

Alkaline Fuel Cells. Calculating and Comparing Overall Currents of Hydrophobized Cathodes with Thin Regular-Structure and Thick Stochastic-Structure Active Layers

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Abstract—A concept of active hydrophobized active layers with regular structure is introduced. In these layers, a hydrophobizer takes part in the development of gas pores representing a set of straight identical rods (cylinders) uniformly distributed over the active layer and extended in a direction perpendicular to the cathode surface. An advantage of cathodes with a thin regular-structure active layer is the reproducibility of their characteristics and a low content of platinum catalyst (up to tenth and even hundredth fractions of mg/cm²). A comparison of current characteristics of thin (with the thickness of several tens of μm) active layers with a regular structure and thick (with the thickness of several hundreds of μm) with the stochastic distribution of the hydrophobizer (with randomly distributed polytetrafluoroethylene). For a fuel cell with an alkaline electrolyte (7 M KOH at 60°C), calculations show that at potentials below 0.5 V (RHE), the cathodes with thin regular-structure active layers demonstrate higher overall currents as compared with cathodes covered with thick active layers with a stochastic structure. However, the opposite trend is observed at potentials above 0.5 V. To increase the current in cathodes with thin regular-structure active layers, it is possible to, first, increase the active layer thickness and, second, decrease the size of hydrophobizer grains in them.

Keywords: alkaline fuel cell, hydrophobized cathodes, thin active layers with regular structure, thick active layers with stochastic structure, computer simulation

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INTRODUCTION

The first wave of interest in the hydrogen–oxygen (air) fuel cells with hydrophobized electrodes dates back to the 70s of the past century. Then, the key problems in the theory of such systems included the mechanism of gas delivery to the electrode active mass and the explanation of the fact that hydrophobized electrodes can work without pressure drop. The literature of those years contains descriptions of several types of hydrophobized electrodes with different structure, where catalysts represented a fine-grain platinum powder as such (platinum black) or were deposited on inert carriers (asbestos, carbon) [1]. Polytetrafluoroethylene (PTFE) or polyethylene served as hydrophobizers and simultaneously as binding agents.

For hydrophobized electrodes, the largest body of information can be retrieved from I vs. c_{PTFE} curves, where c_{PTFE} is the weight concentration of the hydrophobizer (polytetrafluoroethylene) in the active layer of a porous electrode. Such I vs. c_{PTFE} curves demonstrate a current peak, which can easily be explained. At $c_{\text{PTFE}} = 0$ (pure catalyst, gas virtually fails to penetrate inside

the porous electrode) and at $c_{\text{PTFE}} = 1$ (pure hydrophobizer, catalyst is absent), the overall current is obviously equal to zero. Hence, in the intermediate range, where all factors necessary for sustaining the electrochemical process operate simultaneously, the current I should reach an extremum.

To explain the experimental data obtained in studying the hydrophobized electrode (data on measuring liquid and gas porosity, recording I vs. c_{PTFE} curves for several values of electrode overpotential, etc. [2, 3]), two competitive theoretical models were proposed.

In [4], it was proposed to explain the structure of hydrophobized electrodes as follows. First, a mental picture of the mutual arrangement of agglomerates of PTFE particles and agglomerates of catalyst particles was drawn. Then, catalyst agglomerates were approximated as cylinders (later, cylindrical agglomerates were changed for spherical) of the average radius R and the height H (actually coinciding with the active layer thickness). The gas was flowered along the outer surface of cylinders, while the electrochemical reaction occurred on their inner surface.

This model, which was called the “agglomerate model”, posed the problems of the theoretical (or

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experimental) determination of the cylinder diameter, the surface separating the catalyst agglomerates from the gas-filled PTFE agglomerates, the effective coefficient of ionic conductivity, etc. These problems were solved neither in [4] nor in the later theoretical and experimental studies carried out in the framework of the “agglomerate mode” (the latest model included a thin moisture film that separated the electrolyte-soaked agglomerates from the gas phase).

A serious drawback of the “agglomerate model” is that the latter does not allow one to interpret the I vs. c_{PTFE} dependences. It remains totally unclear in which c_{PTFE} concentration range this model can be used. Most probably, the Giner–Hunter model [4] is fulfilled only in the right descending segment of I vs. c_{PTFE} curves when the active electrode mass contains a large amount of PTFE and a small amount of catalyst, where an adequate gas supply is provided but the currents should be low. This model leaves open the question on the gas-delivery channel in hydrophobized electrodes, which is the central problem in the general theory of porous electrodes with a gaseous reactant.

The second approach to the theory of hydrophobized electrodes was the “model of cylindrical gas pores” proposed in [5]. This model made it possible to plot I vs. c_{PTFE} dependences. Later, it was shown that “gas pores” represent chains of PTFE grain in contact with one another [6]. The grains are porous and contain pores with hydrophobic walls; the pores are not filled with the electrolyte and serve as the natural channels for the gas delivery to the active layer. Such a channel is independent of the pressure drop. These concepts were later successfully used in describing the mechanism of operation of cathodes based on platinum black and PTFE for a fuel cell with alkaline electrolyte and also in calculating their overall characteristics [7].

However, neither the “agglomerate model” nor the “model of cylindrical gas pores” can be considered as the complete theoretical models intended to describe the mechanism of operation of hydrophobized electrodes. A fundamental shortcoming of theoretical approaches proposed in [4] and [5] is the fact that many parameters that enter into equations and formulas were taken from experiments. On the other hand, a complete theoretical study should not rely on experimental data. In this case only, after calculating the overall characteristics of electrodes, such a theory can be compared with experiment.

Such a complete theory of hydrophobized electrode was recently put forward in [8]. The latter study considered a statistical model of the electrode active layer, a model of equidimensional hydrophobic (PTFE) and hydrophilic (carrier particles with catalyst) grains, i.e., a “model of equidimensional grains”. The proposed [8] theory allowed one to calculate the electrode characteristics without using experimental data. This made it possible to gain insight into the mechanism of opera-

tion of a porous hydrophobized electrode and optimize its characteristics.

In this study, developing further the approaches proposed in [8] for electrodes with a stochastic active layer (we called such active layers “thick”), we extend the similar computer simulation procedures to the case of “thin” active layers but with a regular structure. The calculations and comparison of overall characteristics of “thick” and “thin” active layers will be carried out by the example of a cathode of a fuel cell with an alkaline electrolyte.

THICK AND THIN ACTIVE LAYERS OF HYDROPHOBIZED CATHODES

The formal difference between thick and thin active layers lies in the fact that their thickness reaches several hundreds of μm for the former and several tens of μm for the latter. As in [8], we consider a model of a cathodic active layer with the dimensions of $N \times N \times N$ arbitrary units. Assume that the layer contains two kinds of grains-cubes of the similar size and the edge length d .

Hydrophobic grains (agglomerates of PTFE particles). In these grains, pores are free of moisture so that gas can be transported via them to the active layer. An active layer volume fraction filled with hydrophobic grains is designated as g . This is the main parameter of this model.

Hydrophilic grains (carbon black agglomerates covered with catalyst particles). They are also porous and for the most part filled with the electrolyte solution. The role of hydrophilic grains is to provide the delivery of ions and electrons to the current generation zone.

Next, assume that the active layer lacks voids, and the volume fraction of voids $g_0 = 0$. This assumption seems quite reasonable because actually the hydrophobizer and carrier grains distributed over the size so that we can assume the presence of a sufficiently dense packing of hydrophobic and hydrophilic grains in the active layer. Therefore, we assume that the whole space in the studied model electrode is filled by exclusively hydrophobic and hydrophilic grains, i.e.,

$$g + g_s = 1, \quad (1)$$

where g_s is the active layer volume fraction accounted for by hydrophilic grains.

In our case, it is important to stress the qualitative difference between the gas-filled thick ($N \sim$ several hundred) and thin ($N \sim$ several tens) active layers. The proper operation of an active layer requires the development of channels to deliver gas, ions, and electrons throughout its thickness. Generation of a non-zero overall current in the active layer requires that a gas cluster of a microscopic size, i.e., an agglomerate of hydrophobic grains bound with one another and with the active layer surfaces, was developed in the layer. If the hydrophobic grain concentration is small, the gas

fills only the grains located near the back surface of the active layer (from the side of the gas-diffusion layer (GDL)), and gas clusters account for merely a small part of the active layer. As a result, the current generated in it is low.

According to the percolation theory [9], the situation radically changes with the attainment of a threshold value of the hydrophobic grains fraction, i.e., $g = 0.298$ [10]. Now, a gas cluster, i.e., an agglomerate of gas-filled PTFE grains, extends over the whole thickness of the active layer. Hence, the current generated in the active layer becomes substantial. As was shown in [8], the peak of current generated on cathodes with thick active layers is reached at approximately $g = g^* = 0.4$.

Thus, the general picture of current generation with the varied parameter g in a thick active layer is as follows. Up to approximately $g = 0.3$, the generated current is negligibly low, after which it rapidly increases to reach the maximum (at $g^* = 0.4$) where the carrier with catalyst (hydrophilic grains) occupies only about 60% of the active layer volume. Then, the effective ionic conductivity k^* in the active layer starts to decrease. It rapidly drops and vanishes together with the current at $g \sim 0.7$.

A principally different picture is observed in thin active layers. There, it is not necessary for g to reach any threshold value. Even for a very small g , there exist chains of interbound PTFE grains that connect the face and back surfaces of the active layer. This means that there is always a probability of the development of proper gas pores, the presence of which can considerably intensify the current generation. Yet another advantage of thin active layers is that they contain much lower catalyst concentrations (platinum group elements) as compared with thick active layers. The catalyst content m (g/cm²) in an active layer of a thickness Δ in the absence of voids in the active layer can be assessed as

$$m = (1 - g)(1 - \nu)\rho_s[g_w/(1 - g_w)]\Delta, \quad (2)$$

where ν is the carrier grain porosity, ρ_s is the carbon black density, $\rho_s = 1.8 \text{ g cm}^{-3}$, g_w is the weight content of platinum in the carrier grains. Assuming $g = 0.4$ (here, the generated current has a maximum in thick active layers with a stochastic structure [8]), $\nu = 0.5$, $g_w = 10 \text{ mass } \%$, we obtain that at $\Delta = 10 \text{ }\mu\text{m}$, $m = 0.6 \text{ mg/cm}^2$. As g_w increases, m also rapidly increases. For $g_w = 40 \text{ mass } \%$ and the same values of the rest parameters, $m = 0.36 \text{ mg/cm}^2$ in a thin active layer and $m = 3.6 \text{ mg/cm}^2$ in a thick active layer.

An unavoidable drawback of thin active layers with the stochastic structure is the bad reproducibility of their overall characteristics. Moreover, the distribution of the small amount of PTFE grains in them most likely differs from the optimum in which all grains are involved in gas pores. As a result, the number of gas pores is small, and the generated current is low. At the

same time, in thick active layers with stochastic structure, a gas cluster formed at $g = 0.3$ is well reproducible; hence, the overall characteristics are also reproducible.

Now, we summarize the pluses and minuses of thick and thin active layers with the stochastic structure. Thick layers are characterized by good reproducibility of overall characteristics and the possibility of generating considerable currents (up to several A/cm²). Their drawback is the high content of platinum catalysts in active layers (about several mg/cm² and more) and the fact that the generated current is non-zero only in a limited range $0.3 \leq g \leq 0.7$. Thin active layers are much more economical as regards the platinum catalyst consumption and the PTFE concentration in them can take all values ($0 \leq g \leq 1$). Their drawbacks are the bad reproducibility of overall characteristics and the overall currents much lower than in thick active layers.

The properties of thin hydrophobized active layers can be considerably improved by passing from thin layers with stochastic structure to thin layers with regular structure. Let us calculate the overall characteristics of cathodes with such layers and compare them with the overall characteristics of cathodes with thick stochastic-structure active layers.

PARAMETERS OF CALCULATIONS

Assume that in thin active layers with regular structure, for any values of parameter g , absolutely all grains of hydrophobizer (PTFE) are involved in the development of gas pores. In the model of thin active layers with regular structure under consideration, all gas pores has a square cross-section with the area d^2 and represent a set of similar straight rods normal to the active layer surface (Fig. 1). These rods are spatially arranged in such a way that the centers of gas pores that exit to the active layer surface form a regular square network. The distance between the centers of neighboring gas pores is designated as $2L$. If n is the number of gas pores per cm² of the active layer outer surface, then, obviously,

$$g = nd^2. \quad (3)$$

Because, by definition,

$$n = 1/4L^2, \quad (4)$$

then, in place of Eq. (3), we ultimately obtain

$$g = (d/2L)^2. \quad (5)$$

Condition (5) makes it possible to relate L/d with g . As g approaches zero, the distance between gas pores increases and becomes infinitely large. For $g = 1.0$, $L = d/2$, i.e., all grains in the cathodic active layer are accessible for gas, and the distance between the centers of neighboring grains decreases to the minimum, i.e., the grain diameter.

The further calculations require the use of the effective conductivity of electrolyte k^* . Obviously, in the taken model (the regular structure of a thin active layer)

$$k_{\text{thin}}^* = kv g_s = kv(1 - g), \quad (6)$$

where k is the electrolyte conductivity.

In the present study, the calculations are carried out by the example of a cathode of a fuel cell with alkaline electrolyte, namely, 7 N KOH, at 60°C. Catalyst represents platinum deposited on a carbon carrier (carbon black). When choosing parameters, we rely on experiments carried out in [5]. The Tafel plot of oxygen reduction on platinum in an alkaline solution has two slopes; let the steady-state potential $E^{\text{st}} = 1.07$ V, the potential of the break in the Tafel plot $E^* = 0.97$ V, the slope of the first Tafel plot segment $b_1 = 2.6 \times 10^{-2}$ V, the second slope $b_2 = 5.2 \times 10^{-2}$ V, the exchange current $i_0 = 2 \times 10^{-8}$ A/cm² (at 25°C), the number of electrons involved in the electrochemical process $n = 4$, the Faraday number $F = 9.6 \times 10^4$ C/mol, the diffusion coefficient of oxygen in electrolyte $D = 6 \times 10^{-6}$ cm²/s, carrier grain porosity $v = 0.5$, oxygen solubility in electrolyte $c_0 = 1.2 \times 10^{-7}$ mol/cm³, electrolyte conductivity $k = 0.42 \Omega^{-1} \text{cm}^{-1}$.

The calculations of overall characteristics of active layers both thick and thin are carried out using formulas shown in [8]. The difference between thick active layers with the stochastic structure and thin active layers with the regular structure lies only in the form of dependence of the distance between neighboring gas pores L on the volume concentration of hydrophobizer g . For thin layers with the regular structure, this dependence turns out to be more complicated, the details of the L vs. g dependence for this case can be found in [8].

Now we choose the main parameters of models under study, namely, the grain size d and the characteristic current density j_1 in the high potential range $E^{\text{st}} > E > E^*$ (in the low potential range, for $E < E^*$, the j_2 value is determined by the relationship $j_2 = j_1 \exp\{(E^{\text{st}} - E^*)(b_2 - b_1)/b_2 b_1\}$). The characteristic bulk current density generated in a volume unit filled by 100% with the carrier and catalyst j_1 , represents the product of the exchange current i_0 by the specific surface S of platinum particles deposited on the carrier and really involved in the electrochemical process

$$j_1 = i_0 S. \quad (7)$$

In turn,

$$S = S^* \mu, \quad (8)$$

where S^* is the specific surface of carrier particles, μ is the electrochemical roughness factor introduced in [11].

To assess S^* , we represent the carrier particles as microcubes with the edge length d_s . Then, the carrier grains form a set of randomly distributed carrier particles and voids. According to the percolation calculations carried out in [12], the maximum surface of con-

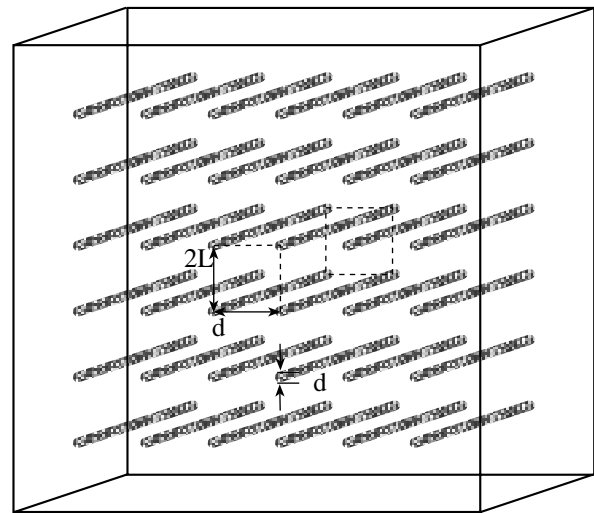


Fig. 1. Illustration of the porous space structure for a thin active layer with a regular structure. PTFE particles form a set of straight rods with the thickness d , which are perpendicular to the outer surface of the active layer. These rods are spatially oriented in such a way that the centers of their exit to the active layer surface form a regular square network with a step $2L$.

tact between a cluster formed by carbon black particles and a cluster of voids (the voids can also be represented as microcubes with the edge length d_s) is reached for equal volume concentrations of the carrier and void grains, i.e., if the grain porosity $v = 0.5$. In this case [12],

$$S^* = 1.33/d_s. \quad (9)$$

Now, we consider the electrochemical roughness factor μ . Its value increases with an increase in the platinum content g_w in carrier grains. If we represent the platinum particles as microcubes with edges d_p and try to pack them uniformly and densely (without gaps and voids) on the external surface of carrier microcubes, we obtain a catalyst layer with the thickness τ (dimensionless quantity) on the surface of carrier particles. As was shown in [11], if the average size of carrier particles far exceeds the average size of platinum particles $d_s \gg d_p$, which is indeed the case (according to [13], in average, $d_p = 2$ nm, $d_s = 30$ nm), then the relationship between μ and τ has the form

$$\mu = 3.845\tau. \quad (10)$$

It remains to find the dependence of parameter τ on the content of platinum in the carrier grains g_w . By the definition of the quantity g_w ,

$$g_w = V_p \rho_p / (V_p \rho_p + V_s \rho_s), \quad (11)$$

where V_p , V_s are the volumes and ρ_p , ρ_s are the specific densities of platinum and carbon black. In view of obvious relationships

$$V_s = d_s^3, \quad (12)$$

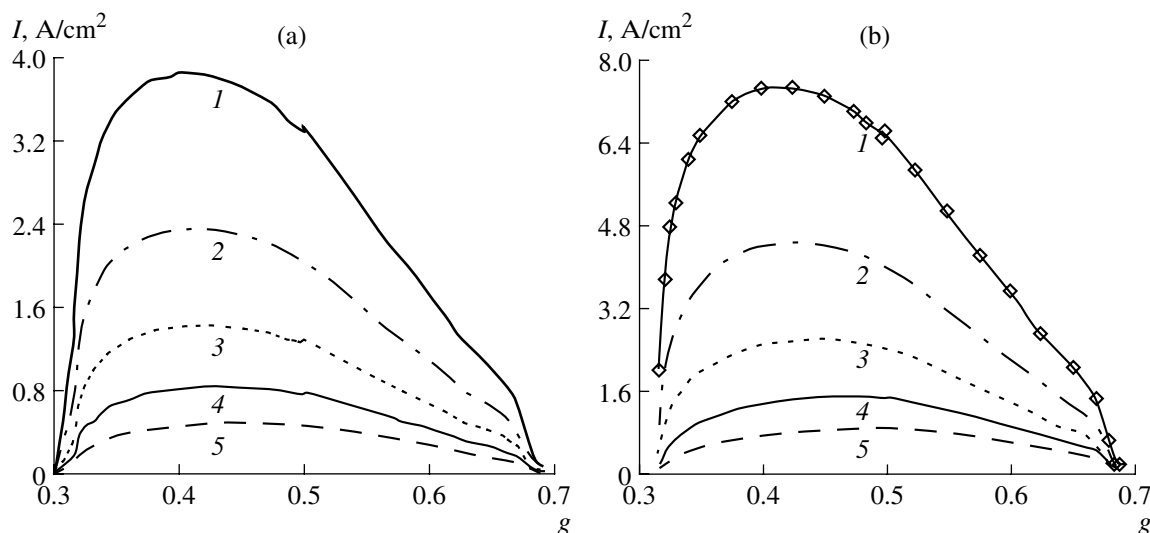


Fig. 2. Dependence of the overall current of a cathode with a thick active layer with the stochastic structure on the volume fraction of hydrophobizer grains: (a) $d = 4 \mu\text{m}$, $\Delta = 400 \mu\text{m}$; (b) $d = 1 \mu\text{m}$, $\Delta = 100 \mu\text{m}$; E, V : (1) 0.3, (2) 0.4, (3) 0.5, (4) 0.6, (5) 0.7.

$$V_P = 6d_s^2 d_P \tau, \quad (13)$$

we obtain that

$$\tau = (\rho_s/\rho_P)(d_s/6d_P)[g_w/(1-g_w)]. \quad (14)$$

Ultimately, taking into account Eq. (10), we have

$$\mu = 3.845(\rho_s/\rho_P)(d_s/6d_P)[g_w/(1-g_w)]. \quad (15)$$

Now, we pass to estimates. For $\rho_s = 1.8 \text{ g cm}^{-3}$, $\rho_P = 21.5 \text{ g cm}^{-3}$, $d_s = 30 \text{ nm}$, $d_P = 2 \text{ nm}$, and $g_w = 10 \text{ mass } \%$ $\mu = 0.089$, $S^* = 4.43 \times 10^5 \text{ cm}^{-1}$, $3.94 \times 10^4 \text{ cm}^{-1}$. Then,

Table 1. Overall current (I) of cathodes with a thick active layer of stochastic structure as a function of potential (E) for three versions of hydrophobizer grain size (d) and active layer thickness (Δ), $g = 0.4$

E, V	$d = 4 \mu\text{m}$, $\Delta = 400 \mu\text{m}$	$d = 1 \mu\text{m}$, $\Delta = 100 \mu\text{m}$	$d = 1 \mu\text{m}$, $\Delta = 400 \mu\text{m}$
	$I, \text{A/cm}^2$	$I, \text{A/cm}^2$	$I, \text{A/cm}^2$
0.9	0.104	0.052	0.152
0.8	0.234	0.249	0.494
0.7	0.445	0.681	1.090
0.6	0.805	1.348	1.892
0.5	1.393	2.493	3.060
0.4	2.334	4.396	4.894
0.3	3.837	7.457	7.846
0.2	6.249	12.34	12.62
0.1	10.14	20.17	20.36
0.0	16.41	32.76	32.89

according to Eqs. (7)–(9), the characteristic bulk current density in the high potential range $j_1 = i_0 S^* \mu = 7.88 \times 10^{-4} \text{ A/cm}^3$.

Let us take into account that in [5], the experiments were carried out at 25°C ; hence, for 60°C , corrections should be introduced for the exchange current. If we use a formula proposed in [14] to relate the exchange current with the temperature, then at 60°C , we have $j_1 = 1.75 \times 10^{-2} \text{ A/cm}^3$, $j_2 = 1.12 \times 10^{-1} \text{ A/cm}^3$.

Finally, we choose the grain size value d . The average grain size was assessed experimentally in [15, 16]. It was shown that d is of an order of magnitude of several μm . In our calculations, we assume $d = 4 \mu\text{m}$.

CHARACTERISTICS OF CATHODES WITH A THICK ACTIVE LAYER OF A STOCHASTIC STRUCTURE

According to the definition of a thick active layer, we assume in this model that $N = 100$. This is the minimum possible thickness of a thick active layer. For $d = 4 \mu\text{m}$, then $\Delta = 100d = 400 \mu\text{m}$. Then, according to Eq. (2), for a thick layer with $g = 0.4$, $v = 0.5$, and $g_w = 10 \text{ mass } \%$, the platinum content $m = 2.4 \text{ mg/cm}^2$ and for a similar layer with $g_w = 40 \text{ mass } \%$, $m = 14.4 \text{ mg/cm}^2$.

Figure 2 partly illustrates the calculations of the dependence of the overall current of a cathode with a thick stochastic-structure active layer on the volume concentration of PTFE grains for several potential values E (RHE). These calculations were carried out (see also the data shown in Table 1) for three versions of the PTFE grain size (d) and the active layer thickness (Δ). Version no. 1: $d = 4 \mu\text{m}$, $\Delta = 400 \mu\text{m}$; version no. 2: $d = 1 \mu\text{m}$, $\Delta = 100 \mu\text{m}$; version no. 3: $d = 1 \mu\text{m}$, $\Delta = 400 \mu\text{m}$ (Table 1).

As mentioned above, in thick active layers of the stochastic structure, the non-zero overall current was

observed within a range of $0.3 \leq g \leq 0.7$ and reached its maximum at the hydrophobizer volume concentration $g = g^* = 0.4$.

The catalyst content in the active layer m corresponding to versions nos. 1–3 and calculated using Eq. (2) for $g = 0.4$, $v = 0.5$, $g_w = 10$ mass % was 2.4, 0.6, and 2.4 mg/cm², respectively.

In versions nos. 2 and 3 with $d = 1 \mu\text{m}$ (Table 1) at potential $E = 0.3$ V, the overall currents were approximately twice higher than in version no. 1 with $d = 4 \mu\text{m}$. This result confirms a theoretical conclusion that with a decrease in the grain size in thick active layers with stochastic structure, the overall current I increases, namely,

$$I \sim (1/d)^{1/2}. \quad (16)$$

This theoretical conclusion was checked experimentally. In [17], electrodes were fabricated from PTFE of two types, namely, coarse FP-4D with the grain size d of 0.2–0.5 μm before sintering and also fine-grain FP-4MD with particles of 0.05–0.1 μm . The electrochemical characteristics of electrodes containing PTFE with finer grains were better, which was apparently associated with the smaller average size of hydrophobic grains in the case of FP-4MD.

Comparing the currents in the third and fourth columns of Table 1 shows that $\Delta = 400 \mu\text{m}$ in the low potential range corresponds to a virtually infinitely thick active layer, because the transition from the active layer thickness $\Delta = 100 \mu\text{m}$ to $\Delta = 400 \mu\text{m}$ had an insignificant effect of the current. At the same time, in the ranges of medium and high potentials, the currents were sensitive to the increase in the active layer thickness (for example, at $E = 0.9$ V, as the thickness increased 4-fold, the current increased approximately 3-fold).

The explanation of such a dependence lies in the fact that with the increase in the potential, the characteristic Ohmic length L_{ohm} decreases [8]. According to Table 1 (the third and fourth columns), at potentials $E < 0.3$ V, it can be assumed that the characteristic Ohmic length $L_{\text{ohm}} \leq 100 \mu\text{m}$, whereas at potentials $E \geq 0.3$ V, the characteristic length $L_{\text{ohm}} > 100 \mu\text{m}$. The same reasons explain why in Table 1 (contrary to the trend expressed by formula (16)), the overall currents are higher in version no. 2 with $d = 1 \mu\text{m}$ as compared with version no. 1 with $d = 4 \mu\text{m}$.

The above reasoning is confirmed by theoretical estimates. According to [8], the thick active layers under study are characterized by two characteristic Ohmic lengths, expressed as

$$L_{\text{ohm}, m} = (b_m k k^* / \xi_m)^{1/2}, \quad (17)$$

where subscript m takes values 1 and 2 depending on the potential region described by Eq. (17), namely, the high ($E \geq E^*$) or low ($E < E^*$) potentials; b_m is the polarization curve slope, k is the electrolyte conductivity,

k^* is the specific effective electrolyte conductivity, and the characteristic effective bulk current density

$$\xi_m = 3\pi d N (n F D v c_o j_m \lambda)^{1/2}, \quad (18)$$

where N is the number of gas pores per cm² of the external surface of the active layer and parameter λ is the fraction of the active layer thickness located beyond the gas cluster, more exactly, the space fraction where the electrochemical process can really occur.

According to estimates [8], at $g = 0.4$ (i.e., $\lambda = 0.89$), the characteristic Ohmic lengths $L_{\text{ohm}, m=1} = 390 \mu\text{m}$, $L_{\text{ohm}, m=2} = 347 \mu\text{m}$. However, these quantities only demonstrate the size of current generation regions in a thick active layer. According to calculations, as the overpotential increases, the current generation process is shifted towards the frontal surface of the active layer (plane of the contact between the active layer and the electrolyte chamber) and the current generation regions are narrowed at low potentials to several tens of μm .

CHARACTERISTICS OF CATHODES WITH THIN ACTIVE LAYERS OF REGULAR STRUCTURE

For cathodes with thin active layers with regular structure, we repeat the procedure of calculations carried out for thick active layers with stochastic structure in the above section. However, now we assume that in a model electrode $N = 10$ (this value should be considered as the minimum acceptable for a thin active layer). Then, for $d = 4 \mu\text{m}$, the minimum thickness of an active layer $\Delta = 10d = 40 \mu\text{m}$. If $d = 1 \mu\text{m}$, then $\Delta = 10d = 10 \mu\text{m}$.

Figure 3 shows the results of calculating the overall current on a cathode with a thin regular-structure active layer as a function of the volume concentration of hydrophobizer for the cathodic potentials E (RHE) from 0.7 to 0.3 V. In contrast to cathodes with thick active layers of stochastic structure (Fig. 2), now the non-zero overall current lies in the range of $0 \leq g \leq 1$ rather than in a range of $0.3 \leq g \leq 0.7$. The current reaches maximum at the PTFE volume concentration $g^* = 0.7$ rather than at $g^* = 0.4$.

We considered (Fig. 3 and data in Table 2) three combinations of the hydrophobizer grain size (d) and the active layer thickness (Δ). Version no. 1: $d = 4 \mu\text{m}$, $\Delta = 40 \mu\text{m}$; version no. 2: $d = 1 \mu\text{m}$, $\Delta = 10 \mu\text{m}$; version no. 3: $d = 1 \mu\text{m}$, $\Delta = 40 \mu\text{m}$. Data in Table 2 suggest that in this case, the active layer thickness is far below the characteristic Ohmic length L_{ohm} .

A comparison of currents in versions nos. 2 and 3 (Table 2) shows that at potentials $E \geq 0.8$ V, the currents increase in direct proportion to the active layer thickness; however, later, at $E < 0.8$ V, their growth decelerates because the characteristic Ohmic length also decreases with decreasing potential. It also follows from the comparison of versions nos. 1 and 2 (Table 2) that the minimum possible active layer thickness is smaller than the characteristic Ohmic length. In the

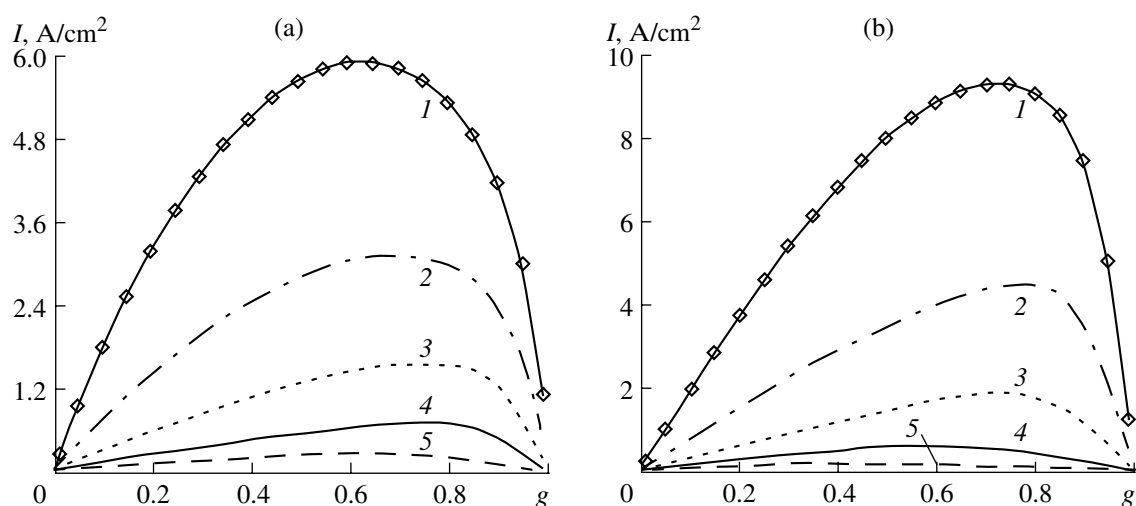


Fig. 3. Dependences of the overall current of a cathode with a thin active layer with a regular structure on the volume fraction of hydrophobizer grains. (a) $d = 4 \mu\text{m}$, $\Delta = 40 \mu\text{m}$; (b) $d = 1 \mu\text{m}$, $\Delta = 10 \mu\text{m}$; E , V: (1) 0.3, (2) 0.4, (3) 0.5, (4) 0.6, (5) 0.7.

potential range $E \geq 0.7$ V, the currents in version no. 2 are lower than in version no. 1, although it would seem obvious that a 4-fold decrease in the grain size should make the currents in version no. 2 exceed those in version no. 1. Only in the potential range $E < 0.7$ V, everything returns in its place, because the reduced characteristic Ohmic length becomes commensurable to the active layer thickness and even smaller than the latter.

Table 2. Overall current (I) of cathodes with a thin active layer of regular structure as a function of potential (E) for three versions of hydrophobizer grain size (d) and active layer thickness (Δ), $g = 0.7$

E , V	$d = 4 \mu\text{m}$, $\Delta = 40 \mu\text{m}$	$d = 1 \mu\text{m}$, $\Delta = 10 \mu\text{m}$	$d = 1 \mu\text{m}$, $\Delta = 40 \mu\text{m}$
	I , A/cm ²	I , A/cm ²	I , A/cm ²
0.9	8.708×10^{-3}	2.086×10^{-3}	8.922×10^{-3}
0.8	0.055	0.015	0.059
0.7	0.253	0.099	0.352
0.6	0.698	0.547	1.475
0.5	1.550	1.871	3.890
0.4	3.142	4.408	7.507
0.3	5.845	9.305	12.94
0.2	10.20	17.94	21.47
0.1	17.14	32.11	35.1
0.0	28.22	54.72	57.02

Now, we explain the fact that in thin active layers with regular structure, the current reaches the maximum at a hydrophobizer volume concentration $g^* = 0.7$, i.e., higher than for thick active layers with stochastic structure for which $g^* = 0.4$ (Figs. 2 and 3).

In hydrophobized active layers, with an increase in the hydrophobizer concentration, the current increases by two reasons [8], namely, the increase in the number of gas pores N and the decrease in the average distance L between them. The latter means that the current generation mechanism gradually passes from the less effective innerdiffusion mechanism to the more effective kinetic mechanism. However, the current increases to a certain limit, because with an increase in g , the catalyst concentration in the active layer also begins to decrease, and the effective electrolyte conductivity drops. Eventually, this leads to the appearance of peaks in the dependences of overall current on the volume concentration of hydrophobizer (Figs. 2 and 3).

In thick active layers with stochastic structure, the conductivity decreases to zero at $g = 0.7$, whereas in thin active layers with regular structure, according to Eq. (6), the electrolyte conductivity drops to zero only for $g = 1$. Table 3 shows the dependence of the effective conductivity for the active layers both thick with stochastic structure and thin with regular structure (for $v = 0.5$) on the volume concentration of hydrophobic grains. It is these data that explain why the optimum concentration of hydrophobizer g^* in thin active layers with regular structure lies in a range of higher values as compared with thick active layers with stochastic structure.

Now it becomes clear why in the low potential range (for $E < 0.5$ V), the currents in Table 2 exceed the corresponding values in Table 1. This is observed because the effect of factors favoring the increase in the overall current (the number of gas pores with the smaller aver-

age gap between them) is exceeded by the effect factors that prevent the overall current growth (a decrease in the catalyst concentration in the active layer and a decrease of the effective electrolyte concentration in this layer) at the higher volume concentrations of PTFE, namely, at $g^* = 0.7$ rather than at $g^* = 0.4$.

Moreover, it should be mentioned that a shift of the optimal value of parameter g towards values larger than $g^* = 0.4$ additionally reduces the catalyst consumption in thin active layers with regular structure as compared with thick active layers with stochastic structure. According to formula (2), the catalyst content in the active layer $m \sim (1 - g)$. If we take a value $g^* = 0.7$ which is the optimum as regards the current generation, then the catalyst content in the thin active layer corresponding to versions nos. 1–3 and calculated using Eq. (2) with $g = 0.7$, $v = 0.5$, $g_w = 10$ mass % is equal to 0.12, 0.03, and 0.12 mg/cm², respectively. Thus, the changeover from thick active layers with stochastic PTFE distribution to thin active layers with regular PTFE distribution provides a 20-fold decrease in the catalyst consumption.

Let us again compare the data in Tables 1 and 2. Throughout the practically important potential range $E > 0.5$ V, the currents in the second and third columns of Table 2 are lower than the currents in the same columns of Table 1, which is natural, because we consider the minimum possible thicknesses of thin active layers with regular structure (10 and 40 μm), and the latter are noticeably smaller than the characteristic Ohmic length. However, the overall current on cathodes with thin active layers of regular structure in the high potential range (for $E > 0.5$) can be increased by increasing their thickness within certain limits.

The dependence of the overall current on a cathode with a thin active layer of regular structure on the active

Table 3. Dependence of the specific effective electrolyte conductivity for thick active layers with stochastic structure and thin active layer with regular structure on the volume concentration of hydrophobic grains

g	k_{thick}^*/k	k_{thin}^*/k
0.320	0.339	0.340
0.358	0.287	0.321
0.456	0.152	0.272
0.606	0.023	0.192
0.702	0.000	0.149

layer thickness is shown in Fig. 4 for the average size of PTFE grains $d = 4$ μm and $d = 1$ μm. As the active layer thickness increases from 40 μm (the extremely thin active layer, for $d = 4$ μm, Fig. 4a) to 200 μm, the overall currents at potentials 0.7, 0.6, and 0.5 V increase from 0.253, 0.698, and 1.55 A/cm² (the second column in Table 2) to 0.635, 1.374, and 2.446 A/cm², respectively. Obviously, the increase in overall current is still more pronounced when the active layer thickness increases from 10 μm (the extremely thin active layer, for $d = 1$ μm, Fig. 4b) to 100 μm. Here, the currents at potentials 0.7, 0.6, and 0.5 V increase from 0.099, 0.547, and 1.871 A/cm² (the third column in Table 2) to 0.605, 1.883, and 4.316 A/cm², respectively.

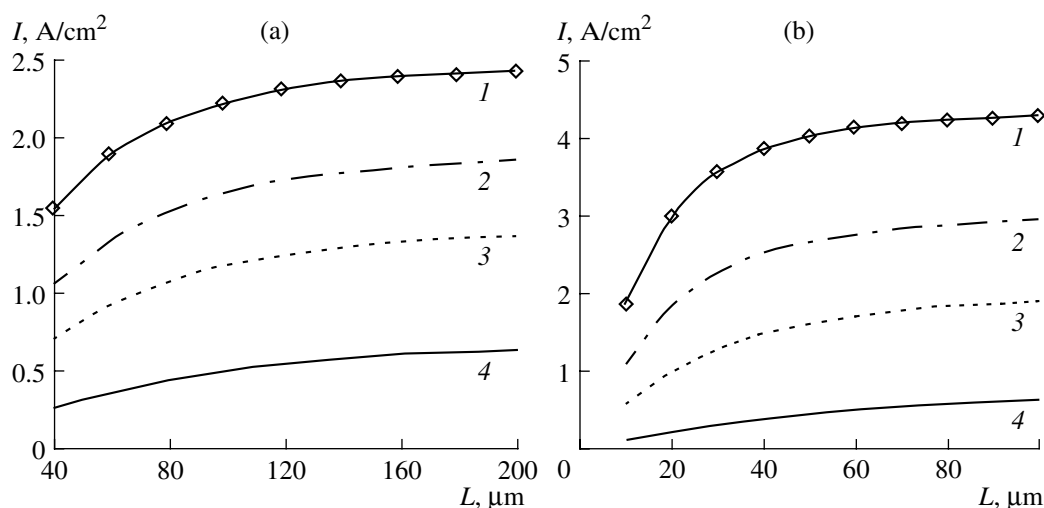


Fig. 4. Dependences of the overall current of a cathode with a thin active layer of a regular structure on the active layer thickness; d , μm: (a) 4, (b) 1; E , V: (1) 0.5, (2) 0.55, (3) 0.6, (4) 0.7; $g = 0.7$.

CONCLUSION

Within the framework of the "model of equidimensional grains" (both the hydrophilic grains consisting of a carrier with a catalyst and the hydrophobic, PTFE grains), for hydrophobized active layers, the concepts of thick layers with stochastic structure and thin layers with regular structure were introduced. A thickness of about 10-fold grain size corresponds to extremely thin layers; thickness of about 100-fold grain size corresponds to extremely thick layers.

In hydrophobized thin active layers with regular structure, all hydrophilic grains are involved in the development of gas pores, and these pores represent a set of identical straight rods uniformly distributed throughout the active layer (normally to the overall surface of the cathode). The advantage of thin active layers with regular structure lies in reproducibility of their characteristics and their platinum content which is lower by an order of magnitude (up to tenth and even hundredth fractions of mg/cm²).

In calculating the overall characteristics of thick active layers with stochastic PTFE distribution and thin active layers with the regular structure, we used the procedures proposed earlier and described in [8]. According to our calculations, in thin active layers with regular structure at potentials below 0.5 V, the generated overall currents proved to be higher than in thick active layers with stochastic structure. However, in the range of medium and high potentials (for $E > 0.5$ V), thin active layers with regular structure are inferior to thick active layers with stochastic structure as regards the current.

Two methods can help to improve this relationship of currents for thin active layers with regular structure. First, one can increase the thickness of thin active layers with regular structure starting from the minimum possible thickness equal to $10d$ (where d is the average PTFE grain size; sizes of 1 and 4 μm correspond to minimum possible thicknesses of 10 and 40 μm). Actually, this will proportionally increase the platinum content in the active layer.

Second, it is possible to increase overall currents by decreasing the average size of PTFE grains in the layer, thus passing from conventionally used active layers with the average size of PTFE grains of about several μm to the active layers with the average grain size of 1 μm and less. In this case, the current will increase in an inverse proportion to the square root of the average grain size.

DESIGNATIONS CHARACTERIZING THE CATHODE ACTIVE LAYER AND THEIR VALUES TAKEN IN CALCULATIONS

$t = 60^\circ\text{C}$ is the working temperature of a fuel cell

$P = 101$ kPa is pressure

$E_{\text{st}} = 1.07$ V is the steady-state potential

$E^* = 0.97$ V is the potential of the break in the Tafel plot

$b_1 = 2.6 \times 10^{-2}$ V is the Tafel plot slope in the high potential range

$b_2 = 5.2 \times 10^{-2}$ V is the Tafel plot slope in the low potential range

$n = 4$ is the number of electrons involved in the electrochemical process

$F = 9.6 \times 10^4$ C/mol is the Faraday number

$i_0 = 2 \times 10^{-8}$ A/cm² is the exchange current in the high potential range at $t = 25^\circ\text{C}$

$j_1 = 1.75 \times 10^{-2}$ A/cm³ is the characteristic bulk current density in the high potential range

$j_2 = 1.12 \times 10^{-1}$ A/cm³ is the characteristic bulk current density in the low potential range

$D = 6 \times 10^{-6}$ cm²/s is the oxygen diffusion coefficient in the electrolyte

$c_0 = 1.2 \times 10^{-7}$ g-mol/cm³ is the oxygen solubility in electrolyte

$d = 1$ and 4 μm is the average edge length of the hydrophobizer and carrier grains

$d_p = 2$ nm is the average edge length of catalyst (platinum) particles

$d_s = 30$ nm is the average edge length of carrier (carbon black) particles

$g_w = 10$ mass % is the platinum content in carrier grains

$g_0 = 0$ is the volume concentration of grains-voids

$S = 3.94 \times 10^4$ cm⁻¹ is the specific surface of platinum particles deposited on the carrier and involved in the electrochemical process

$S^* = 4.43 \times 10^5$ cm⁻¹ is the specific surface of the carrier (carbon black) particles

$\Delta = 100$ and 400 μm is the active layer thickness

$k = 0.42$ Ω^{-1} cm⁻¹ is the specific conductivity of electrolyte

$\nu = 0.5$ is the carrier grain porosity

$\mu = 0.089$ is the electrochemical roughness factor

$\rho_s = 1.8$ g cm⁻³ is the carrier (carbon black) density

$\rho_p = 21.5$ g cm⁻³ is the catalyst (platinum) density

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