

# Active Layer of Fuel Cell Electrode with Polymer Electrolyte: Nature of Proton and Oxygen Supply Channels

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**Abstract**—The nature of proton and oxygen supply channels in the active layer of a cathode of fuel cell with polymer electrolyte is discussed. There are three types of electron, proton, and oxygen carriers in the active layer: agglomerates of carbon particles with supported platinum (support grains), agglomerates of Nafion molecules (Nafion grains), and void grains. In computer simulation of the active layer structure, the three types of grains were assumed equal-sized, cube-shaped and arranged into a cubic node lattice (in the terms of the percolation theory). Impossibility of forming on the basis solely the above three grain types of three percolation clusters (“electron”, “proton”, and “gas”) that could supply all that is required for the electrochemical process is proved. But in this, the following question arises: how can satisfactory operation of the cathode with polymer electrolyte be provided? The required supply of protons and oxygen can be provided only if the support grains can feature not only electronic conductivity, but can also participate in transport of both protons and oxygen. As a result, the transport of protons and oxygen is carried out via special combined percolation clusters that must include apart from the support grains either Nafion grains (combined “proton” cluster) or void grains (combined “gas” cluster). The paper describes the technique of calculation of effective specific conductivity of a combined “proton” cluster. The effective specific diffusion coefficient of a combined “gas” cluster can also be calculated in a similar way.

**Keywords:** fuel cell with polymer electrolyte, active layer, supply channels of protons and oxygen in the active layer, computer simulation, percolation, percolation threshold, combined percolation clusters, calculation of effective specific conductivity of a combined “proton” cluster

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## 1. PROBLEM STATEMENT

Low-temperature hydrogen–oxygen (air) fuel cells with polymer electrolyte (Nafion) and platinum as a catalyst remain one of the main candidates for the role of self-contained high-performance sources of environmentally clean electric power. The issue of the greatest concern is the active cathode layer where the oxygen reduction process occurs. Here, it is important above all to identify the nature of supply channels across the whole active layer depth of the three electrochemical process participants: electrons, protons, and oxygen.

A cathode with polymer electrolyte is a representative of the third generation of electrodes for hydrogen–oxygen fuel cells. The first two generations are hydrophilic electrodes with a pressure drop and barrier layer [1] and hydrophobized electrodes [2].

The first generation of cathodes was based on Raney catalysts. The active cathode layer was obtained by the sintering of metal (catalyst) particles in the presence of a pore agent. Removal of the latter resulted in development of porous space with large (free of pore

agent) “gas” pores (electrolyte was removed from them with the help of a pressure drop) and small (space between the catalyst particles) “electrolyte” pores filled by liquid electrolyte. The main problem of the first generation of cathodes consisted in development of a connected system of large pores. It was such a “gas” cluster that provided access to the active cathode layer of gas reagents (oxygen or air).

Thus, porous agglomerates of catalyst metal particles impregnated by solution of electrolyte in hydrophilic electrodes had a double function: they supplied both electrons (metallic phase) and ions (liquid electrolyte) into the active layer. And the gas was supplied via specially formed large pores free of electrolyte.

The second generation of cathodes was prepared by the mixing and further sintering of agglomerates (let us further denote them as grains) catalyst particles and agglomerates of hydrophobic (fluoroplast) particles (grains). Now, the gas was supplied into the active layer via chains of interconnected hydrophobic grains (their internal small hydrophobic pores remained unfilled by electrolyte, there was already no need in the pressure drop). Thus, a “gas” cluster was developed and elec-

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trons and ions were supplied through porous catalyst grains wetted by electrolyte.

Thus, the mechanism of reagent supply in the first two generations of cathodes was practically similar. It was required to organize two clusters extending across the whole depth of the active layer: the gas cluster and “electron–ion” cluster. And no fundamental problems appeared here.

The active layer of the third generation of cathodes represents already a three-component mixture. These are agglomerates (grains) of Nafion molecules (liquid electrolyte is replaced by solid polymer electrolyte). Agglomerates (grains) of particles of conducting carbon support with platinum black (catalyst) nanoparticles applied on the surface. These are also void grains inevitably appearing in the course of cathode active layer manufacturing.

Active layer formation includes the most important stage of preparation of the so called catalytic ink, a suspension of a mixture of carbon particles and Nafion molecules. Herewith, the suspension undergoes prolonged ultrasonic treatment favoring the vigorous mixing of carbon particles and Nafion molecules.

The active layer structure becomes most complicated in cathodes with polymer electrolyte. The number of clusters required for adequate cathode operation is increased to three. These are: the “gas” cluster (void grains, the potential channel for gas supply and removal of the electrochemical reaction product, water vapors), “electron” cluster (the system of support grains conducting electrons), and “ion” cluster (a system of Nafion grains conducting protons). Each of these clusters must be macroscopic: it must be extended across the whole active layer depth.

Here, as shown below, problems appear. The aim of this study is to answer the question whether it is possible to generate in the active layer with polymer electrolyte three independent clusters providing transport of electrons, protons, and oxygen molecules. If it appears that it is impossible in principle, then, the question is as to the true nature of the support channels of all electrochemical process participants is in the third generation of the cathodes.

The answer to the above questions can be obtained using computer simulation of the active layer structure in a cathode with polymer electrolyte.

## 2. ACTIVE LAYER STRUCTURE

The active layer microstructure was experimentally studied in detail in a large number of works. The presence of the support particle agglomerates (grains) was shown. It was assumed at first that the carbon particle sizes of which these were composed were in the range of ~20–40 nm. The size of their agglomerates was ~200–300 nm. Voids between the support grains were estimated as ~40–300 nm. It was assumed that this space was partially filled by agglomerates (grains) of

molecules of polymer electrolyte (Nafion). The size of individual platinum particles in the support grains was ~2–3 nm.

The intention to increase the specific surface area of the carbon support and enhance the intensity of the electrochemical process resulted in the fact that the carbon particle size is at present down to ~5–10 nm. The support grain size is estimated already as ~30–100 nm [3, 4].

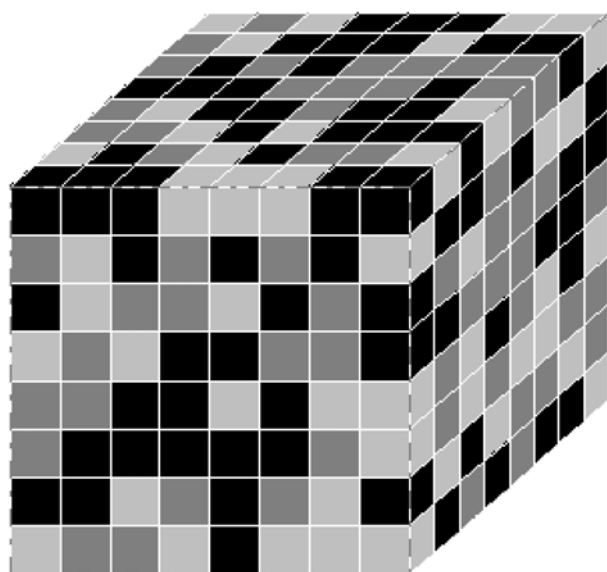
The processes of self-organization of elements forming the structure of the active layer of the cathode with polymer electrolyte (different techniques of catalytic ink preparation) were studied, e.g., in [4, 5]. This research trend has the common name of molecular dynamics simulations. The illustrative material presented in [4] demonstrates how carbon particles and Nafion molecules form the corresponding support and Nafion agglomerates (grains). One can also clearly see the presence of void grains.

The early attempts to describe the active layer microstructure employed experimental techniques allowing destructive serial sectioning of pore casts with the following attempts to reconstruct the pore space using mathematical calculations [6, 7]. Later, research techniques without destruction of the initial material appeared. X-ray techniques and magnetic resonance computed microtomography were used [8, 9].

The most interesting approach in such studies consists in the following. At first, the whole microstructure of the active layer in a cathode with Nafion and platinum on a carbon support is studied using the electron microscopy techniques: TEM (transmission electron microscopy) and SEM (scanning electron microscopy). Then, the obtained 2D statistical information is processed mathematically (stochastic technique): thus, the active layer structure can be reconstructed and its 3D image can be reproduced on the basis of its 2D images. The details of the techniques used here can be seen in [3, 10–13].

Thus, the microstructure of the active layer of the cathode with polymer electrolyte appears as a composite of support grains, Nafion grains, and void grains. Of course, these components feature a certain size distribution and have different 3D configuration. However, one can attempt to the first approximation to represent this grain triad in the form of a model of equal-size and similar-shape grains of three types and start working with the “model of equally sized grains”.

Now it is necessary to agree about the shape of these grains. It would appear that the grains have the shape of spheres. However, the model of equally sized spheres has obvious faults. Firstly, regular porosity (intersphere space) of strictly fixed value appears at any packing of spheres. The volume of void grains in the active layer can be arbitrary and these voids are randomly distributed in the active layer.



**Fig. 1.** Model of the active layer of a cathode with polymer electrolyte. A model cube with the size of  $8 \times 8 \times 8$  of three types of equally sized cubic grains. Black microcubes: support grains (their volume is 40%); dark-gray microcubes: Nafion grains (their volume is 30%); light-gray microcubes: void pores (their volume is 30%).

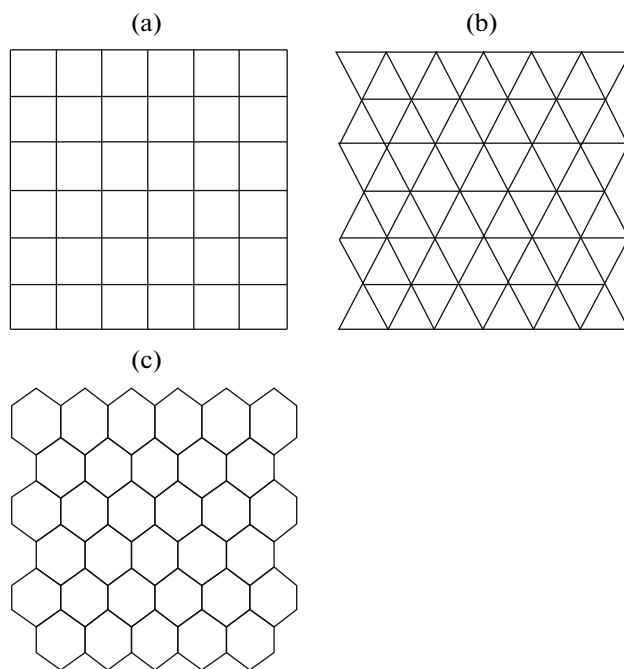
Secondly, in the sphere model, the junction surface of grains, where the electrochemical process basically occurs and where protons and oxygen molecules must be supplied represents the sum of junction surfaces of geometric points, so that the area of this surface is actually zero.

With account for the above, it is preferable to characterize the active cathode layer not on the basis of the model of equally sized spheres, but the model of equally sized cubic grains. This model is presented in Fig. 1. One can see that the packing of cubic grains can be characterized by arbitrary gas porosity and significant (different from zero) surface of contacts of grains of different types.

A model cube representing the active layer of a cathode with Nafion meant for computer simulation of the structure and processes in the cathode with polymer electrolyte must be macroscopic. The sizes of grains are  $\sim 100 \text{ nm} = 10^{-5} \text{ cm}$ ; the active layer thickness is  $\sim 10 \text{ }\mu\text{m} = 10^{-3} \text{ cm}$ . Therefore, the studied model cube simulating the active layer must be sufficiently large. Let us assume that the model cube volume of  $100 \times 100 \times 100 = 10^6$  consists of a million of grains of three types.

Let us introduce some notations. Let  $g$  be the bulk concentration (fraction) of support grains in the model cube,  $g_i$  is the fraction of Nafion grains,  $g_{\text{gas}}$  is the volume fraction of voids. Obviously, the following relationship is true:

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



**Fig. 2.** Planar regular lattices: (a) square, (b) triangular, (c) honeycomb.

Clusters (sets of interconnected grains of various types) appear spontaneously in the model cube (Fig. 1). The presence of such clusters extended across the whole active layer depth (model cube) and provides full progress of the electrochemical process in the cathode. Conditions at which formation of such clusters being channels for supply of electrons, protons, and oxygen molecules into the active layer becomes possible and properties of such clusters must be discussed within the terms of a special branch of mathematics and theoretical physics denoted as the percolation theory [14].

### 3. PERCOLATION THRESHOLD: EXACT FORMULAS

The percolation problem is as follows [14, 15]. A certain regular infinite lattice is set (examples of three planar lattices are shown in Fig. 2); its main elements are sites and bonds (bonds connecting neighboring sites).

Let us moisten an arbitrary (fluid-permeable) lattice site by an imaginary liquid. Let us also assume that lattice sites are only partially fluid-permeable (bonds with probability  $\gamma$  and sites with probability  $\omega$ ). It is necessary to calculate probability  $P(\gamma, \omega)$  of the fact that the liquid moving from site to site, from bond to bond via directly contacting, fluid-permeable sites and bonds would moisten an infinite number of these (the liquid may move away infinitely from the liquid source site).

**Table 1.** Exact values of percolation thresholds obtained for three planar regular lattices

Lattice type	$\gamma_*$	$\omega_*$
Square	0.5	It is assumed that the exact value is absent
Triangular	$2\sin(\pi/18) = 0.3473\dots$	0.5
Honeycomb	$1 - 2\sin(\pi/18) = 0.6527\dots$	It is assumed that the exact value is absent

This probability is denoted as percolation probability. Obviously, if the values of parameters  $\gamma$  and  $\omega$  are low, the liquid can penetrate only to a small distance, as it is blocked by bonds and sites impenetrable for liquid. In this range of values of parameters  $\gamma$  and  $\omega$ , percolation probability  $P(\gamma, \omega)$  is identically equal to zero.

However, when critical values of parameters  $\gamma$  and  $\omega$  are reached when they fall on curve  $\gamma_* = f(\omega_*)$  denoted here as percolation line, it becomes possible for the liquid to spread already infinitely. Herewith, in the region of two parameters  $\gamma > \gamma_*$  and  $\omega > \omega_*$ , percolation probability  $P(\gamma, \omega)$  starts differing from zero.

The problem of determination of percolation lines appears most general and is usually not considered. Only two limiting cases are studied. In the lattice of sites (site problem), the value of parameter  $\omega$  is varied and it is assumed herewith that parameter  $\gamma$  is equal to 1 (all lattice bonds are penetrable for liquid). In the lattice of bonds (bond problem), the value of parameter  $\gamma$  is varied and it is assumed herewith that parameter  $\omega$  is equal to 1 (all sites are penetrable for liquid). The critical values of parameters  $\gamma_*$  and  $\omega_*$  for these two limiting cases (time moments when percolation probability starts differing from zero) were denoted as percolation thresholds.

Determination of exact values of percolation thresholds is an extremely difficult problem. Indeed, it is necessary to consider here an infinite number of closed loops through which our imaginary liquid can leak. It is assumed at present that the exact values of percolation thresholds are known only for some planar lattices. Thus, for lattices in Fig. 2, we have only 4 values of percolation thresholds. They are given in Table 1. And it is commonly assumed that exact values of percolation thresholds for 3D lattices remain as yet unknown. This is however not true.

In [15], the overall method of calculation of exact values of percolation thresholds is described for bond lattices and site lattice and even for percolation lines. Exact values of percolation thresholds could be found for the important class of lattices simulating porous media, such as rectangular lattices: planar square, 3D cubic and their counterparts in a space with any number of dimensions.

For rectangular lattices, the general shape of percolation lines could be established for any number of dimensions  $d$ . They are determined for solution of the following characteristic equation:

$$2(d-1)\gamma^2\omega^3 + (2d-3)\gamma\omega - 1 = 0. \quad (2)$$

Assuming  $\omega = 1$  in (2), solution of the obtained square equation yields the general expression for the value of percolation threshold in the bond problem:

$$\gamma_* = 1/2(d-1). \quad (3)$$

At  $d = 2$  (square lattice in Table 1)  $\gamma_* = 0.5$ ; for a 3D cubic lattice ( $d = 3$ )  $\gamma_* = 0.25$ ; in a 4D space in a rectangular lattice ( $d = 4$ )  $\gamma_* = 1/6$ .

Assuming  $\gamma = 1$  in (2), solution of the obtained square equation yields the general expression for the value of percolation threshold in the bond site problem:

$$\omega_* = \{[1 + \{1 + 2(2d-3)^3/27(d-1)\}^{1/2}]/4(d-1)\}^{1/3} + \{[1 - \{1 + 2(2d-3)^3/27(d-1)\}^{1/2}]/4(d-1)\}^{1/3}. \quad (4)$$

We need the formulas just above to solve the problem stated in the first section of this paper. Is it possible to generate three independent macroscopic clusters providing transport of electrons, protons, and oxygen molecules in the active layer of the cathode with polymer electrolyte?

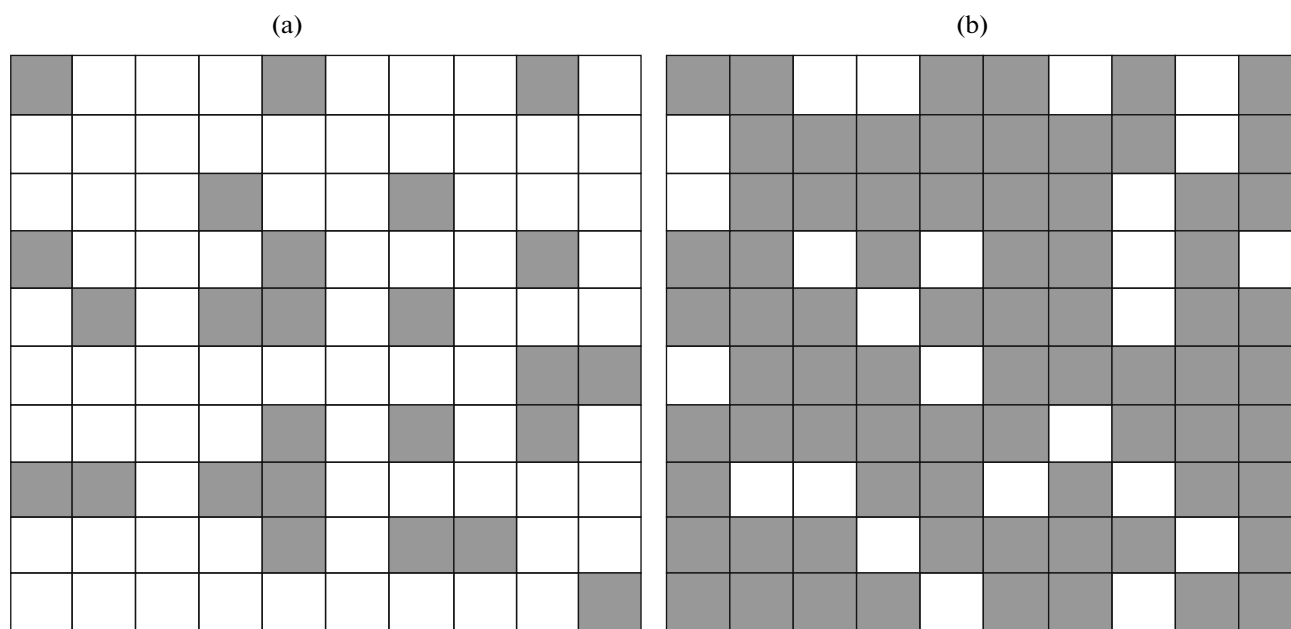
#### 4. PERCOLATION CLUSTERS IN PLANE AND IN BULK

Electrochemical processes occur in active layers of any chemical power sources, whether a primary cell, rechargeable battery, or fuel cell. Here, it is at least required to generate two percolation clusters, an electron and gas one, in active layers. This brings up a question. If electron and ion carriers are presented in the form of microcubes arbitrarily distributed across the cells of a macroscopic planar square (Fig. 2a), then, one may ask if two percolation clusters can be located in this region.

The answer to this question is given by formula (4). In the terms of the percolation theory, the model of equally sized grain (whether microcubes located in plane or in bulk, Fig. 1) has to deal with the site problem. Here, each microcube is connected through its faces either with four (in plane, Fig. 2a) or six (in bulk, Fig. 1) neighboring microcubes.

For a square site lattice, the exact critical value of the concentration (percolation threshold in the site problem) is (formula (4), let us substitute in it  $\omega$  by  $g$  and assume  $d = 4$ ) the only real equation root being [15]

$$2g^3 + g - 1 = 0. \quad (5)$$



**Fig. 3.** Regular square lattice of sites with the size of  $10 \times 10$ . Black squares: grains with electron conductivity; light squares: grains with ionic conductivity. (a) The concentration of electron grains is 0.25; there is an ion percolation cluster; it hinders appearance of an electron percolation cluster. (b) The concentration of electron grains is 0.75; there is only an electron percolation cluster; it hinders appearance of an ion percolation cluster.

Then, we have for the critical fraction of grains providing supply of electrons to the active layer:

$$g_* = \left[ \frac{1}{4} + \frac{(29/3)^{1/2}}{12} \right]^{1/3} + \left[ \frac{1}{4} - \frac{(29/3)^{1/2}}{12} \right]^{1/3} = 0.58975 \approx 0.59. \quad (6)$$

We see that if an electron percolation cluster is present in the planar macroscopic square, the fraction of grains providing supply of ions into the active layer cannot exceed  $1 - 0.59 = 0.41$ . But this value is already insufficient for appearance of an ion percolation cluster in the same region.

The result of our discussion is: two percolation clusters, electron and ion, in a planar square lattice cannot exist simultaneously. Fig. 3 helps visualizing this circumstance. In the square site lattice with the size of  $10 \times 10$ , black (conventional electron conductors) and light (conventional ion conductors) square grains are distributed randomly. If the concentration of electron grains  $g = 0.25$  (Fig. 3a), then only an ion (white) percolation cluster exists and it hinders appearance of an electron (black) percolation cluster. If  $g = 0.75$  (Fig. 3b), then there is an electron cluster and an ion cluster is absent.

Let us now pass from planar percolation clusters to 3D percolation clusters. Let us ask now whether it is possible to arrange simultaneous existence of three percolation clusters at once (electron, ion, and gas) in a 3D model cube composed of equally sized microcubes of three types.

Let us again turn to percolation theory. Again, we deal with a cubic lattice of sites. And again we can use formula (4). Let us assume now  $d = 3$ .

In the solution of the characteristic equation

$$4g^3 + 3g - 1 = 0, \quad (7)$$

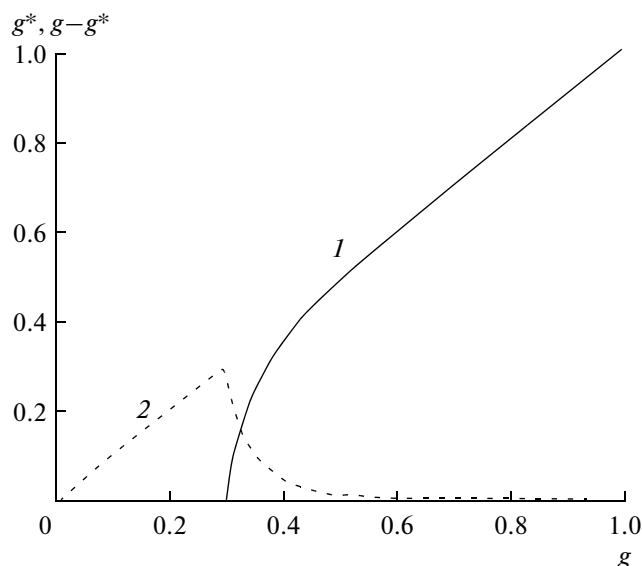
we find the percolation threshold:

$$g_* = \left[ \left( 1 + 2^{1/2} \right)^{1/3} + \left( 1 - 2^{1/2} \right)^{1/3} \right] / 2 = 0.298 \approx 0.30. \quad (8)$$

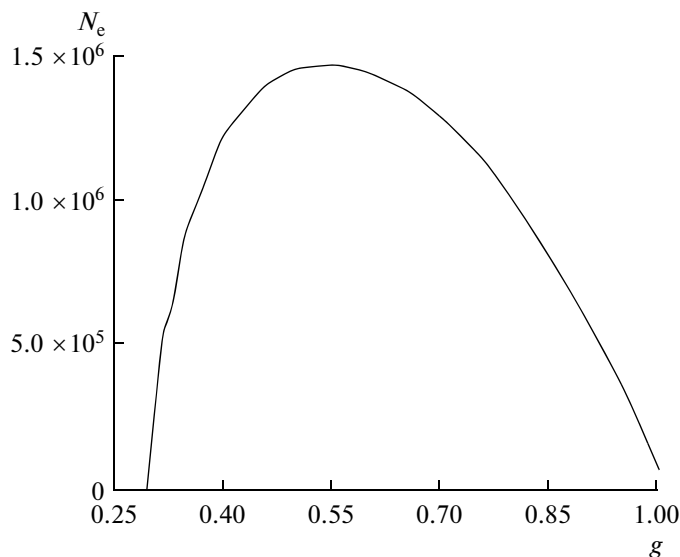
It would seem that we obtained a positive answer to the question: yes, it appears that it is possible to generate simultaneously functioning channels for supply of electrons, protons, and oxygen molecules into the macroscopic active layer (across its whole depth). Indeed, the sum of  $0.30 + 0.30 + 0.30$  does not exceed 1. Equality condition (1) can be satisfied. And even a certain excess of vacancies remains in the active layer that we can dispose of ad libitum.

And still, detailed consideration brings to light the fact that the three formed percolation clusters cannot be considered as full-fledged structures. As shown in [16], the percolation cluster is yet weakly developed bear the percolation threshold (at concentration  $g$  little differing from  $g^*$ ); its main “mass” encompasses only a small fraction of the model cube volume.

There is also another reason preventing work with bulk concentrations close to the threshold value. The point is that not all the grains within a particular percolation cluster but only their fraction actually take part in the transport of all the required substances into the active layer of the cathode: these are “through”



**Fig. 4.** Process of formation of electron percolation cluster in the active layer of a cathode with polymer electrolyte, as dependent on support grain fraction  $g$ . (1) Fraction of support grains in percolation cluster  $g^*$  (solid line), (2) fraction of grains isolated from percolation cluster,  $g - g^*$  (dashed line). A model cube with the size of  $100 \times 100 \times 100$ .



**Fig. 5.** Dependence of the amount of faces in support grains  $N_e$  in electron percolation cluster accessible for supply of protons and oxygen molecules on the fraction of support grains  $g$ . A model cube with the size of  $100 \times 100 \times 100$ .

grains. The “deadlock” grains are obviously closed for transport. In a percolation cluster, one can distinguish its “trunk” responsible for the transport and the rest percolation cluster elements: its “crown” [17].

The percolation cluster trunk may be obtained using a special procedure: the elements are eliminated (“deadlock” elements) that do not assist transport of substances. Therefore, the transport of electrons, protons, or oxygen molecules in the corresponding percolation clusters can be noticeably improved, only if the bulk concentration of the corresponding grains of electrolyte is considerably enhanced as compared to the value pertaining to the percolation threshold.

## 5. ELECTRON PERCOLATION CLUSTER

In the active layer of a cathode with Nafion, the central role is played by the electron percolation cluster consisting of support grains. The electrochemical process occurs within these grains and on their surface, an expensive and scarce catalyst, platinum, is also here. Therefore, it is so important to choose the optimum concentration of support grains,  $g = g_{\text{opt}}$ .

Let us vary the concentration (fraction) of support grains in the model cube with the volume of  $100 \times 100 \times 100$ . In the range of  $0 \leq g \leq g_* = 0.298$  (formula (8)), the percolation cluster has not yet appeared and the number of disconnected support grains not united into a single cluster grows linearly at an increase in  $g$  (dashed curve 2 in Fig. 4).

The number of support grains within the generated percolation cluster after the percolation threshold is reached (denoted here as  $g^*$ ) starts growing rapidly and

the growth of  $g^*$  becomes linear approximately at  $g \sim 0.5$  (solid curve 1 in Fig. 4). And the amount of support grains isolated from the percolation cluster in the range of  $0.298 \leq g \leq 1$  fast decreases (dashed curve 2 in Fig. 4).

One can also calculate how the number of support grain faces within the electron percolation cluster  $N_e$  open for supply of protons and oxygen molecules changes in the range of  $0.298 \leq g \leq 1$ . The curve of the dependence of  $N_e$  on  $g$  is shown in Fig. 5. This is a curve with an extremum.

The dependence of the main parameters of the electron percolation cluster on the support grain fraction in range of  $0.298 \leq g \leq 1$  is presented in Table 2. Here,  $g^*$  is the fraction of support grains within the electron percolation cluster,  $g - g^*$  is the fraction of support grains isolated from the electron percolation cluster,  $(g - g^*)/g$ , % is the ratio (percentage) of the fraction of isolated grains to the overall number of support grains. And parameter  $N_e$  is the number of support grain faces within the electron percolation cluster and open for supply of protons and oxygen molecules to the support grains.

Of great interest are the data of column 4 in Table 2. It appears that at  $g = 0.35$ , about one-third (precisely: 29%) of the support grains are not included into the electron percolation cluster, no electrons are supplied to it and therefore these grains take no part in current generation. And this does not only imply problems in current generation, but means to large losses of the valuable catalyst, platinum. At  $g = 0.40$ , though the situation is improved, the losses in the current generation ability and consumption of platinum are still high. And only at  $g = 0.50$ , the losses become tolerable, as here, already practically all support grains become the part of the percolation cluster.

**Table 2.** Dependence of main parameters of an electron percolation cluster on the concentration (fraction) of support grains (the model cube with the size of  $100 \times 100 \times 100$ )

G	$g^*$	$g - g^*$	$(g - g^*)/g, \%$	$N_e$
0.298	0.0	0.298	100	0.0
0.30	0.03	0.27	90.0	$1.1 \times 10^5$
0.31	0.09	0.22	71.0	$3.60 \times 10^5$
0.32	0.14	0.18	56.0	$5.25 \times 10^5$
0.33	0.18	0.15	45.0	$6.25 \times 10^5$
0.35	0.25	0.10	29.0	$8.98 \times 10^5$
0.40	0.35	0.05	12.5	$1.22 \times 10^6$
0.45	0.43	0.02	4.44	$1.38 \times 10^6$
0.50	0.49	0.01	2.0	$1.45 \times 10^6$
0.55	0.54	0.01	1.82	$1.47 \times 10^6$
0.60	0.597	0.003	0.5	$1.45 \times 10^6$
0.65	0.649	0.001	0.15	$1.39 \times 10^6$
0.70	0.699	0.001	0.14	$1.29 \times 10^6$
0.75	0.7498	$2 \times 10^{-4}$	$2.7 \times 10^{-2}$	$1.16 \times 10^6$
0.80	0.7999	$1 \times 10^{-4}$	$1.25 \times 10^{-2}$	$1.00 \times 10^6$
0.85	0.85	0.00	0.00	$8.11 \times 10^5$
0.90	0.90	0.00	0.00	$5.90 \times 10^5$
0.95	0.95	0.00	0.00	$3.40 \times 10^5$
1.00	1.00	0.00	0.00	$6.00 \times 10^4$

**Table 3.** Distribution across the active layer of a cathode with polymer electrolyte of availability of protons  $N_i$  and oxygen molecules  $N_{\text{gas}}$  to support grains within an electron percolation cluster (a model cube with the size of  $100 \times 100 \times 100$ )

$N$	$N_i$	$N_{\text{gas}}$	$N^*$	$g^*$	Dg
1	0	$1.182 \times 10^4$	0	$1.9678 \times 10^4$	$3.679 \times 10^3$
2	0	$3.133 \times 10^3$	0	$2.2459 \times 10^4$	872
3	0	678	0	$2.2484 \times 10^4$	862
4	0	153	0	$2.2492 \times 10^4$	865
5	0	39	0	$2.2492 \times 10^4$	866
6	0	16	0	$2.2497 \times 10^4$	862
7	0	4	0	$2.2475 \times 10^4$	873
8	0	0	0	$2.2472 \times 10^4$	863
9	0	0	0	$2.2487 \times 10^4$	867
10	0	0	0	$2.2491 \times 10^4$	861
11	0	0	0	$2.2472 \times 10^4$	872
12	0	0	0	$2.2481 \times 10^4$	876
13	0	0	0	$2.2480 \times 10^4$	868
14	0	0	0	$2.2492 \times 10^4$	865
15	0	0	0	$2.2466 \times 10^4$	870
16	10	0	0	$2.2472 \times 10^4$	867
17	18	0	0	$2.2476 \times 10^4$	868
18	133	0	0	$2.2468 \times 10^4$	873
19	$1.339 \times 10^3$	0	0	$2.2497 \times 10^4$	866
20	$9.126 \times 10^3$	0	0	$1.9669 \times 10^4$	$3.700 \times 10^3$

What is the optimum concentration (fraction) of the support grains to be chosen as the optimum one,  $g = g_{\text{opt}}$ ? Should the support grain fraction be increased above the value of  $g = 0.55$ ? No, as in this case, the number of faces in the electron percolation cluster (the fifth column in Table 2), through which protons and oxygen molecules are supplied into the active support grains (the grains capable of participating in the electrochemical process) starts rapidly decreasing (Fig. 5). At  $g = 1.0$ , the whole model cube bulk was filled by support grains and of  $10^6$  support grains the active ones are only those that are adjacent to the 6 faces of the model cube faces. It is easy to count them:  $6 \times 100 \times 100 = 6 \times 10^4$ .

And now, here is an important conclusion following from all the above. If the optimum values of  $g_{\text{opt}} = 0.5$  or  $g_{\text{opt}} = 0.55$  are chosen for a fraction of support grains, then there is no place in the model cube for another two full-fledged percolation clusters. Such clusters would be unable to appear. Thus, we come to the following conclusion: it is practically impossible within the model of equal-size microcube grains of three types to organize a full-fledged process with significant generated current in bulk structures.

## 6. AVAILABILITY OF PROTONS AND OXYGEN TO SUPPORT GRAINS

Nevertheless, despite the just obtained negative theoretical estimates, active layers of cathodes with polymer electrolyte are capable of generating considerable currents. What is the cause of disparity between the theoretical predictions and experimental data? Let us again turn to the results of studies of reconstruction of the active layer microstructure [18]. And let us also point out that a number of such works established the spectrum of concentrations (fractions) of the three phases in the active layer: the support with platinum, Nafion, and gas pores. In [18], e.g., the following set of values is given. In our notations,  $g = 0.467$ ,  $g_i = 0.257$ ,  $g_{\text{gas}} = 0.276$ .

Let us perform yet another computer modeling of the active layer structure within the model of equally sized microcube grains of three types. In this case, the aim of the modeling was to establish for the active layer the degree of supply of protons and oxygen molecules to support grains.

Above all, the choice of the fraction of support grains in the active layer close to optimum was made in [18]:  $g = 0.467$ . This was discussed in the previous section (the data in Figs. 4, 5 and Table 2). This value of support grains corresponds to a relatively low amount of isolated (with no electron supply) proton grains. And simultaneously, the value of the outer surface of the electron percolation cluster  $N_e$  is practically maximum.

Let us now see if good access of protons and oxygen to support grains can be provided at the concentration values of  $g_i = 0.257$ ,  $g_{\text{gas}} = 0.276$ . Support grains must

be made electrochemically active. Results of computer modeling are presented in Table 3 and in Fig. 6.

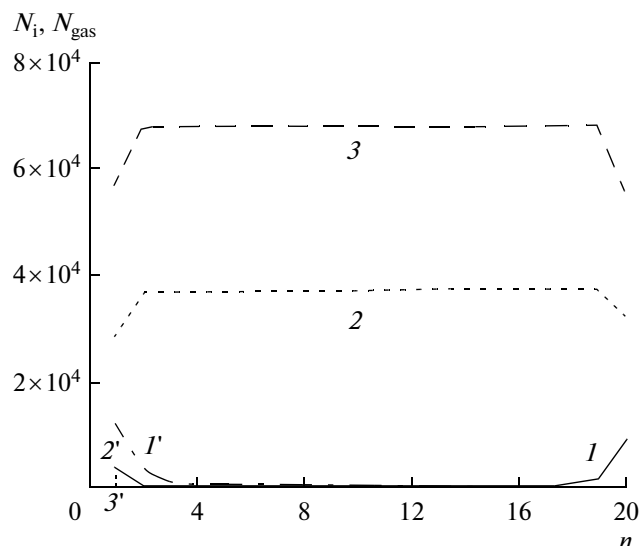
A model cube of  $100 \times 100 \times 100$  grains simulating the active layer of a cathode with polymer electrolyte located between a membrane of Nafion (proton source) and gas diffusion layer (oxygen source) was divided into 20 layer sections. In each, the number of support grains within the electron percolation cluster  $g^*$  and number of isolated support grains  $\Delta g = g - g^*$  were calculated (the averaging by 100 configurations of equally sized grains of three types in the model cube). These are the data of the last two columns in Table 3. One can see that apart from layers 1 and 20 where the effect of the active layer edge is observed, the distribution of support grains included and not included into the electron percolation cluster is rather uniform.

Now, to the degree of availability of protons and oxygen to support grains within the electron percolation cluster. Let us introduce some notations. Here,  $N_i$  is the number of grains of active support grains to which protons are supplied,  $N_{\text{gas}}$  is the number of active support grains to which oxygen is supplied,  $N^*$  is the number of active support grains to which both protons and oxygen are supplied.

The data of Table 3 shown in columns 1–4 ( $N$  is the number of the layer section) are rather trivial. The concentration of Nafion grains  $g_i = 0.257$  and gas pores  $g_{\text{gas}} = 0.276$  are small, below the percolation threshold of 0.298. Therefore, protons from the membrane (Nafion) adjacent to layer 20 of the model cube penetrate only a limited space (through 5 layers). But the amount of oxygen supplied from the opposite side of the model cube also penetrates only to a limited depth (7 layers, as the concentration of voids is above the concentration of Nafion grains). Due to this, the amount of support grains provided both by protons and gas  $N^*$  (column 4 in Table 3) proves to be equal to zero in all model cube layers.

All the above is demonstrated in Fig. 6. Three variants of concentration of support, Nafion, and void grains were chosen. Variant 1:  $g = 46.7\%$ ,  $g_i = 25.7\%$ ,  $g_{\text{gas}} = 27.6\%$  (the data of [18]). Variant 2:  $g = 46.7\%$ ,  $g_i = 37.0\%$ ,  $g_{\text{gas}} = 16.3\%$  (the fraction of Nafion grains is increased). And variant 3:  $g = 46.7\%$ ,  $g_i = 53.3\%$ ,  $g_{\text{gas}} = 0.0\%$  (the fraction of Nafion grains is maximum). In total, concentrations  $g$ ,  $g_i$ , and  $g_{\text{gas}}$  must satisfy the conditions of equality (1): the model cube must be fully filled by grains of three types.

Figure 6 shows a quite obvious fact. When the amount of void grains decreases and the fraction of Nafion grains grows, it becomes possible (curves 2 and 3 in Fig. 6) to provide increasingly protons to support grains across the whole active layer depth, but supply of oxygen to support grains remains herewith practically zero.



**Fig. 6.** Distribution of the amount of faces in active support grains in the electron percolation cluster across the active layer depth. (1–3) Amount of faces in support grains with supplied protons  $N_i$ . (1'–3') Amount of faces with supplied oxygen molecules  $N_{\text{gas}}$ . Variant 1: (1, 1')  $g = 0.467$ ,  $g_i = 0.257$ ,  $g_{\text{gas}} = 0.276$ ; variant 2: (2, 2')  $g = 0.467$ ,  $g_i = 0.370$ ,  $g_{\text{gas}} = 0.163$ ; variant 3: (3, 3')  $g = 0.467$ ,  $g_i = 0.533$ , and  $g_{\text{gas}} = 0.0$ .

Thus, we seem to find again that it is completely impossible to organize full current generation in the active layer of a cathode with polymer electrolyte. What is the fault of theoretical interpretation? It is that the potential possibility of intrinsic probability both by protons and by gas in support grains is neglected.

It should be noted that the structure of the active layer of a cathode with polymer electrolyte actually consists of some two “levels”. The upper level is supply channels of all participants of the electrochemical process through clusters of the corresponding grains: the support, Nafion, and voids. There is yet the lower level: the microstructure of support grains, where the current generation process occurs. In [4, 12], microphotographs of support grains show rather clearly both the presence of Nafion and micro voids in them.

If so, then transport of oxygen and protons can occur in the active layer not only through Nafion and void grains, but also through support grains. And then supply of protons and oxygen to support grains ceases being zero (the data of Table 3). And the current generation process would already occur through the whole active depth.

The only issue now is whether high ohmic (proton supply) and diffusion (oxygen supply via the mechanism of Knudsen diffusion) limitations would appear in the active layer of a cathode with polymer electrolyte? Indeed, proton conductivity and diffusion coefficient of support grains can prove very low. Let us test the relevance of these concerns.



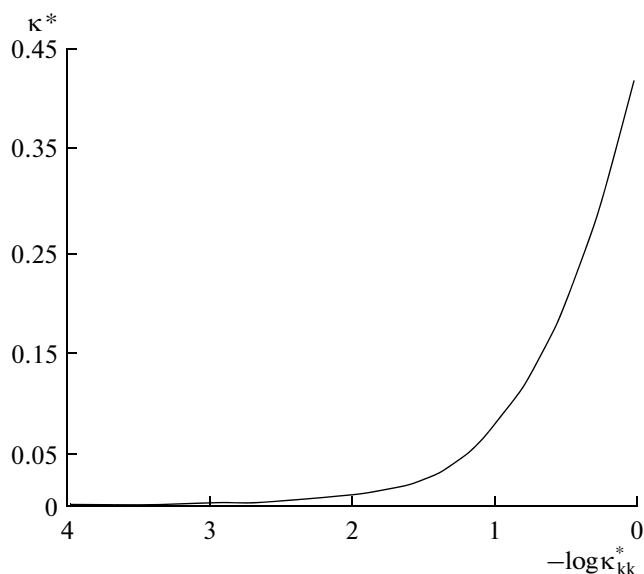


Fig. 7. Dependence of effective specific proton conductivity of combined percolation proton cluster  $\kappa^*$  on protonic conductivity of support grains  $\kappa_{kk}^*$ .

## 7. CALCULATION OF EFFECTIVE PROTON CONDUCTIVITY

Let us perform numeric estimations. Let us assume for simplicity that all support grains both within the electron percolation cluster and isolated from it feature similar proton conductivity  $\kappa_{kk}^*$ . Assuming conductivity of a Nafion grain to be unity, let us vary conductivity of a support grain within the unit fractions.

Let it vary from the minimum value of  $\kappa_{kk}^* = 0.01$  to the maximum, naturally arbitrary value (the volume

Table 4. Dependence of effective specific proton conductivity of combined percolation cluster  $\kappa^*$  on protonic conductivity of support grains  $\kappa_{kk}^*$  (a model cube with the size of  $100 \times 100 \times 100$ ).  $g = 46.7\%$ ,  $g_i = 25.7\%$

$\kappa_{kk}^*$	$\kappa^*$
0.01	0.011
0.05	0.041
0.10	0.078
0.20	0.140
0.32	0.198
0.40	0.233
0.50	0.273
0.63	0.317
0.79	0.366
1.00	0.420

occupied by a support grain cannot be 100% filled by Nafion) of  $\kappa_{kk}^* = 1.0$ .

Thus, let us start studying the conducting properties of a so called combined proton percolation cluster. Its composition is:  $g = 46.7\%$ ,  $g_i = 25.7\%$ . The base of the combined cluster is the already formed electron percolation cluster. And the set of those support grains isolated from the electron cluster and Nafion grains that prove connected with the electron percolation cluster through continuous chains extends the size of the combined cluster.

In a combined proton percolation cluster, there are already three bond types with different conductivity. Conductivity in the case of contact between two coupled Nafion grains is naturally assumed equal to 1 (ion conductivity of Nafion). Conductivity appearing in the case of contact of two coupled neighboring support grains is assumed equal to  $\kappa_{kk}^*$  (proton conductivity of support grains). Conductivity appearing under contact of two neighboring grains of Nafion and support is assumed equal to the following (serial coupling of two elements in the electric circuit):

$$\kappa^{**} = 2\kappa_{kk}^* / (1 + \kappa_{kk}^*). \quad (9)$$

Thus, a combined proton percolation cluster with an arbitrary distribution of conducting bonds of three types can be realized in the course of computer simulation in a model cube. Here, it is necessary to point out again that not every bond of a combined percolation cluster can generate proton current. The contribution to conductivity can be provided only by the bonds within the "trunk" of the combined percolation cluster [17].

Let us also add that effective proton conductivity in a combined percolation cluster was calculated using numeric computer simulation based on the Monte-Carlo technique [19, 20]. The main positions of the chosen calculation approach were described in [21].

The results of calculation of effective proton conductivity of the combined percolation cluster  $\kappa^*$  as dependent on the value of proton conductivity of support grains  $\kappa_{kk}^*$  are given in Fig. 7 and in Table 4. If the support grain consists of 100% of Nafion ( $\kappa_{kk}^* = 1$ ), then  $\kappa^* = 0.42$  (the last line in Table 4). Indeed, the reaching of such a  $\kappa^*$  value in the above example of the combined percolation cluster appears problematic. And many questions arise here. What is the limiting content of Nafion in a support grain? And what is the maximum possible value of conductivity of a support grain  $\kappa_{kk}^*$ ? But this is an issue for other studies.

Let us make another useful addition to the above. Let us assume that support grains feature no proton conductivity. Let us calculate dependences of effective specific proton conductivity  $\kappa_i^*$  in the percolation ion cluster in a model cube with the size of  $100 \times 100 \times 100$

**Table 5.** Dependence of effective specific proton conductivity of ion percolation cluster  $\kappa_i^*$  on the concentration of Nafion grains  $g_i$  (a model cube with the size of  $100 \times 100 \times 100$ )

$g_i$	$\kappa_i^*$
0.30	$5.7 \times 10^{-4}$
0.40	$1.5 \times 10^{-2}$
0.50	0.10
0.60	0.23
0.70	0.39
0.80	0.59
0.90	0.79
1.00	1.00

consisting now only of Nafion grains on the concentration of Nafion grains  $g_i$ .

The results of this calculation are given in Table 5. It appears that the fraction of Nafion grains in the active layer must be brought to the value of  $g_i = 0.50$  to obtain a more or less adequate value of conductivity, at least  $\kappa_i^* = 0.10$  (the data of Table 5). But then it is quite unclear how full supply of oxygen atoms into the active layer can be provided under these conditions. Indeed, then the fraction of void grains that may potentially supply oxygen decreases to a tiny amount, to  $g_{\text{gas}} = 1 - 0.467 - 0.50 = 0.033$ .

## CONCLUSIONS

The mechanism of reagent supply was in fact similar in the first two generations of cathodes of low-temperature hydrogen–oxygen (air) fuel cells (with hydrophilic electrodes with a pressure drop and a barrier layer and with hydrophobized electrodes). It was required to organize two clusters extending across the whole depth of the active layer: the gas cluster and “electron–ion” cluster. And no fundamental problems appeared here.

A different situation was formed for fuel cells with solid polymer electrolyte. Experiments with determination of the composition and structure of active layers of such fuel cells show that the number of clusters required for adequate cathode operation increase now to three. It is usually assumed that transport of protons and oxygen molecules to agglomerates (support grains) in the active layer of the cathode with polymer electrolyte (Nafion) with electron conductivity of carbon particles coated by platinum (catalyst) nanoparticles is carried out accordingly via agglomerates (grains) of Nafion and void grains. Thus, formation in the active layer of three macroscopic percolation clusters extended across the whole active layer depth becomes necessary: “electron”, “proton”, and “gas.”

The aim of this study was to answer the question whether it was possible to generate in the active layer with polymer electrolyte three independent clusters providing transport of electrons, protons, and oxygen molecules. The answer to the above questions was obtained using computer simulation.

Many attempts of researchers to establish the active layer structure register the presence of support, Nafion, and void grains. To the first approximation, these can be assumed to be of equal size. It is suggested in the paper to simulate this grain set using a model cube with the size of  $100 \times 100 \times 100 = 10^6$  grains. Herewith, the grains are microcubes. In the terms of percolation theory, the model of equally sized microcube grains of three types represents a cubic lattice of sites.

It is shown in the paper that formation of any percolation cluster (of the three) requires that the volume corresponding to grains of this type was at least 30%. Development of a full electron percolation cluster requires that the concentration (fraction) of support grains within this cluster is already about 50% of the whole model cube volume. Only then one can provide the minimum catalyst (platinum) losses and simultaneously the maximum outer surface of faces of its support grains open for supply of protons and oxygen.

It is clear that only one more percolation cluster (either “proton”, or “gas”) can be arranged within the volume that remains free of support grains in the model cube (this volume is about 50%). And the simultaneous existence of three percolation clusters in the active layer already becomes quite impossible.

But then a problem appears that requires an explanation: how can one explain the experimentally observed rather satisfactory operation of the active layer of fuel cell cathodes with polymer electrolyte? What is the true nature of proton and oxygen supply channels to the support grains?

Numeric estimates and results of computer simulation in the paper show that the required supply of protons and oxygen can be provided only in the case when the very support grains can feature not only electron conductivity. Indeed, they can also participate in a rather effective transport in the active layer of a cathode with polymer electrolyte of both protons and oxygen molecules.

As intrinsic proton and diffusion conductivity of support grains naturally cannot be high, in third-generation fuel cells, as opposed to fuel cells of the first two generations, large problems arise regarding proton and oxygen transport to support grains where the electrochemical process actually occurs. Thus, there is a fundamental difference in the mechanism of operation of fuel cells of the third and the first two generations, where there were no actual problems with ion and gas transport.

It is shown in the paper that supply of protons and oxygen in fuel cells of the third generation must be car-

ried out already using the corresponding combined percolation clusters basically consisting of support grains and additionally of Nafion grains (then, a combined "proton" cluster appears) or void grains (which allows generating a combined "gas" cluster).

It is shown in the paper how effective coefficients can be calculated for the corresponding combined percolation clusters in the active layer: effective specific proton conductivity and effective Knudsen diffusion coefficient are to be determined.

There is yet another fundamental difference between the fuel cells of the third generation and fuel cells of the first two generations consisting in polyvariance of the possible mechanisms of proton and oxygen supply in system with polymer electrolyte: transport of protons and oxygen can now occur via different mechanisms. In cathodes of the first two generations, supply of ions and oxygen into the active layer occurred via a single initially determined mechanism.

The latter circumstance leads to the necessity of searching for the optimum routes for transport of protons and oxygen in active layers of fuel cell cathodes with polymer electrolyte. Herewith, optimization criteria can be different: attempts to decrease the key factor of the degree of cost effectiveness of platinum consumption (its amount per kW of electric power generated in the membrane electron assembly), increase in degree of platinum utilization in the active cathode layer, control of cathode pore flooding by water etc.

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