

A Cathode for Solid Polymer Electrolyte Fuel Cells: Designing the Optimal Structure of the Active Layer

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Abstract—The complete computer simulation of the cathodic active layer with solid polymer electrolyte (Nafion) is carried out. The active layer structure can be described by 8 parameters. In designing the optimal structure, it is shown that to provide the high overall characteristics of the cathode and save the catalyst, 0.5 of the active layer volume should be set aside for the support grains (agglomerates of carbon particles covered with platinum and containing Nafion incorporations and microvoids). Protons and oxygen molecules must be supplied to the active layer by means of peculiar combined percolation clusters. The latter consist of a combination of support grains with either Nafion grains (to produce “protonic” clusters) or grains-voids (to afford “gas” clusters). The volume fractions of Nafion grains and grain-voids are assumed to be 0.25 and 0.25. The computer simulation of the support grain structure is also carried out. Their composition, i.e., the volume fractions of the carbon component (g_c), Nafion (g_{ii}), and microvoids (g_{gg}), is varied. The support grains play the key role in the active layer functioning. It is impossible to organize three full-value percolation clusters (electronic, protonic, and gas); hence, one has to have one or two combined clusters in the active layer. Thus the double load falls on the support grains. Their optimal structure should not only sustain the transport of protons and electrons in the active layer but also create the best conditions for the electrochemical process in each grain. The maximum current I_{\max} (realized upon reaching the optimal active layer thicknesses Δ^*) is calculated. The dependences of I_{\max} and Δ^* on the main parameters characterizing the support grains (g_c and g_{ii}) are analyzed. Here, two goals are sought: (1) to obtain the high currents, (2) to provide the low consumption of platinum per power unit. To solve the first problem, one has to work with high values of g_c . The second problem requires the opposite: the values of g_c must be minimal possible.

Keywords: cathode of solid polymer electrolyte fuel cell, active layer, computer simulation, full-value and combined percolation clusters, support grains, calculation of overall characteristics

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1. FORMULATION OF THE PROBLEM

Even now in the XXI century, the low-temperature hydrogen-oxygen (air) fuel cells with solid polymer electrolyte (Nafion) and platinum as the catalyst are considered as the chief candidates for the main autonomous sources of environmentally clean electric energy. Their part that poses the most serious problem is the cathode active layer in which the very slow process of oxygen reduction to water proceeds.

The cathode active layer has a complex structure. First of all, it should contain channels for the delivery of all participants of the electrochemical process, namely, oxygen molecules, protons, and electrons and the removal of the reaction product, water vapors. All this makes up the transportation, “upper” level of the active layer.

There should also be the “lower level” in the active layer structure, i.e., its elements where the electrochemical process as such occurs. Such structural formations we call the “support grains” (grains of the catalyst carrier). These are agglomerates of electron-conducting carbon particles with platinum deposited on their surface. The composition of support grains includes also microvoids and Nafion-filled loci incorporated into the grain bulk. The latter components provide the transport of oxygen and protons from the grain surface to the catalyst-coated surface of carbon microparticles.

The active layer structure was experimentally studied in many works. Thus, the structure of support grains was studied [1–3]. Due to the tendency for increasing the specific surface of the carbon support at any price in order to intensify the electrochemical process, the particle size is now only 5–10 nm and the support grain size is assessed as 30–100 nm [4].

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The processes of self-assembling of elements that form the active layer structure of cathodes in polymer electrolyte fuel cells (various methods of preparation of catalytic ink [2, 3] were considered) were also studied, e.g., in [5, 6]. This direction has the general name: the molecular dynamics simulations. In the illustrative material of [5] it is demonstrated how carbon particles and Nafion molecules are gathered together to form agglomerates of support particles and Nafion; the presence of voids is also clearly distinguishable.

The most interesting procedure used in such studies is as follows. First, the structure of the cathode active layer containing Nafion and platinum on the carbon support is studied by the microscopy techniques: transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Then, the obtained two-dimensional statistical information is mathematically processed (the stochastic method). This allows the active layer structure to be reconstructed and its three-dimensional images to be created based on two-dimensional images. The peculiarities of these procedures can be found in several studies [4, 7–10].

Thus, in the first approximation, the “upper level” of the microstructure of the cathode active layer with solid polymer electrolyte can be represented as the composite of support grains, Nafion grains (agglomerates of Nafion molecules), and grains-voids. Indeed, these components are size-distributed and have various shapes; however, in the first approximation, this triad of grains can be represented as the model of equal-sized and equal-shaped grains of three types.

Below, we characterize the “upper level” of the cathode active layer in terms of the model of equal-sized cubic grains of three types (for the first time, such a model was proposed in [11]). Figure 1 illustrates this model. The model cube we have chosen for calculations must have the macroscopic dimensions, because the grain size $\sim 100 \text{ nm} = 10^{-5} \text{ cm}$ and the active layer thickness is $\sim 10 \text{ }\mu\text{m} = 10^{-3} \text{ cm}$. Hence, the active-layer-imitating model cube should be sufficiently large. We assume the model cube volume to be $100 \times 100 \times 100 = 10^6$ and comprise one million of grains of three types.

Let us introduce designations. Let g be the volume concentration (fraction) of support grains in the model cube, g_i be the fraction of Nafion grains, and g_{gas} be the volume fraction falling to voids. Obviously, the following relationship is true:

$$g + g_i + g_{\text{gas}} = 1. \quad (1)$$

In the model cube (Fig. 1), the clusters (conglomerates of interconnected grains of one or another type) are formed. Such clusters that stretch to the whole thickness of the active layer provide the proper development of the electrochemical process in any section of the active layer. The conditions at which such clusters, i.e., the channels for the delivery of electron, protons, and oxygen molecules to the active layer, can be

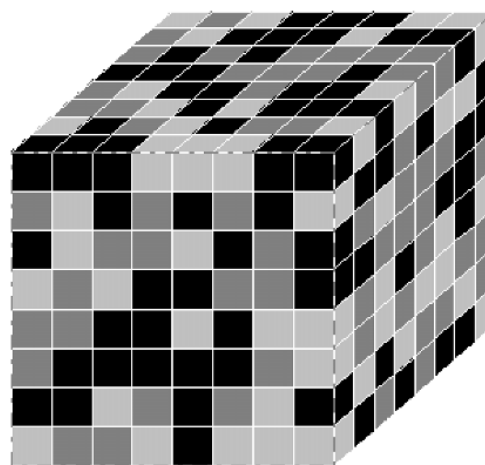


Fig. 1. The model of “the upper level” of the active layer of the cathode with solid polymer electrolyte: the model cube ($8 \times 8 \times 8$) built of three types of equal-sized cubic grains. Black microcubes are the support grains (40 vol %), dark-grey microcubes are the Nafion grains (30 vol %), and light-grey microcubes are the pores-voids (30 vol %)

formed and the properties of these clusters should be discussed in terms of the special division of mathematics and theoretical physics – the percolation theory [12].

Now, we consider the “lower level” of the active layer structure – the support grains. Figure 2 shows the model of an individual support grain. Let us list the average parameters that characterize the structure of this segment of the active layer. Let $L = 100 \text{ nm} = 10^{-5} \text{ cm}$ be the length of the edge of support grains (as well as the length of edges of Nafion grains and void-grains), $d = 10 \text{ nm} = 10^{-6} \text{ cm}$ be the edge of carbon particles-cubes within support grains, and $\delta = 2 \text{ nm} = 2 \times 10^{-7}$ be the size of edges of Nafion cubes within support grains.

Further, let g_c be the volume concentration of carbon microcubes in the support grain, g_{ii} be the volume concentration of Nafion entering the composition of the Nafion cluster in the support grain, and g_{gg} be the porosity accounted for by support grain. Obviously, the sum of volume fractions of the carbon material, Nafion, and voids within the support grain fulfils the relationship

$$g_c + g_{ii} + g_{gg} = 1. \quad (2)$$

Thus, the total number of variables that characterize the structure of the active layer as a whole is 8. Let us name them once more. These are any pair of quantities involved in Eq. (1) (the third quantity is determined by equality (1)), any pair of quantities in Eq. (2), three sizes of components present in the support grain (L , d , and δ), and, ultimately, the active layer thickness Δ .

The large number of such parameters and also the vast number of possible combinations of 8 parameters

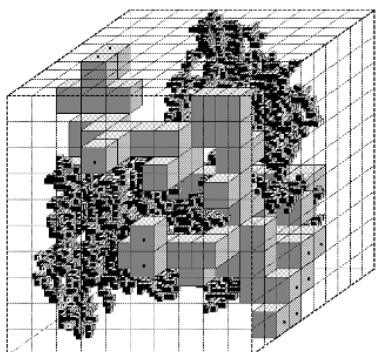


Fig. 2. The model of the support grain: the cluster of large grey cubes is the carbon “skeleton”, the cluster of fine Nafion cubes makes possible the transport of protons from the support grain boundary to the carbon cluster surface where the catalyst (platinum) is localized. The volume fraction of carbon particles $g_c = 0.072$, the volume fraction of Nafion particles $g_{ii} = 0.0396$, the volume fraction of gas pores $g_{gg} = 0.8884$. The edge of carbon particles-cubes $d = 10$ nm, the edge of Nafion cubes $\delta = 2$ nm for the model cube of $10 \times 10 \times 10$.

severely complicate the problem that consists of seeking the optimal combination of parameters which would allow obtaining the maximum possible current in the cathode active layer. This difficult task represents to a certain extent the main subject of our further speculations and calculations.

2. THE OPTIMAL ELECTRONIC PERCOLATION CLUSTER

We start our study with assessing the optimal value for g , i.e., the volume fraction of the support. This is the most significant parameter because support grains contain the catalyst—expensive platinum. In total, in the active layer, three percolation clusters should operate: the “electronic” (support grains, this cluster supplies the catalyst with electrons), “protonic” (Nafion grains), and “gas” (of grains-voids) clusters.

In terms of the percolation theory, in the cubic model under consideration (Fig. 1), which represents the cubic lattice of sites, the three percolation thresholds should be reached (the minimum concentration of one or another component at which the corresponding percolation cluster can form). These thresholds for electronic, protonic, and gas clusters are determined by a special equation. Generally, it describes the percolation phenomena on the infinite set of so-called “percolation lattices” (square lattice—on the plane; simple cubic lattice—in the volume, and all analogues lattices in any number of dimensions) [13].

For rectangular lattices, the following characteristic equation is true [13]. It allows the exact percolation thresholds to be found in rectangular lattices:

$$2(z-1)\gamma^2\omega^3 + (2z-3)\gamma\omega - 1 = 0, \quad (3)$$

where z is the spatial dimension, γ is the fraction of sought elements (provided we deal with “the problem of links”), and ω is the fraction of sought elements (provided we deal with “the problem of sites”).

In rectangular lattices, in terms of the problem of links, the percolation thresholds are determined by the following solution of equation (3): the relationship $\gamma^* = 1/2(z-1)$ is true. Then, for the square lattice on the plane ($z = 2$), the percolation threshold is 0.5 (the exact result long known in the percolation theory [12]). For the simple cubic lattice, the threshold is 0.25; in the rectangular lattice of 4-dimensional space, it is 1/6. And so on.

In Eq. (3), assuming $z = 3$ (3-dimensional space) and $\gamma = 1$ (all lattice sites are interconnected), we find the following equation for the problem of sites in the simple cubic lattice in 3-dimensional space:

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

The only real root of Eq. (4) determines the percolation threshold in the lattice of sites in the case of interest (Fig. 1), i.e., for electronic g^{***} (support grains), protonic g_i^{***} (Nafion grains), and gas g_{gas}^{***} (grains-voids) clusters:

$$g^{***} = g_i^{***} = g_{gas}^{***} \\ = [(1 + 2^{1/2})^{1/3} + (1 - 2^{1/2})^{1/3}] / 2 = 0.298. \quad (5)$$

Thus for functioning of the active layer, at least three conditions should be fulfilled simultaneously

$$g \geq 0.30, \quad g_i \geq 0.30, \quad g_{gas} \geq 0.30. \quad (6)$$

Let us make a significant note. As was shown in [14], the full-blown percolation clusters actually appear not at 0.3 but at the higher concentrations of about 0.35. Before this value is reached, the clusters are only being formed and occupy a small part of the volume. Hence, with the permissible concentrations g , g_i , and g_{gas} , one has to consider condition (7) in place of condition (6)

$$g \geq 0.35, \quad g_i \geq 0.35, \quad g_{gas} \geq 0.35. \quad (7)$$

Note that the presence of inequalities (7) clearly suggests that the active layer cannot actually accommodate three full-value clusters, because the sum of values in the left part of inequalities (7) turns out to be larger than 1! This contradicts condition (1).

Everything said above in this section allows the optimal concentration of support grains that form the electronic percolation cluster to be assessed.

After the attainment of the percolation threshold, the fraction of support grains involved in the percolation cluster, which is designated below as g^* (the second column in Table 1), begins to increase quickly. At

Table 1. Dependence of the main parameters of the electronic percolation cluster on the concentration (fraction) of support grains g (model cube of $100 \times 100 \times 100$)

g	g^*	$g - g^*$	$(g - g^*)/g, \%$	S^*	g_0	g_1	g_2	g_3	g_4	g_5
0.35	0.2514	0.0986	28.2	0.895	0.0007	0.0071	0.0315	0.0728	0.0900	0.0493
0.40	0.3567	0.0433	10.8	1.199	0.002	0.0163	0.0583	0.1099	0.1144	0.0557
0.45	0.4278	0.0222	4.9	1.329	0.0048	0.0319	0.0894	0.1365	0.1170	0.0483
0.50	0.4882	0.0118	2.4	1.370	0.0111	0.0566	0.1262	0.1528	0.1050	0.0365
0.55	0.5439	0.0061	1.1	1.332	0.0258	0.0955	0.1619	0.1535	0.0840	0.0232
0.60	0.5969	0.0031	0.5	1.205	0.0627	0.1490	0.1829	0.1320	0.0574	0.0128
0.65	0.6486	0.0014	0.2	0.908	0.1753	0.1964	0.1583	0.0847	0.0287	0.0051

the same time, the number of support grains isolated from the percolation cluster and thus uninvolved in the electrochemical process (unsupplied with electrons) $g - g^*$ (the third column in Table 1) quickly decreases.

The data in the 4th column of Table 1 deserve attention. It turns out that at $g = 0.35$, almost the third (more precisely, 28.2%) of support grains are uninvolved in the electronic percolation cluster, not supplied with electrons, and hence take no part in the current generation. This not only complicates the current generation but also represents a noticeable loss of the valuable catalyst—platinum. For $g = 0.40$, although the situation improves, the losses in the ability to generate current and save platinum are still considerable. It is only at $g = 0.50$ that the losses become bearable because the majority of support grains are now involved in the percolation cluster.

What is fraction of support grains that can be taken as the optimal $g = g_{\text{opt}}$? Shall we continue to increase the fraction of support grains above $g = 0.5$? The answer is no. Let us consider the fifth column in Table 1. S^* is the normalized specific surface of the electronic percolation cluster (its true specific surface $S = S^*/L$, where L is the length of the support grain edge). It is through this surface that the active support grains (those that can take part in the electrochemical process) are supplied with protons and oxygen molecules. As seen from the data in Table 1, this surface first increases with the increase in g , reaches the maximum at $g = 0.5$, and then begins to decrease.

The concentration $g = 0.5$ should be considered as the optimal also due to the following. Let us consider the data of columns 6–11 in Table 1. Here, the fractions of grains involved in the electronic percolation cluster with n of their 6 faces open are shown, i.e., the grains with all faces close (g_0), with a single open face (g_1), with two open faces (g_2), and so on up to the maximum, five open faces.

In the first column of Table 1, the fraction of isolated support grains g_0 is negligible (0.0007) and the number of grains with open faces is large. However, as g increases, the ratio g_0 also quickly increases (see the data in the last column in Table 1 in which $g_0 = 0.1753$).

However, such grains are virtually blocked from oxygen and protons and hence cannot take part in the electrochemical process, representing the complete loss of platinum confined in them. This is why, ultimately, the optimal concentration of support grain should be $g_{\text{opt}} = 0.5$ or close to this value.

3. PROTONIC AND PERCOLATION CLUSTERS

In [15], we have demonstrated that the cathodic active layer with Nafion cannot have three macroscopic percolation clusters capable of becoming full-value suppliers of everything required for the electrochemical process to occur. Moreover, it should be especially stressed that it is quite natural to image each cluster as consisting of grains of a single type. Particularly, the electronic cluster can be imaged to contain only support grains, the protonic cluster—only Nafion grains, and the gas cluster—only grains-voids. However, it is impossible to have simultaneously three percolation clusters.

But if it is impossible to create three such clusters then how the experimentally observed sufficiently adequate functioning of the active layer of cathodes in polymer electrolyte fuel cells can be explained. What is the real nature of channels for the delivery of protons and oxygen to the support grains and where does the electrochemical process of oxygen reduction occur?

The estimates obtained in [15] suggest that the necessary delivery of protons and oxygen molecules can be organized only if the support grains are capable of providing not only the electronic conduction. In addition this they should render considerably efficient assistance to the proper transport of both protons and oxygen in the active layer of the cathode with polymer electrolyte.

In fuel cells of the third generation (with solid polymer electrolyte), the delivery of protons and oxygen (in the presence of the full-value electronic cluster with $g = 0.5$) has to proceed in the corresponding “combined” percolation clusters [15]. The latter consist basically of the combination of support grains with either Nafion grains (to produce the combined “pro-

Table 2. Characteristics of the carbon support grain structure (model cube of $10 \times 10 \times 10$, Nafion is absent in the support grain)

g_0	g_e	g_{gg}	S_{out}	$S_{in,0}$	S_0	D_0^*	$D_{kn}, \text{cm}^2/\text{s}$	$D_{kn}D_0^*, \text{cm}^2/\text{s}$
0.21	0.072	0.928	12	254	266	0.842	2.475×10^{-3}	2.083×10^{-3}
0.25	0.124	0.876	22	421	443	0.743	2.336×10^{-3}	1.735×10^{-3}
0.27	0.179	0.821	35	612	647	0.639	2.189×10^{-3}	1.398×10^{-3}
0.30	0.219	0.781	61	740	801	0.569	2.083×10^{-3}	1.185×10^{-3}
0.33	0.279	0.721	84	888	972	0.505	1.923×10^{-3}	9.716×10^{-4}
0.35	0.310	0.690	78	998	1076	0.434	1.840×10^{-3}	7.979×10^{-4}
0.37	0.335	0.665	138	1045	1183	0.392	1.773×10^{-3}	6.944×10^{-4}
0.40	0.376	0.624	163	1149	1312	0.350	1.664×10^{-3}	5.822×10^{-4}
0.45	0.431	0.569	198	1317	1515	0.264	1.517×10^{-3}	4.006×10^{-4}
0.50	0.494	0.506	257	1365	1622	0.151	1.349×10^{-3}	2.032×10^{-4}
0.55	0.549	0.451	298	1386	1684	0.090	1.203×10^{-3}	1.079×10^{-4}
0.60	0.594	0.406	284	1390	1674	0.015	1.083×10^{-3}	1.602×10^{-5}
0.65	0.647	0.353	354	1293	1647	0.0094	9.413×10^{-4}	8.847×10^{-6}

tonic” cluster) or grains-voids (to produce the combined “gas” cluster).

In [16], it was demonstrated how the effective coefficients of proton conductivity and oxygen diffusion in the active layer can be calculated in the presence of the corresponding combined percolation clusters, i.e., how to determine the effective specific proton conductivity and the effective diffusion coefficient of oxygen. Ultimately, this allows the overall characteristics of the active layers of cathodes with polymer electrolyte to be found.

It was shown in Section 2 that the optimal concentration of support grains $g = 0.5$. Let us take this as the working value. Then half of the active layer volume belongs to Nafion grains and grains-void. The question is how to organize this volume, which values of parameters g_i and g_{gas} should be taken. In this point, we could have begun discussing various versions, but we will not do this and follow the recommendations found experimentally. Note that in several studies, attempts were undertaken to find the approximate range of concentrations (fractions) of three phases in the cathode active layer, namely, the concentrations of the support with platinum, Nafion, and gas pores. For example, in [17] the following figures were shown. In our designations, they are $g = 0.467$, $g_i = 0.257$, $g_{gas} = 0.274$. Thus in the further calculations we assume for the sake of simplicity that in the cathode active layer $g = 0.5$, $g_i = 0.25$, $g_{gas} = 0.25$.

4. SUPPORT GRAINS WITHOUT NAFION

It is clear that the concentrations $g_i = 0.25$ and $g_{gas} = 0.25$ are insufficient for the formation of full-value protonic and gas percolation clusters. The latter have to be the combined clusters, i.e., involve also the support grains. However, then one has to know the proton and gas conductivity of the support grains. Let us consider this problem.

Let us start with simulating the support grain structure (Fig. 2). The first stage is to create the “skeleton” of support grain. Assume that the edge of support grains cubes $L = 100$ nm. The carbon particles in support grains are assumed to be the equal size. They also are cubes and form the cubic lattice together with voids (also cubes). We also assume that the size of carbon cubes and cubic voids in the support grains $d = 10$ nm.

Let us randomly distribute the carbon cubes throughout the support grain (the model cube of $10 \times 10 \times 10$). The initial concentration of carbon cubes is varied. The final concentration of carbon cubes in the support grain should satisfy several strict requirements.

First, the carbon structure of the grain, its “skeleton” should represent a connected cluster which can sustain the transport of electrons. Hence, the components that make zero contribution into the electron transport should be eliminated from the initial configuration of cubes within the model cube. It is their removal that creates the final carbon structure in the support grain (Fig. 2). The carbon cubes exposed to the support grain surface are marked by dots in Fig. 2.

Second, we select only those structures of carbon grains within a support grain that demonstrate connectivity along the chains of these cubes from each support-grain face to the opposite face. This is the natural requirement to the support grain—the latter should be electron conductive along three coordinates, because the support grains should constitute the full-value contribution into the active layer composition (“the upper level”). Due to this limitation, the initial concentration of cubes in the support grain g_0 cannot be arbitrary small. As was shown by computer experiments (see the data in the 1st column in Table 2), the initial concentration of carbon cubes should begin with $g_0 = 0.21$.

Third, in the connected carbon cluster (Fig. 2), we have to determine the overall external surface of its

faces S . On this surface, the electrochemical process can proceed. For the sake of definiteness, we assume that this surface is maximally large.

The latter requirement is achieved as follows. For the chosen initial concentration of cubes g_0 , the procedure of simulation of the carbon cluster such as that shown in Fig. 2 is repeated many times (tens and hundreds of versions). Every new value of $S = S_2$ is compared with the previous value $S = S_1$. If $S_2 > S_1$, the first configuration is discarded. If $S_2 < S_1$, the second configuration is discarded and the next attempt is made to find the new cluster structure.

The resulting carbon cluster with the maximum reactivity of its faces should be assessed as regards several parameters shown in Table 2. The 1st column of Table 2 contains the volume concentration of carbon cubes. The 2nd column shows the volume concentration of carbon cubes in the optimal cluster (g_c is simultaneously the fraction of porosity that falls on carbon cubes within the support grain). The 3rd column shows the porosity corresponding to the voids in the support grain composition ($g_c + g_{gg} = 1$).

Assume that S_{out} is the number of optimal-cluster faces emerged to the surface of the support grain, $S_{in,0}$ is the number of carbon-cluster faces located in the bulk of the support grain, $S_0 = S_{out} + S_{in,0}$ is the total number of faces of the optimal carbon cluster.

D_0^* is the effective diffusion coefficient of gas in the support grain (thus we take into account the role of the support-grain microstructure, D_0^* is dimensionless parameter). Note that for the optimal cluster, D_0^* is calculated in three versions (along three coordinate axes). The final value $D_0^* = (D_1 + D_2 + D_3)/3$. In calculations, it was assumed that gas diffusion proceeds via voids from any support-grain face to the opposite face (or back). In the process, the remaining four faces are closed for diffusion.

In Table 2, D_{kn} (cm²/s) is the coefficient of Knudsen diffusion in pores of the support grain. It is calculated by Eq. (8) with allowance made for g_{gg} values taken from Table 2 (assuming that the average pore radius in the support grain is conditionally equal to 10 nm)

$$D_{kn} = (3.2 \times 10^{-3}) g_{gg,0}/1.5. \quad (8)$$

It should be noted that the assessment of Knudsen diffusion was carried out in [16]; it is there that Eq. (8) was derived.

The last column of Table 2 houses the values of the final effective coefficient of Knudsen diffusion in support grains D_e . The latter was assessed by Eq. (9) [16]

$$D_e = D_{kn} D_0^*, \text{ cm}^2/\text{s}. \quad (9)$$

In Table 2, several parameters are marked with index 0. It indicates that no Nafion molecules are present in the carbon support grains.

Concluding, it should be noted that the details of the model of individual support grain containing no Nafion can be found in [16].

5. SUPPORT GRAINS WITH NAFION

Now, we begin to fill the initial gas porosity $g_{gg,0}$ (Table 2) in support grains by Nafion particles. We gradually increase the Nafion content in grains. The individual Nafion particles shaped as microcubes with the edge $\delta = 2$ nm (all identical) are randomly distributed throughout the volume free of the carbon cluster (Fig. 2). The initial concentration of Nafion is g_{i0} . The cluster-forming Nafion particles with the volume concentration g_{ii} remain in the support grain, whereas the Nafion particles isolated from this cluster are eliminated; hence, $g_{i0} > g_{ii}$.

The problem is to create the full-value cluster of Nafion particles, which would fulfill the following conditions.

1. It must be in contact with the carbon cluster within the support grain, because the electrochemical process can occur in these loci.

2. This Nafion cluster should contact all faces of the model cube, because this cluster must provide proton conductivity to the support grain along all three mutually perpendicular coordinate axes.

The effective conductivity of protons in the fractal film (the protonic cluster) of Nafion particles within the support grain k^{***} was calculated three times (along three coordinate axes). The ultimate value $k^{***} = (k_1^{***} + k_2^{***} + k_3^{***})/3$. When calculating k^{***} , it was assumed that the proton flow travels in a support grain via Nafion microparticles from any face of the support grain to the opposite face (or back) when the side faces are closed for proton migration.

In avoid complications in our calculations, from the total list of porosity values for the corresponding carbon cubes g_c (the second column in Table 2), we selected five reference values: 0.072, 0.179, 0.279, 0.376, 0.494. The further operations were carried out with these values (the lower two values in Table 2 were not taken because the effective diffusion coefficient begins to dramatically decrease there).

The new (different from those shown in Table 2) parameters of support grains with Nafion are taken from Tables 3–7 which are much similar to Table 2. Columns 1 and 2 are different from those in Table 2 (in Table 3–7, g_{i0} is the initial concentration of Nafion in the support grain, g_{ii} is the Nafion concentration after the removal of Nafion cubes uninvolved in the cluster).

Column 3 is also different from that in Table 2, because the gas porosity becomes lower with the addition of Nafion. Column 4 in Tables 2–7 remains apparently unchanged but the dimensionality of values is expressed not in the number of faces (Table 2) but in cm².

Table 3. Characteristics of the support grain (model cube of $10 \times 10 \times 10$, Nafion is present in the grain, $g_e = 0.072$): $S_0 = 2.66 \times 10^{-10} \text{ cm}^2$

g_{i0}	g_{ii}	g_{gg}	$S_{\text{out}}, \text{cm}^2$	$S_{\text{in}}, \text{cm}^2$	S, cm^2	D^*	$D_{\text{kn}}, \text{cm}^2/\text{s}$	$D_{\text{kn}} D^*, \text{cm}^2/\text{s}$	k^{***}
0.28	0.038	0.890	1.2×10^{-11}	7.68×10^{-12}	1.97×10^{-11}	0.880	2.37×10^{-3}	2.09×10^{-3}	3.25×10^{-4}
0.41	0.383	0.545	1.2×10^{-11}	1.05×10^{-10}	1.17×10^{-10}	0.207	1.46×10^{-3}	3.00×10^{-4}	0.045
0.54	0.535	0.393	1.2×10^{-11}	1.50×10^{-10}	1.62×10^{-10}	0.035	1.05×10^{-3}	3.69×10^{-5}	0.205
0.67	0.669	0.260	1.2×10^{-11}	1.88×10^{-10}	2.00×10^{-10}	0	6.92×10^{-4}	0	0.432
0.80	0.798	0.130	1.2×10^{-11}	2.22×10^{-10}	2.34×10^{-10}	0	3.47×10^{-4}	0	0.650

Table 4. Characteristics of the support grain structure (model cube of $10 \times 10 \times 10$, Nafion is present in the grain, $g_e = 0.179$): $S_0 = 6.47 \times 10^{-10} \text{ cm}^2$

g_{i0}	g_{ii}	g_{gg}	$S_{\text{out}}, \text{cm}^2$	$S_{\text{in}}, \text{cm}^2$	S, cm^2	D^*	$D_{\text{kn}}, \text{cm}^2/\text{s}$	$D_{\text{kn}} D^*, \text{cm}^2/\text{s}$	k^{***}
0.26	0.043	0.778	3.5×10^{-11}	2.78×10^{-11}	6.28×10^{-11}	0.786	2.07×10^{-3}	1.63×10^{-3}	2.93×10^{-4}
0.37	0.347	0.474	3.5×10^{-11}	2.53×10^{-10}	2.88×10^{-10}	0.148	1.26×10^{-3}	1.87×10^{-4}	0.036
0.48	0.480	0.342	3.5×10^{-11}	3.63×10^{-10}	3.98×10^{-10}	0.023	9.11×10^{-4}	2.10×10^{-5}	0.171
0.60	0.597	0.225	3.5×10^{-11}	4.52×10^{-10}	4.87×10^{-10}	0	5.99×10^{-4}	0	0.365
0.71	0.709	0.112	3.5×10^{-11}	5.35×10^{-10}	5.70×10^{-10}	0	2.99×10^{-4}	0	0.456

Table 5. Characteristics of the support grain structure (model cube of $10 \times 10 \times 10$, Nafion is present in the grain, $g_e = 0.279$): $S_0 = 9.72 \times 10^{-10} \text{ cm}^2$

g_{i0}	g_{ii}	g_{gg}	$S_{\text{out}}, \text{cm}^2$	$S_{\text{in}}, \text{cm}^2$	S, cm^2	D^*	$D_{\text{kn}}, \text{cm}^2/\text{s}$	$D_{\text{kn}} D^*, \text{cm}^2/\text{s}$	k^{***}
0.23	0.038	0.683	8.4×10^{-11}	2.55×10^{-11}	1.10×10^{-10}	0.472	1.82×10^{-3}	8.61×10^{-4}	2.46×10^{-4}
0.33	0.301	0.420	8.4×10^{-11}	3.57×10^{-10}	4.41×10^{-10}	0.094	1.12×10^{-3}	1.06×10^{-4}	0.032
0.43	0.420	0.301	8.4×10^{-11}	5.20×10^{-10}	6.04×10^{-10}	0.019	8.03×10^{-4}	1.50×10^{-5}	0.103
0.53	0.522	0.199	8.4×10^{-11}	6.46×10^{-10}	7.30×10^{-10}	0	5.30×10^{-4}	0	0.227
0.62	0.620	0.101	8.4×10^{-11}	7.65×10^{-10}	8.49×10^{-10}	0	2.68×10^{-4}	0	0.348

Table 6. Characteristics of the support grain structure (model cube of $10 \times 10 \times 10$, Nafion is present in the grain, $g_e = 0.376$): $S_0 = 1.312 \times 10^{-9} \text{ cm}^2$

g_{i0}	g_{ii}	g_{gg}	$S_{\text{out}}, \text{cm}^2$	$S_{\text{in}}, \text{cm}^2$	S, cm^2	D^*	$D_{\text{kn}}, \text{cm}^2/\text{s}$	$D_{\text{kn}} D^*, \text{cm}^2/\text{s}$	k^{***}
0.21	0.049	0.576	1.63×10^{-10}	6.16×10^{-11}	2.25×10^{-10}	0.262	1.53×10^{-3}	4.02×10^{-4}	3.06×10^{-4}
0.25	0.189	0.435	1.63×10^{-10}	2.98×10^{-10}	4.61×10^{-10}	0.199	1.16×10^{-3}	2.30×10^{-4}	0.015
0.29	0.269	0.355	1.63×10^{-10}	4.68×10^{-10}	6.31×10^{-10}	0.051	9.46×10^{-4}	4.81×10^{-5}	0.019
0.38	0.368	0.257	1.63×10^{-10}	6.72×10^{-10}	8.35×10^{-10}	0.013	6.84×10^{-4}	8.57×10^{-6}	0.072
0.41	0.403	0.221	1.63×10^{-10}	7.38×10^{-10}	9.01×10^{-10}	2×10^{-4}	5.90×10^{-4}	1.19×10^{-7}	0.180
0.46	0.452	0.173	1.63×10^{-10}	8.28×10^{-10}	9.91×10^{-10}	0	4.60×10^{-4}	0	0.204
0.50	0.494	0.131	1.63×10^{-10}	9.04×10^{-10}	1.07×10^{-9}	0	3.48×10^{-4}	0	0.242

Table 7. Characteristics of the support grain structure (model cube of $10 \times 10 \times 10$, Nafion is present in the grain, $g_e = 0.494$): $S_0 = 1.622 \times 10^{-9} \text{ cm}^2$

g_{i0}	g_{ii}	g_{gg}	$S_{\text{out}}, \text{cm}^2$	$S_{\text{in}}, \text{cm}^2$	S, cm^2	D^*	$D_{\text{kn}}, \text{cm}^2/\text{s}$	$D_{\text{kn}} D^*, \text{cm}^2/\text{s}$	k^{***}
0.19	0.068	0.438	2.57×10^{-10}	1.49×10^{-10}	4.06×10^{-10}	0.089	1.17×10^{-3}	1.04×10^{-4}	5.26×10^{-4}
0.25	0.223	0.283	2.57×10^{-10}	5.70×10^{-10}	8.27×10^{-10}	0.019	7.54×10^{-4}	1.44×10^{-5}	0.015
0.32	0.292	0.214	2.57×10^{-10}	7.70×10^{-10}	1.03×10^{-9}	3.27×10^{-4}	5.71×10^{-4}	1.86×10^{-7}	0.036
0.38	0.354	0.152	2.57×10^{-10}	9.35×10^{-10}	1.16×10^{-9}	0	4.05×10^{-4}	0	0.071
0.44	0.413	0.093	2.57×10^{-10}	1.09×10^{-9}	1.35×10^{-9}	0	2.48×10^{-4}	0	0.111

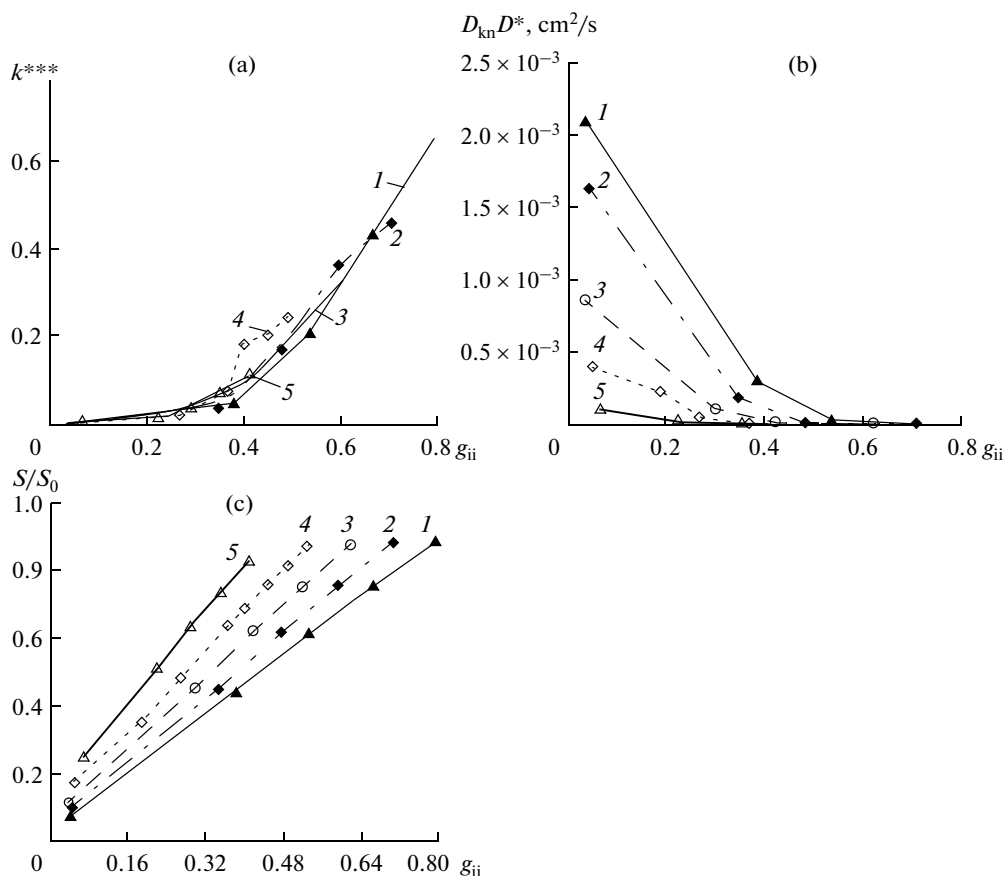


Fig. 3. In the support grains: the dependences of (a) the normalized effective conductivity of the protonic percolation cluster k^{***} , (b) the effective Knudsen diffusion coefficient of gas D^* , and (c) the normalized total active surface of the carbon cluster S/S_0 on the volume fraction of Nafion in support grains g_{ii} . The values of g_c : (1) 0.072, (2) 0.179, (3) 0.279, (4) 0.376, (5) 0.494.

At the same time, columns 5 and 6 (Table 2) are renewed ($S_{in,0}$ and S_0): now S_{in} is the total number of contacts of the inner faces of the carbon cluster with Nafion particles involved in the cluster. Column 6 in Tables 3–7 represents the sum of surfaces S_{out} and S_{in} .

The next three columns in Tables 3–7 are similar to those in Table 2 but take account of the fact that in addition to the carbon cluster (Table 2), one more cluster of Nafion particles has appeared (the free space in the support grain decreases and so are the diffusion coefficients).

The last column in Tables 3–7 shows the effective specific proton conductivity. This quantity is dimensionless. The true effective specific proton conductivity of support grains k^{**} , $S \text{ cm}^{-1} = k_0 k^{***}$, where $k_0 = 0.1 \text{ S cm}^{-1}$ is the specific optimal proton conductivity of Nafion.

Note once more that the grains of all types in the cathode active layer are considered as identical. Thus, we will calculate the electrochemical characteristics of active layers with the regular and optimized structure.

The brief inspection of data in Tables 3–7 reveals the evident: as the support grain are filled with Nafion

(columns 2, values g_{ii}), the effective proton conductivity k^{***} steadily increases (Fig. 3a). Moreover, irrespective of parameter g_c , all the curves are described by approximately the same dependence.

The quite different situation is with the dependence of the effective Knudsen diffusion coefficient of oxygen $D_e = D_{kn}D^*$ on g_{ii} (Fig. 3b), because the carbon- and Nafion-free volume in the support grain decreases and the diffusion coefficient also rapidly falls to zero.

On the other hand, the surface fraction of the carbon cluster involved in the electrochemical process S_0 increases (Fig. 3c, S_0 in Tables 3–7 is the optimal surface of the carbon cluster corresponding to the carbon component content in support grains g_c and gradually increases with the increase in g_c). Figure 3c also shows that at considerable concentrations g_{ii} , the electrochemical process can involve about 90% of the carbon cluster surface.

The analysis of data shown in Tables 3–7 evidently poses the question of what the optimal filling of the support grains with Nafion should be and, generally, how the main parameters of support grains, i.e., g_c (the

Table 8. Dependence of effective characteristics of the active layer on the component composition of support grains (model cube of $100 \times 100 \times 100$)

g_c	g_{ii}	$k^{**}, S \text{ cm}^{-1}$	$D^{**}, \text{cm}^2/\text{s}$	S, cm^2	S_0, cm^2
0.072	0.038	0.0114	0.0255	1.97×10^{-11}	2.66×10^{-10}
	0.383	0.0164	0.0232	1.17×10^{-10}	
	0.535	0.0268	0.0228	1.62×10^{-10}	
0.179	0.043	0.0114	0.0249	6.28×10^{-11}	6.47×10^{-10}
	0.347	0.0156	0.0230	2.88×10^{-10}	
	0.480	0.0251	0.0228	3.98×10^{-10}	
0.279	0.038	0.0114	0.0239	1.09×10^{-10}	9.72×10^{-10}
	0.301	0.0152	0.0229	4.41×10^{-10}	
	0.420	0.0210	0.0228	6.04×10^{-10}	
0.376	0.049	0.0114	0.0233	2.25×10^{-10}	1.312×10^{-9}
	0.269	0.0138	0.0228	6.31×10^{-10}	
	0.403	0.0256	0.0227	9.01×10^{-10}	
0.494	0.068	0.0114	0.0229	4.06×10^{-10}	1.622×10^{-9}
	0.223	0.0133	0.0228	8.27×10^{-10}	
	0.292	0.0333	0.0228	1.03×10^{-9}	

volume concentration of carbon particles in the support grain), g_{ii} (the volume concentration of Nafion particles in the support grain), and g_{gg} (the volume concentration of voids in the support grain, its value can be determined based on the known g_c and g_{ii} by using the condition (2)) affect the current on the cathode with polymer electrolyte.

Thus, we have to determine the conditions at which the effective coefficients of the active layer, namely, the effective proton conductivity k^{**} and the effective diffusion coefficient of oxygen in the active layer D^{**} are optimal.

6. EFFECTIVE COEFFICIENTS OF THE ACTIVE LAYER

In the case under study, the active layer includes the full-value electronic percolation cluster (the fraction of support grains $g = 0.5$) and two combined percolation clusters: protonic (the fraction of Nafion grains $g_i = 0.25$) and gas (the fraction of voids $g_{gas} = 0.25$). The concentration 0.25 is insufficient for the appearance of full-value protonic and gas percolation clusters. In Section 2, it was shown that the concentrations of the corresponding grains should exceed 0.35.

The combined clusters are added up of grains of one or another type and the support grains that, as was demonstrated in Section 5 (data of Table 3–7), exhibit intrinsic proton conductivity and are capable of taking part in the diffusion process.

As was mentioned above, the method of calculating the effective proton conductivity $k^{**}, S \text{ cm}^{-1}$ and the effective diffusion coefficient of oxygen $D^{**}, \text{cm}^2 \text{ s}^{-1}$ was described in [16]. Table 8 shows the results of thorough calculations for the case under consideration (columns 3 and 4) and also contains information on the surface of the carbon cluster in support grains S_0

and its part S accessible to the electrochemical process, because it is on the latter surface that the platinum-covered surface of the carbon cluster comes in contact with the proton-supplying cluster of Nafion particles.

The first column of Table 8 shows the selected reference values of the carbon material concentration in support grains g_c . The carbon clusters corresponding to these parameters have the active surface S, cm^2 and are shown in next to last column of Table 8. As the content of carbon particles in support grains increases, the carbon cluster surface S_0 increases very rapidly. However, according to Table 2 (column 6), this increase is limited and when the concentration $g_c = 0.549$ is reached the surface of carbon clusters begins to decrease.

Column 2 in Table 8 contains the concentrations of Nafion g_{ii} in support grains taken from Tables 3–7. As this parameter increases, the effective proton conductivity of the active layer k^{**} naturally increases. Moreover, the fraction of the active (proton-supplied) surface of the carbon cluster S also increases. It is clear that the effective diffusion coefficient D^{**} should decrease with the increase in g_{ii} if for no other reason than the decreasing gas porosity.

The bulk of data shown in Table 8 makes it possible to begin calculating the overall currents and the optimal thicknesses of cathode active layers.

7. OVERALL CHARACTERISTICS OF CATHODES

At the reduction of oxygen on platinum in acidic media, the polarization curves demonstrate two slopes: 60 mV (high potentials) and 120 mV (low potentials) [18–21]. The method of calculating the currents on cathodes based on polarization curves with two different slopes was demonstrated in [22].

We carry out the calculations of overall characteristics of cathodes under the assumption that the cathode potential $E_0 = 0.6$ V, the fuel cell temperature $t = 80^\circ\text{C}$, the gas-chamber pressure $p^* = 101$ kPa, the oxygen solubility in Nafion at $p^* = 101$ kPa, $c_0 = 5 \times 10^{-6}$ g-mol/cm³, the optimal specific conductivity of Nafion $k = 0.1$ S cm⁻¹, and the active layer thickness Δ is varied in order to find the optimal active layer thickness Δ^* which provides the maximum possible current.

When calculating, allowance should be made for the fact that the characteristic ohmic length L_{ohm} and the characteristic ohmic current I_{ohm} in the high potential region take the form

$$L_{\text{ohm}} = [b_1 k^{**} L^3 / gS i_0]^{1/2}, \quad (10)$$

$$I_{\text{ohm}} = [b_1 k^{**} gS i_0 / L^3]^{1/2}. \quad (11)$$

The characteristic diffusion length L_d and the characteristic diffusion current I_d in the high potential region are described as

$$L_d = [nFc_0 D^{**} L^3 / gS i_0]^{1/2}, \quad (12)$$

$$I_d = [nFc_0 D^{**} gS i_0 / L^3]^{1/2}. \quad (13)$$

Here, $b_1 = 2.6 \times 10^{-2}$ V and $b_2 = 5.2 \times 10^{-2}$ V are two slopes of the polarization curve of oxygen reduction on platinum (in the regions of high and low potentials, respectively), $L = 100$ nm is the edge length of grains in the active layer, S is the surface of carbon cluster faces in support grains, open to the electrochemical process, $i_0 = 1.01 \times 10^{-7}$ A/cm² is the exchange current in the high potential region at $t = 80^\circ\text{C}$, $n = 4$ is the number of electrons involved in the electrochemical process, F is the Faraday number, $g = 0.5$ is the fraction of support grains in the active layer, and, finally, k^{**} is the specific proton conductivity and D^{**} is the effective diffusion coefficient of oxygen in the active layer.

Table 9 shows the results of calculations of the maximum currents on cathodes I_{max} , A/cm² which are attained at the optimal thickness Δ^* and the set of main parameters of support grains, namely, g_c , g_{ii} , and g_{gg} .

The data of Table 9 show that the maximum current I_{max} increases monotonously with the increase in the volume content of the carbon component in support grains g_c , while the optimal thickness of the active layer Δ^* decreases from 100 to 10 μm . The same tendency towards the increase in the current is observed as the volume concentration of Nafion in support grains g_{ii} increased (at the fixed value of parameter g_c).

If now for triads of concentrations g_{ii} (Table 9) we take the average values at fixed g_c (the series of values 0.383, 0.347, 0.301, 0.269, 0.223), then we can see how the dependences of the maximum current I_{max} (curve 1, axis of currents on the left) and the optimal thickness of the active layer Δ^* (curve 2, axis of thicknesses on the right) depend on the carbon component content in support grains g_c . The higher the maximum possible current, the lower the active layer thickness and vice versa.

Table 9. The cathode maximum current I_{max} and the corresponding optimal thickness of the active layer Δ^* as a function of the support grain composition. The pressure in the gas reagent supplying chamber $p^* = 101$ kPa, the temperature $t = 80^\circ\text{C}$, the cathode potential $E_0 = 0.6$ V (all calculations were carried out with the model cube of $100 \times 100 \times 100$)

g_c	g_{ii}	g_{gg}	I_{max} , A/cm ²	Δ^* , μm
0.072	0.038	0.890	0.66	89.9
	0.383	0.545	1.90	37.8
	0.535	0.393	2.76	34.1
0.179	0.043	0.778	1.18	50.1
	0.347	0.474	2.91	23.8
	0.480	0.342	4.21	21.6
0.279	0.038	0.683	1.56	37.4
	0.301	0.420	3.56	19.1
	0.420	0.301	4.80	17.1
0.376	0.049	0.576	2.24	25.7
	0.269	0.355	4.08	15.7
	0.403	0.221	6.39	14.3
0.494	0.068	0.438	3.32	17.3
	0.223	0.283	4.59	13.7
	0.292	0.214	7.64	13.7

Now we consider Fig. 5. It shows how the conditional consumption of the catalyst (platinum) per unit of electric power generated in the cathode of a fuel cell with polymer electrolyte depends on the carbon mass concentration in the support grains g_c . More precisely, it shows the ratio g_c/W_{max} , where $W_{\text{max}} = 0.6I_{\text{max}}$. Thus the platinum consumption is the minimum at the low filling of grains; as the latter increases g_c/W_{max} also increases.

The latter conclusion may appear quite trivial but this is not true. The point is that at low loads of support grains with carbon, the advantageous conditions are created for generation of current in support grains as compared with the higher loads. Were not this true, curve 5 would take the strictly horizontal position.

In Table 9, we select certain "average" values of grain parameters. For instance, let $g_c = 0.279$ and $g_{\text{ii}} = 0.420$ (then, $g_{\text{gg}} = 0.301$). Now, we see how the main parameters of the fuel cell cathode change with variations in the temperature (Fig. 6). As the temperature increases, the exchange current changes (these changes are shown in the legend to Fig. 6). This is why the maximum current I_{max} increases and the optimal active layer thickness Δ^* decreases with the increase in the temperature.

And finally, we vary also the cathode potential (Fig. 7). The result is also obvious: the current increases and the active layer optimal thickness decreases with the decrease in the cathode potential.

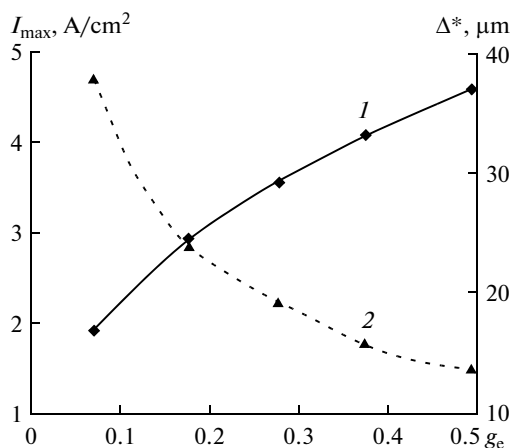


Fig. 4. Dependences of (1) the maximum current in the cathode of a solid polymer electrolyte fuel cell I_{\max} and (2) the corresponding optimal thickness Δ^* of the active layer on the composition of components in support grains (for explanation, see text). The pressure in the gas reagent supplying chamber $p^* = 101$ kPa, the cathode potential $E_0 = 0.6$ V, the temperature $t = 80^\circ\text{C}$.

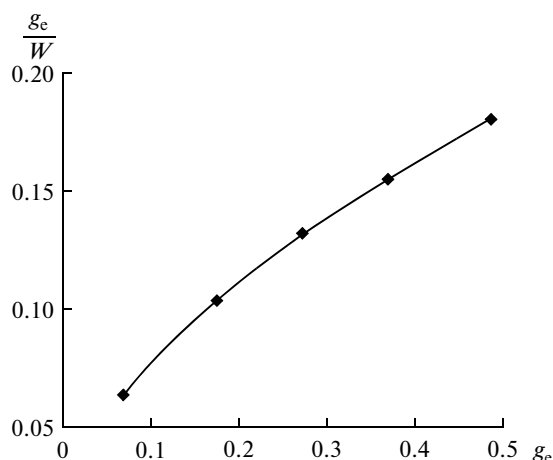


Fig. 5. Dependence of the conditional consumption of the catalyst (platinum) per unit of electric power generated in the cathode of a solid polymer electrolyte fuel cell on the volume concentration of the catalyst in support grains. The pressure in the gas reagent supplying chamber $p^* = 101$ kPa, the cathode potential $E_0 = 0.6$ V, the temperature $t = 80^\circ\text{C}$.

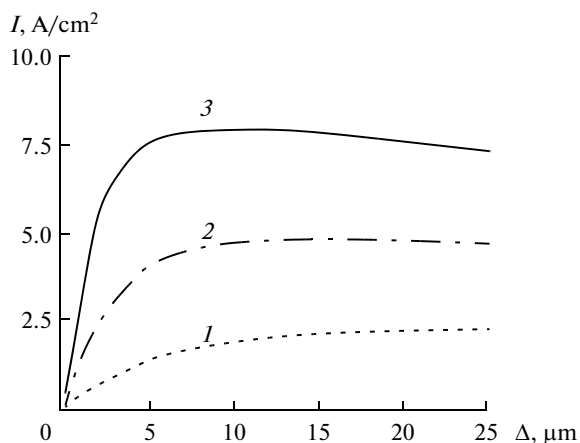


Fig. 6. Dependence of the current on the cathode with solid polymer electrolyte I on the active layer thickness Δ . Parameters of support grains: $g_e = 0.279$, $g_{ii} = 0.420$. $t, ^\circ\text{C}$: (1) 60 ($i_0 = 2.27 \times 10^{-8}$ A/cm², $\Delta^* = 36$ μm , $I_{\max} = 2.28$ A/cm²), (2) 80 ($i_0 = 1.01 \times 10^{-7}$ A/cm², $\Delta^* = 17$ μm , $I_{\max} = 4.80$ A/cm²), (3) 95 ($i_0 = 2.80 \times 10^{-7}$ A/cm², $\Delta^* = 10$ μm , $I_{\max} = 8.0$ A/cm²). The pressure in the gas reagent supplying chamber $p^* = 101$ kPa, the cathode potential $E_0 = 0.6$ V.

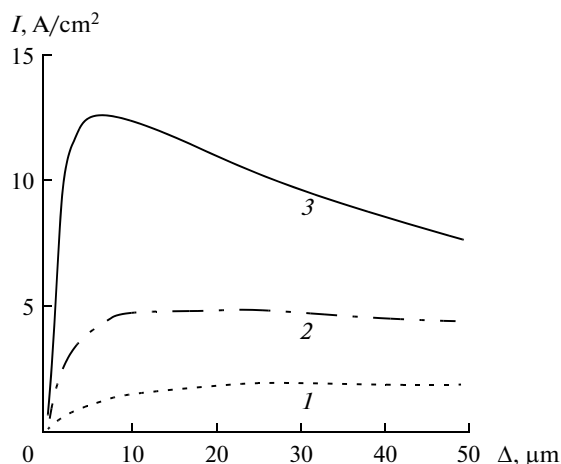


Fig. 7. Dependence of the current of cathode with solid polymer electrolyte I on the active layer thickness Δ . Parameters of support grains: $g_e = 0.279$, $g_{ii} = 0.420$. Cathode potential, E_0, V : (1) 0.7 ($\Delta^* = 45$ μm , $I_{\max} = 1.84$ A/cm²), (2) 0.6 ($\Delta^* = 17$ μm , $I_{\max} = 4.80$ A/cm²), (3) 0.5 ($\Delta^* = 7$ μm , $I_{\max} = 12.6$ A/cm²). The pressure in the gas reagent supplying chamber $p^* = 101$ kPa, the temperature $t = 80^\circ\text{C}$, the exchange current $i_0 = 1.01 \times 10^{-7}$ A/cm².

The results of Figs. 6 and 7 could have been still more impressive had we taken the support grain parameters (the value g_e and g_{ii}) from the lower part of Table 9. For example, the pair $g_e = 0.494$ and $g_{ii} = 0.292$ (in this case, $g_{gg} = 0.214$).

On the other hand, here, on the attainment of such high values of the maximum current, the limitations may arise associated with the removal of the electro-

chemical reaction product—water. This is why the values of I_{\max} and Δ^* obtained in calculations would no longer reflect the situation.

The problem of the removal of the electrochemical reaction product from the active layer of the cathode in polymer electrolyte fuel cells is very complicated. However, it is beyond the scope of our studies.

8. CONCLUSIONS

The active layer of the cathode in polymer electrolyte fuel cells is a very complicated structure characterized by 8 parameters. Let us list them.

They include three transport parameters that determine the delivery of everything necessary for the electrochemical process (electrons, protons, and oxygen molecules) to the active layer, namely, the volume fractions of support grains g , Nafion grains g_i , and grains-voids g_{gas} . Insofar as the sum of these fraction gives unity, we have only two independent parameters and assume them to be the pair of g and g_i . Together they form the parameters of the so-called "upper level" of the active layer structure.

The "lower level" of the active layer structure represents the support grains in which the electrochemical reaction as such is realized. The process occurs on the catalyst(platinum)-covered surface of carbon particles within the support (they are assembled into carbon clusters). The protons and oxygen molecules are delivered from the support grain surface to its bulk via the clusters of Nafion particles and fine pores-voids in which the Knudsen diffusion of oxygen (or air) occurs.

The structural peculiarities of support grains are also determined by three parameters: the volume concentration of the carbon material g_c , the volume concentration of Nafion in the support grain g_{ii} , and the total volume of voids in the support grain g_{gg} . When added up these values also produce unity; thus, only two of them can be considered as independent parameters. For definiteness sake, we assume that these are g_c and g_{ii} .

Thus we have listed four active-layer parameters. As to the support grains (they were assumed to be identical in all calculations, as well as the Nafion grains and the grains-voids), they are characterized by three more parameters. The grain size L (the edge of the model grain cube), the edge of small carbon cubes d and the edge of small Nafion cubes δ . In our calculations, we have assumed that $L = 100$ nm, $d = 10$ nm, and $\delta = 2$ nm. These three parameters have probably reached their smallest values and should hardly be varied.

There remains the 8th structural parameter, the active layer thickness Δ . The necessity arises to determine the optimal thickness as Δ^* at which the current reaches its maximum value I_{max} . Thus, the properties of the active layer are in fact determined by five parameters: Δ^* , g , g_i , g_c , and g_{ii} .

The optimum g value was found in this paper. It was concluded that the value $g = 0.5$ should be taken, if one wants to maximally save the catalyst (platinum) and simultaneously obtain the maximum currents. The value g_i (and also g_{gas} , because $g_i + g_{\text{gas}} = 0.5$) can be selected conditionally, in view of problems in hand. In this study, when calculating the cathode characteristics, we assumed $g_i = g_{\text{gas}} = 0.25$.

The peculiarity of the system under study is that a large number of parameters make it polyvariant. The required sets of parameters should be selected depending on the goal.

Let us list the problems posed by the practice:

1. Organization of the efficient removal of water, the electrochemical reaction product from the active layer.

2. Attainment of the high currents and, correspondingly, the high overall power.

3. Provision of the low amounts of consumed platinum per unit of electric power realized in the fuel cell.

The first problem was beyond the scopes of our study. As was shown by the analysis accomplished here, to solve the second problem one has to operate with the high values of parameter g_c (the concentration of platinum-filled carbon material in support grains), disregarding the high expenditures of platinum. It was demonstrated that the solution of the third problem requires the opposite: the maximum possible g_c should be provided in support grains.

The last important remark. Insofar as three full-value percolation clusters—electronic, protonic, and gas—cannot be organized in the active layer, one has to deal with one or even two peculiar combined percolation clusters in the active layer; however, in this case, the double load falls on the support grains. Their optimal structure should not only provide the electrochemical process in the grain but also sustain the processes of transportation of protons and oxygen molecules in the active layer.

LIST OF ABBREVIATIONS OF PARAMETERS CHARACTERIZING A FUEL CELL WITH NAFION AND PLATINUM AND THEIR VALUES USED IN CALCULATIONS

The "Upper Level" Parameters of the Cathode Active Layer Structure

$t = 60, 80, 95^\circ\text{C}$ is the fuel cell temperature

$p^* = 101$ kPa is the pressure in the gas chamber

$c_0 = 5 \times 10^{-6}$ g-mol/cm³ is the oxygen solubility in Nafion at $p^* = 101$ kPa

Δ is the active layer thickness, it is varied

Δ^* is the optimal active layer thickness

$L = 100$ nm = 10^{-5} cm is the length of the edge of support grains, Nafion grains, and grains-voids

$k = 0.1$ S cm⁻¹ is the specific optimal proton conductivity of Nafion

I , A/cm² is the current

W , W/cm² is the power

g is the fraction of support grains in the active layer

g_i is the fraction of Nafion grains in the active layer

g_{gas} is the fraction of grains-voids in the active layer

$g^{***} = 0.298$ is the percolation threshold for the electronic cluster

$g_i^{***} = 0.298$ is the percolation threshold of the protonic cluster

$g_{\text{gas}}^{***} = 0.298$ is the percolation threshold for the gas cluster

k^{**} , S cm⁻¹ is the effective proton conductivity of the active layer

D^{**} , cm²/s is the effective diffusion coefficient of oxygen (air) in the active layer.

Electrochemical Parameters

E_{st} = 1.05 V is the stationary cathode potential

E^* = 0.825 V is the potential of the break in the polarization curve

E_0 = 0.6 V is the cathode potential

b_1 = 2.6×10^{-2} V is the Tafel curve slope in the region of high potentials

b_2 = 5.2×10^{-2} V is the Tafel curve slope in the low potential region

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

i_0 = 1.01×10^{-7} A/cm² is the exchange current in the high potential region at $t = 80^\circ\text{C}$

F = 9.65×10^4 C/mol is the Faraday number.

Parameters of Support Grains ("the Lower Level" of the Active Layer)

g_0 is the initial volume concentration of carbon microcubes in support grains

g_e is the final volume concentration of carbon microcubes in support grains

S_{out} is the number of faces exposed to the surface of the support grain

S_{in} is the active surface of the optimal carbon cluster inside the Nafion-containing support grain

$S_{in,0}$ is the surface of the optimal carbon cluster inside the Nafion-free support grain

$S_0 = S_{out} + S_{in,0}$ is the total number of faces on the surface of a carbon cluster in a Nafion-free support grain

S is the total active surface of the carbon cluster in a Nafion-containing support grain

S_0 is the total surface of a carbon cluster in the Nafion-free support grain

g_{ii} is the volume concentration of Nafion involved in the Nafion cluster of support grains

$g_{i,0}$ is the initial volume concentration of Nafion in support grains

g_{gg} is the porosity formed by voids in the Nafion-containing support grain

k^{***} (dimensionless value) is the effective conductivity of the protonic cluster in support grains

D_{kn} , cm²/s is the effective Knudsen diffusion coefficient of gas in pores of support grains (takes into account the average pore size)

D^* is the effective Knudsen diffusion coefficient of gas in the Nafion-containing (dimensionless parameter, takes into account the support grain microstructure)

D_0^* is the effective Knudsen diffusion coefficient of gas in the Nafion-free support grain (dimensionless

parameter, describes the role of the support grain microstructure)

$D_e = D_{kn}D^*$, cm²/s is the effective Knudsen diffusion coefficient of gas in support grains

$d = 10$ nm = 10^{-6} cm is the length of edges of carbon grains-cubes in support grains

$\delta = 2$ nm = 2×10^{-7} cm is the length of edges of Nafion particles-cubes in the support grains.

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