of grains  $d$ . A similar system had been investigated experimentally and theoretically in [4, 5]. In the works cited, the specific surface area of the catalyst (platinum) was estimated as  $S = 3.9 \times 10^5$  cm<sup>-1</sup> and the exchange current was evaluated as  $i_0 = 2 \times 10^{-8}$  A cm<sup>-2</sup>. In so doing, no carbonaceous carrier for the catalyst was present. Thus, it had been assumed that the characteristic bulk current density  $j_1 = i_0 S$  was equal to  $7.8 \times 10^{-3}$  A cm<sup>-3</sup>. In our case platinum is diluted by the catalyst carrier and, as a

result, the magnitude of the characteristic bulk current density  $j_1$  must consequently be smaller than this value of  $7.8 \times 10^{-3} \text{ A cm}^{-3}$ . In the subsequent calculations we will presume that  $j_1 = 10^{-3} \text{ A cm}^{-3}$ . Besides, we will also take into account the fact that the experiments in [4, 5] had been conducted at a temperature of  $25^\circ\text{C}$ , which means that we must perform a correction for the temperature of  $60^\circ\text{C}$ . According to [10],

$$i_0 = i_0^{\text{ref}} \exp[8804(1/T_{\text{ref}} - 1/T)], \quad (27)$$

where  $i_0^{\text{ref}}$ , and  $T_{\text{ref}}$  are the initial values of the exchange current and temperature, respectively.

The exchange current in relationship (27) may be replaced by a characteristic bulk current density related to it. Let us now presume that at a temperature of  $25^\circ\text{C}$  in the region of high potentials we will have  $j_1 = 10^{-3} \text{ A cm}^{-3}$ . Then, at a temperature of  $60^\circ\text{C}$  we will have  $j_1 = 2.22 \times 10^{-2} \text{ A cm}^{-3}$ . Thus, elevated temperatures are capable of exerting a considerable influence on the magnitude of the  $j_1$  quantity. The value of  $j_2$  will increase as well. According to formula (15),  $j_2 = 1.53 \times 10^{-1} \text{ A cm}^{-3}$ .

The estimates that had been performed in [11] demonstrated that the average dimensions of grains of polytetrafluoroethylene were on the order of a few micrometers. But let us select for  $d$  the value  $5 \times 10^{-5} \text{ cm}$ . Note that, according to formulas (6) and (25), characteristic bulk current densities  $\xi_m \sim 1/d$ . Consequently, the overall current must also increase with decreasing  $d$ .

#### FORMULAS FOR CALCULATING OVERALL CHARACTERISTICS

Let us present calculating formulas that would allow one to determine characteristics of an electrode in the framework of the above-formulated model for the structure of the active layer of a cathode and the model of cylindrical gas pores.

##### *Region of High Potentials $E^* \leq E \leq E^{\text{st}}$*

In that case the reduced polarization  $\tau_1 = \eta$  and the characteristic bulk current density is equal to  $j_1$ . The distribution of polarization over the thickness of the electrode is described by the equation

$$d^2\eta/dy^2 = \varphi_{m=1}(\eta), \quad (28)$$

where  $y$  is a coordinate, which is perpendicular to the front surface of the active layer and which is counted from it;  $\dot{y} = y/L_{\text{ohm}, m=1}$  is a reduced coordinate; and the characteristic ohmic length is

$$L_{\text{ohm}, m=1} = (b_1 \kappa \kappa^* / \xi_{m=1})^{1/2}. \quad (29)$$

The last equation must be supplemented by the boundary conditions

$$\eta|_{y=0} = \eta_0 = (E^{\text{st}} - E_0)/b_1, \quad d\eta/dy|_{y=\Delta} = 0, \quad (30)$$

where  $E_0$  is the electrode potential and  $\Delta$  is the electrode thickness. The overall current of an electrode  $I_{m=1}$  is defined by the expression

$$I_{m=1}/I_{\text{ohm}, m=1} = 2^{1/2} \left[ \int_{\eta_\Delta}^{\eta_0} \varphi_{m=1}(\eta) d\eta \right]^{1/2}, \quad (31)$$

where the characteristic ohmic current is

$$I_{\text{ohm}, m=1} = (b_1 \kappa \kappa^* \xi_{m=1})^{1/2}. \quad (32)$$

The electrode polarization at the rear side  $\eta_\Delta$  may be determined by integrating equation (28) for a second time

$$\int_{\eta_\Delta}^{\eta_0} d\eta / \left[ \int_{\eta_\Delta}^{\eta} \varphi_{m=1}(x) dx \right]^{1/2} = 2^{1/2} \Delta / L_{\text{ohm}, m=1}. \quad (33)$$

##### *Mixed Region of Potentials $E \leq E^*$*

In this case one can encounter two possibilities.

**Version a:** the potential on the rear side  $E_\Delta < E^*$ . In this case it is obvious that at any point of an active layer one can work with reduced polarization  $\tau_2 = \alpha\eta$  and the characteristic bulk current density  $j_2$ . Consequently, one can introduce additionally the characteristic ohmic length  $L_{\text{ohm}, m=2} = (b_2 \kappa \kappa^* / \xi_{m=2})^{1/2}$  and the characteristic ohmic current  $I_{\text{ohm}, m=2} = (b_2 \kappa \kappa^* \xi_{m=2})^{1/2}$ . However, for performing computer-aided calculations, it is more convenient to use only one characteristic length, specifically, the characteristic ohmic length  $L_{\text{ohm}, m=1}$ , and only one characteristic current, specifically, the characteristic ohmic current  $I_{\text{ohm}, m=1}$  at any values of the electrode potential. Then, in the potential region under investigation, we will have

$$d^2\eta/dy^2 = \gamma \varphi_{m=2}(\alpha\eta), \quad (34)$$

where parameter  $\gamma$  is described by the expression

$$\gamma = \xi_{m=2} / \xi_{m=1} = (j_2 / j_1)^{1/2}, \quad (35)$$

and the boundary conditions for formula (34) are the same as in (30). The reduced overall current is

$$I_{m=2}/I_{\text{ohm}, m=1} = (2\gamma/\alpha)^{1/2} \left[ \int_{\alpha\eta_\Delta}^{\alpha\eta_0} \varphi_{m=2}(\tau) d\tau \right]^{1/2}, \quad (36)$$

and instead of (33) we have

$$\int_{\alpha\eta_\Delta}^{\alpha\eta_0} d\tau / \left[ \int_{\alpha\eta_\Delta}^{\tau} \varphi_{m=2}(\tau) d\tau \right]^{1/2} = (2\alpha\gamma)^{1/2} \Delta / L_{\text{ohm}, m=1}. \quad (37)$$

It is obvious that an electrode with a given thickness  $\Delta$  may fully be described by formulas (34)–(37) provided the reduced polarization at the rear side of the electrode takes on the value  $\eta_\Delta = (E^{\text{st}} - E^*)/b_1 = \eta^*$ , i.e.

at  $E_{\Delta} = E^*$ . Thus, the value of the critical polarization  $\eta_0^*$  (or  $E_0^*$ ) is defined by the expression

$$\int_{\alpha\eta^*}^{\alpha\eta_0^*} d\tau / \left[ \int_{\alpha\eta^*}^{\alpha\eta} \varphi_{m=2}(\tau) d\tau \right]^{1/2} = (2\alpha\gamma)^{1/2} \Delta / L_{\text{ohm}, m=1}. \quad (38)$$

**Version b:** the potential on the rear side is confined in the interval

$$E^* \leq E_{\Delta} \leq E^{\text{st}}. \quad (39)$$

What this means is that the potential on the front side of the electrode  $E_0^*$  must be confined in the interval

$$E^* < E_0 < E_0^* \quad (40)$$

at a given thickness of the electrode  $\Delta$  and the value of  $E_0^*$  that was calculated for this thickness with the aid of formula (38).

If conditions (39) and (40) are fulfilled, the electrode thickness  $\Delta$  must be broken into two parts. One part is the thickness  $\Delta_1$ , which corresponds to coordinates  $0 \leq y \leq \Delta_1$ . The other part is the thickness  $\Delta - \Delta_1$ , which corresponds to coordinates  $\Delta_1 \leq y \leq \Delta$ . It is obvious that the potential at the boundary between these two regions must be equal to the value of  $E^*$ . Then the distribution of polarization over the electrode thickness in the region  $0 \leq y \leq \Delta_1$  is described by equation (34) with boundary conditions

$$\begin{aligned} \eta|_{y=0} &= \eta_0 = (E^{\text{st}} - E_0)/b_1, \\ \eta|_{y=\Delta_1} &= (E^{\text{st}} - E^*)/b_1 = \eta^*. \end{aligned} \quad (41)$$

In the region  $\Delta_1 \leq y \leq \Delta$ , the distribution of polarization over the electrode thickness is described by equation (28) with boundary conditions

$$\eta|_{y=\Delta_1} = \eta^* = (E^{\text{st}} - E^*)/b_1, \quad d\eta/dy|_{y=\Delta} = 0. \quad (42)$$

The value of thickness  $\Delta_1$  and the value of polarization on the rear side of the electrode  $\eta_{\Delta} = \eta|_{y=\Delta}$  is defined by the system of two equations—the equality of current at the boundary between two regions

$$-d\eta/dy|_{y=\Delta_1} = 2^{1/2} \left[ \int_{\eta_{\Delta}}^{\eta^*} \varphi_{m=1}(x) dx \right]^{1/2}, \quad (43)$$

where  $d\eta/dy|_{y=\Delta_1}$  may be determined by solving equation (34), and a condition that is analogous to condition (33), but in which one should replace  $\eta_0$  by  $\eta^*$  and substitute  $\Delta - \Delta_1$  for  $\Delta$

$$\int_{\eta_{\Delta}}^{\eta^*} d\eta / \left[ \int_{\eta_{\Delta}}^{\eta} \varphi_{m=1}(x) dx \right]^{1/2} = 2^{1/2} (\Delta - \Delta_1) / L_{\text{ohm}, m=1}. \quad (44)$$

The only thing that remains to be added is that the current that is generated by in the region of mixed potentials is

$$I = -(I_{\text{ohm}, m=1}) d\eta/dy|_{y=0}, \quad (45)$$

where the quantity  $d\eta/dy|_{y=0}$  may be determined by solving equation (34).

Further on the following should be mentioned. Strictly speaking, currents reach a maximum only at an infinite thickness of the electrode (at  $\Delta = \infty$ ). However, the current  $I$  becomes practically extreme even at relatively moderate values of the electrode thickness  $\Delta$ . Therefore, it makes sense to select, for the effective thickness  $\Delta^*$  of an electrode, the value at which the effective current  $I^*$  reaches 90% of the possible extreme value. Then,

$$I^* = I(\Delta^*) = 0.9I(\Delta = \infty). \quad (46)$$

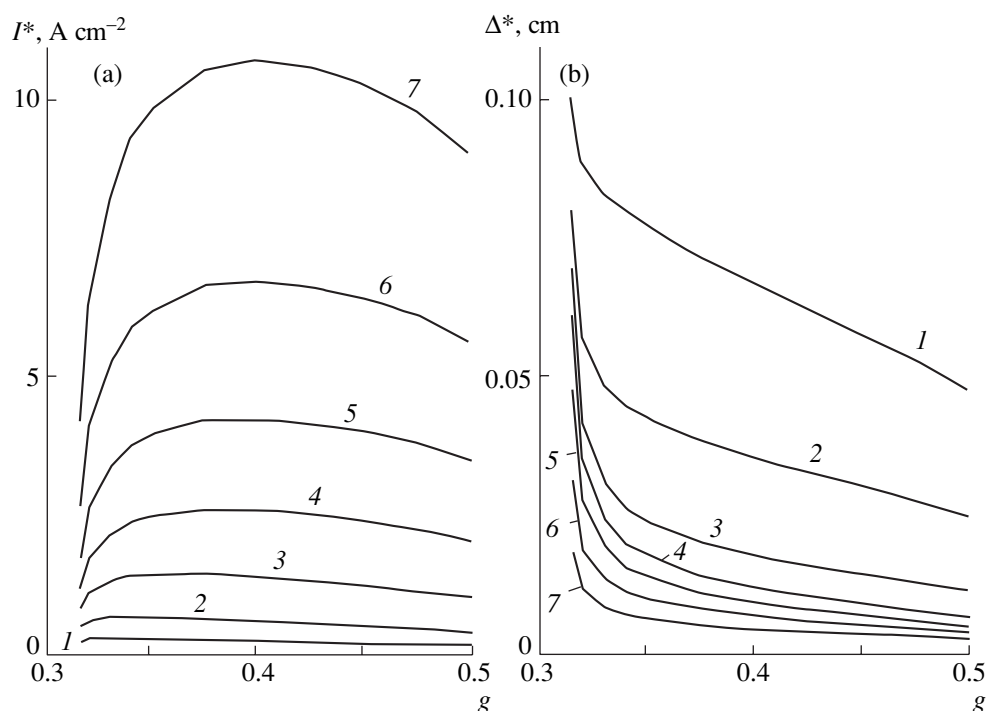
## CONDUCTION OF NUMERICAL CALCULATIONS

At the beginning we will estimate values of the characteristic ohmic length  $L_{\text{ohm}, m=1}$  and the characteristic overall current  $I_{\text{ohm}, m=1}$ . These are presented in Table 4.  $I_{\text{ohm}, m=1}$ ,  $g$  curve reaches a maximum in the interval of values  $0.35 \leq g \leq 0.45$ . At  $g \sim 0.4$ , the overall current  $I_{\text{ohm}, m=1}$  is equal to approximately  $59 \text{ mA cm}^{-2}$ . The dependence of  $L_{\text{ohm}, m=1}$  on  $g$  testifies to a gradual lowering of the effective thickness of the electrode. Characteristic length diminishes from the value equal to 2 mm to  $200 \mu\text{m}$ , which is connected in the first place with the growth of ohmic restrictions.

The results of calculations of optimum values of currents  $I^*$  and thicknesses  $\Delta^*$  for a number of values of the cathode potential  $E_0$  (from 0.9 to 0.3 V) and at potentials on the rear side of the active layer  $E_{\Delta}^*$  are presented in Figs. 3–5. At inconsiderable deviations of potential  $E_0$  from the steady-state value  $E^{\text{st}} = 1.07 \text{ V}$  (Fig. 3a; curves 1, 2), with increasing bulk concentration of the hydrophobizing agent there is observed a monotonic lowering of activity of the electrode. This is connected with that, with the exception of values of parameter  $g$  close to the percolation threshold ( $g_{\text{cr}} = 0.298$ ), the condition  $L \leq L_{d, m=1}$  is fulfilled. Half the distance between neighboring gas pores is smaller than the characteristic diffusion length (formula (20)). That is why in the electrode there takes place a kinetic regime of generation of a current and the overall current lowers down because of an increase of ohmic restrictions with the growth of  $g$ .

A different picture is observed at considerable deviations of potential  $E_0$  from the steady-state value. Now,  $L > L_{d, m=1}$  (Table 5). What this means is that the process of generation of a current is localized near the surface of a gas pore. That is why current  $I$  is proportional to the number of gas pores  $N$  (formula (6)) and rapidly





**Fig. 3.** Dependences of (a) effective overall current and (b) effective thickness of a hydrophobized cathode on the bulk concentration of grains of the hydrophobizing agent at the potential  $E_0$  equal to (1) 0.9, (2) 0.8, (3) 0.7, (4) 0.6, (5) 0.5, (6) 0.4, and (7) 0.3 V;  $j_1 = 2.23 \times 10^{-2} \text{ A cm}^{-3}$ ,  $j_2 = 1.53 \times 10^{-1} \text{ A cm}^{-3}$ ,  $d = 5 \times 10^{-5} \text{ cm}$ .

grows with increasing fraction of the hydrophobizing agent in the electrode  $g$ . However, the growth of the number of gas pores gradually slows down and a decrease in the effective conductance of electrolyte begins to play some role with increasing  $g$ . As a result, a maximum appears in the  $I^*$ ,  $g$  curves (Fig. 3a). This maximum shifts to the right with decreasing  $E_0$ . Though the magnitude of the effective overall current is considerable ( $\sim 10 \text{ A cm}^{-2}$  at  $E_0 = 0.3 \text{ V}$ ), the current

grows with decreasing potential relatively slowly, because, according to theoretical estimates,

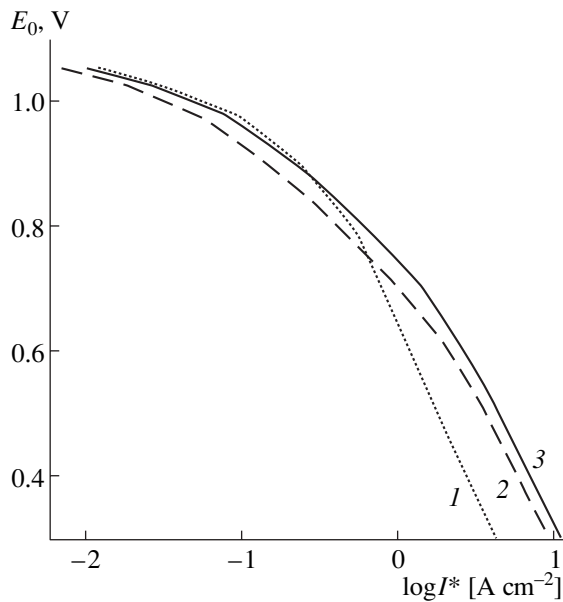
$$I^* \sim (\eta_0)^{1/4} = [(E^{\text{st}} - E_0)/b_1]^{1/4}. \quad (47)$$

Let us note that the overall current grows faster in the kinetic region, here

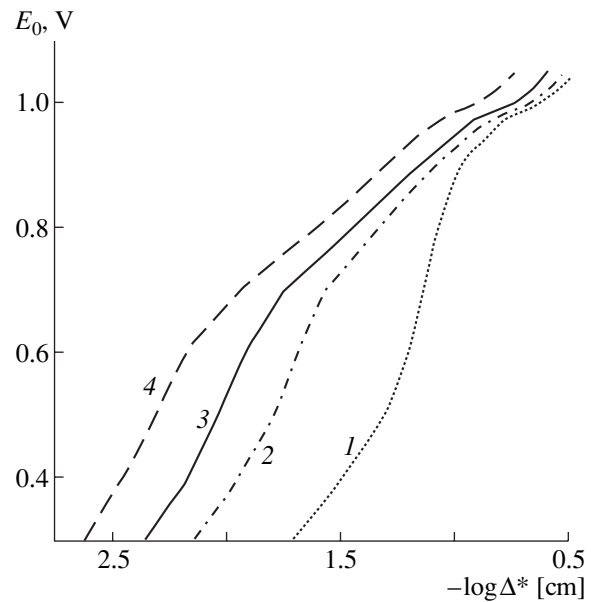
$$I^* \sim (\eta_0)^{1/2} = [(E^{\text{st}} - E_0)/b_1]^{1/2}. \quad (48)$$

**Table 5.** Dependence of characteristic lengths  $L_{d, m=1}$  on the bulk concentrations of the hydrophobizing agent ( $g$ ) and potential of a cathode ( $E_0$ )

$g$	$L \times 10^4, \text{ cm}$	$L_{d, m=1} \times 10^4, \text{ cm at } E_0, \text{ V}$							
		1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3
0.315	1.89	7.64	2.19	0.84	0.32	0.120	0.047	0.018	0.007
0.330	0.94	7.20	2.06	0.79	0.30	0.115	0.044	0.017	0.006
0.350	0.76	6.97	2.00	0.76	0.29	0.110	0.043	0.016	0.006
0.400	0.62	6.73	1.93	0.74	0.28	0.108	0.040	0.016	0.006
0.450	0.55	6.65	1.90	0.73	0.28	0.106	0.040	0.016	0.006
0.499	0.50	6.63	1.90	0.73	0.28	0.106	0.040	0.016	0.006



**Fig. 4.** Current–voltage curves for a hydrophobized cathode at  $g$  equal to (1) 0.315, (2) 0.4, and (3) 0.5;  $j_1 = 2.23 \times 10^{-2} \text{ A cm}^{-3}$ ,  $j_2 = 1.53 \times 10^{-1} \text{ A cm}^{-3}$ ,  $d = 5 \times 10^{-5} \text{ cm}$ .



**Fig. 5.** Dependence of the effective thickness of a hydrophobized cathode on potential at  $g$  equal to (1) 0.315, (2) 0.34, (3) 0.4, and (4) 0.5;  $j_1 = 2.23 \times 10^{-2} \text{ A cm}^{-3}$ ,  $j_2 = 1.53 \times 10^{-1} \text{ A cm}^{-3}$ ,  $d = 5 \times 10^{-5} \text{ cm}$ .

Let us add that

$$I^* \sim (1/d)^{1/2}. \quad (49)$$

That is why the overall current lowers with increasing dimensions of grains  $d$  as well.

Let us note that the larger values of currents ( $I^* \sim 10 \text{ A cm}^{-2}$  at  $E_0 = 0.3 \text{ V}$ ) are caused by two circumstances. In the first place, in the calculations there was selected the practically minimum possible size of grains, specifically,  $d = 0.5 \text{ }\mu\text{m}$ . In the second place, there was not conducted account for outer-diffusion restrictions that emerge when gas is supplied out of the gas chamber towards the active layer. Should one take into consideration the said circumstances, values of currents would substantially diminish.

The obtained results testify that the practically important region of bulk concentrations of the hydrophobizing agent is the region  $0.298 \leq g \leq 0.5$ , because the overall current reaches a maximum value precisely in this region. Moreover, once the electrode polarization is increased, the effective thickness of the electrode lowers from a few millimeters to a few tens of micrometers (Fig. 3b).

Current–voltage curves for three values of the concentration of the hydrophobizing agent ( $g = 0.315, 0.4, 0.5$ ) are presented in Fig. 4. The character, which is exhibited by a dependence of the effective thickness of the electrode on potential for four values of the concentration of the hydrophobizing agent ( $g = 0.315, 0.34, 0.4, 0.5$ ), is demonstrated in Fig. 5.

## CONCLUSIONS

It was demonstrated in the foregoing how one may conduct calculations of overall characteristics intrinsic to a hydrophobized cathode with a liquid electrolyte. In so doing, as had been done in [1, 4, 5], used was the “model of cylindrical gas pores.” And this means that a gas percolation cluster, which really exists in a complicatedly distributed fashion in the active layer of the cathode, transformed into an equivalent (by the volume of gas-filled hydrophobic grains) system of channels of gas supply—system of regularly distributed cylindrical gas pores.

However, there is also a profound fundamental difference between works [4, 5] and this particular investigation. In works [4, 5], calculation formulas contained an enormous number of parameters that should have been obtained experimentally—gas and liquid porosity, specific surface area of the catalyst, radius of gas pores, and so on and so forth. As a result, the mechanism governing the current generation process had not been made ultimately clear. The theory for the current generation process in hydrophobized electrodes that was propounded in the foregoing does not demand for performing a large volume of preliminary experimental works.

Theory now leans only against base quantities: structural (dimensions of primary particles and their agglomerates), coefficients of transfer—diffusion, electroconduction (these data may be found in reference books), external parameters (temperature of medium, pressure of gas, thicknesses of active layer and electrolyte membrane), and finally against parame-

ters that characterize the electrochemical process of reduction of oxygen on the catalyst.

An important distinguishing feature of new approach consists also of that, for calculating overall characteristics of a cathode, used are computer models for the structure of the active layer of the cathode. And for performing calculations we enlist the services of assorted computer programs developed by us for the purpose, which give us a chance to solve complicated percolation and fractal problems that emerge in the course of theoretical description of operation of a hydrophobized electrode.

As an outcome, all this not only gives one a chance to have a clear-cut notion concerning the mechanism governing generation of current in a hydrophobized electrode but also to conduct prognostications and optimization of its working characteristics.

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