

Active Layer of Fuel Cell Electrode with Polymer Electrolyte: Modeling of Support Grains, Calculation of Overall Cathode Characteristics

Yu. G. Chirkov^{a, z} and V. I. Rostokin^b

^a*Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia*

^b*National Research Nuclear University “Moscow Engineer Technical Institute,” Moscow, Russia*

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Abstract—The active layer of the cathode of a fuel cell with polymer electrolyte (Nafion) is considered. The optimum carbon support structure is constructed using computer simulation: its carbon “skeleton” possesses the maximum outer surface area and provides electronic conductivity of the grains, support cubes, along the three coordinate axes. Nafion is absent in the support grain, so that the grain is capable of participating only in the transport of oxygen molecules, it possesses no proton conductivity. An estimate of all parameters of an optimum support grain is provided; in particular, the value of the effective Knudsen diffusion coefficient of oxygen is established. After this, effective proton conductivity and effective Knudsen diffusion coefficient are calculated already on the whole active layer scale, according to the model of equally sized cube grains of three types. In conclusion, the overall current in the active layer of a cathode with a polymer electrolyte was calculated for the percolation cluster consisting only of Nafion grains and the Knudsen diffusion of oxygen created only by a combined gas percolation cluster consisting of void grains and all support grains. The overall current value for $t = 80^\circ\text{C}$ and pressure of $p^* = 101\text{ kPa}$ proved to be low, hundreds of mA/cm^2 . The current value can apparently be increased to several A/cm^2 if the support grains are developed that would simultaneously possess both proton conductivity and ability to sustain oxygen diffusion.

Keywords: fuel cell with polymer electrolyte, active layer, computer simulation, model of equally sized grains of three types, optimum structure of the carbon support grain, combined percolation cluster, Knudsen diffusion

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1. PROBLEM STATEMENT

The active layer of the cathode of a hydrogen–oxygen (air) fuel cell represents a certain “two–level” structure. The “first” level, in agglomerates of carbon particles (in porous support grains), on the surface of which the catalyst (platinum) is applied, locates the electrochemical process. But its reliable occurrence requires the functioning of the “second” level: the whole active layer where the transport of electrons, protons, and oxygen molecules occurs.

The model of the “second” layer of the active layer is a model cube composed of equally–sized cubic grains of three types: support grains, Nafion grains (agglomerates of polymer electrolyte molecules), and void grains [1]. A model cube imitating the active layer must be of macro size: $100 \times 100 \times 100 = 10^6$ grains. Its normal active layer operation requires creating three percolation clusters.

Firstly, an electrochemically active support grain must be included into the “electron” percolation cluster, thus providing entry of electrons into the active layer. Secondly, protons and oxygen molecules must

be supplied to the support grains. And this means that the electron percolation cluster must directly contact two other percolation clusters: the “proton” one (a set of interconnected Nafion grains) and “gas” one (a set of interconnected void grains).

As shown in [1], in the case of the active layers of cathodes with solid polymer electrolyte, as opposed to the first two generations of cathodes with liquid electrolyte [2–4], a simultaneous existence of three percolation clusters consisting only of the corresponding similar–type grains is impossible. In reality, one (or even two) percolation clusters supplying protons and oxygen must be of combined nature. They must consist of Nafion grains (if this is a combined proton percolation cluster) or of void grains (if this is a combined gas percolation cluster) with addition in both cases of support grains that, as shown in the series of works of [5–9], may possess both proton conductivity and the ability to support diffusion of oxygen molecules.

Thus, the mechanism of operation of a cathode with polymer electrolyte fundamentally differs from that of the cathodes of the first two fuel cell generations: hydrophilic cathodes with a pressure drop and a

^z Corresponding author: olga.nedelina@gmail.com (Yu.G. Chirkov).

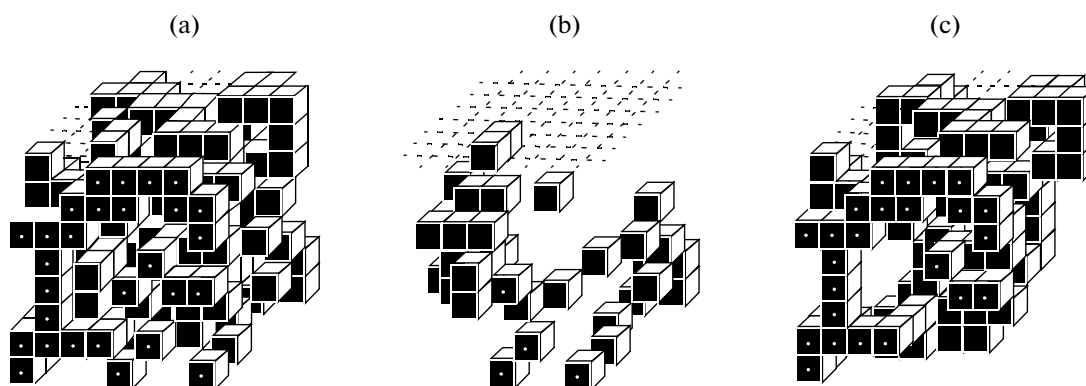


Fig. 1. Process of carbon cluster (skeleton) formation in a support grain: (a) the initial distribution of carbon particles in a support grain (the bulk concentration of carbon microcubes $g_0 = 0.37$), (b) those carbon particles that have no connection with the cluster and therefore must be discarded, (c) the final layout of the carbon cluster (“skeleton”).

barrier layer and hydrophobized cathodes. Accordingly, the requirements to the character of the support grain structure become more complicated in the case of cathodes with polymer electrolyte. In the third-generation cathodes, these grains must not only provide conditions for occurrence of an intensive electrochemical process, but should also support the transport of electrons, protons, and oxygen molecules.

The aim of the present study is to develop using the computer simulation the optimum structure of the carbon support, its carbon “skeleton.” Herewith, as we shall for the moment assume that the support grain is capable of participating only in the transport of oxygen molecules (Nafion would be absent in the support grains). Then, an estimate of all parameters of the optimum support grain structure is provided; in particular, the value of the effective Knudsen diffusion coefficient of oxygen in the support grain is established. After that, effective proton conductivity and effective diffusion coefficient of oxygen are calculated already for the whole active layer. In conclusion, overall current of the active layer of a cathode with polymer electrolyte will be calculated at the assumption that oxygen transport in it is provided by the combined “gas” percolation cluster.

2. MODELING OF CARBON CLUSTER STRUCTURE

Let us start from studying the “first” level of the cathode active layer. According to the literature data [10, 11], the average size of the support grains in the active layer is 100 nm, that of carbon particles is 10 nm. We assume that the size of edges of support, Nafion, and void grains in the active layer model (all these have the shape of microcubes of a similar size arranged into a cubic lattice [1]), $L = 80 \text{ nm} = 8 \times 10^{-6} \text{ cm}$. Herewith, carbon particles in the support grains, also of a similar size, have the shape of microcubes and they constitute together with the void microcubes a cubic lattice. We shall also assume that the size of carbon

microcubes and void microcubes in the support grains are $d = 10 \text{ nm} = 10^{-6} \text{ cm}$.

Further, carbon microcubes are randomly scattered across the support grain bulk with the size of $8 \times 8 \times 8$ microcubes. The initial concentration of carbon microcubes is varied. An example of one of implementations of distribution of the carbon material in the support grain bulk is shown in Fig. 1a. The concentration of carbon microcubes is $g_0 = 0.37$.

The sought-for configuration of carbon microcubes in a support grain must fulfill several requirements. Firstly, naturally, the carbon structure of the support grain, its “skeleton,” must represent a connected cluster, through which the electron transport can occur. Therefore, the cluster components introducing no contribution into electron conductivity must be eliminated from the initial configuration of microcubes (Fig. 1a). These microcubes are shown in Fig. 1b. Their elimination is what creates the final carbon structure in the support grain (“skeleton,” Fig. 1c). The microcubes emerging onto the support grain surface are marked in Fig. 1c by points.

Secondly, not only the implementations of the carbon microcube structures are chosen, for which connectivity across the microcube chains from each support grain face to its opposite face is present. This natural requirement to the support grain is for it to possess electron conductivity on the three coordinates. For this cause, the support grains must later fully enter the active layer (“upper” level). Due to this limitation, the initial concentration of microcubes in a support grain g_0 cannot be arbitrarily small. As shown by computer experiments, the initial concentration of carbon microcubes must start from the value of $g_0 = 0.27$.

Thirdly, in a connected carbon cluster (Fig. 1c), its full total outer surface area of its faces $S = S_1$ must be determined. The requirement must also be imposed for definiteness that this surface area should be as high as possible. Thus, the concept of the “optimum” carbon cluster is finally developed.

Table 1. Characteristics of the optimum carbon cluster structure in an individual support grain

g_0	g	m_0	m	g_e	g_{gas}	S_{out}	S_{in}	S	D^*
0.27	0.1875	138	96	0.1875	0.8125	50	318	368	0.6095
0.30	0.2285	154	117	0.2285	0.7715	87	369	456	0.5195
0.33	0.2734	169	140	0.2734	0.7266	97	441	538	0.4457
0.35	0.3086	179	158	0.3086	0.6914	111	487	598	0.3934
0.37	0.3418	189	175	0.3418	0.6582	113	537	650	0.3593
0.40	0.3730	205	191	0.3730	0.6270	137	581	718	0.2869
0.45	0.4336	230	222	0.4336	0.5664	173	647	820	0.1889
0.50	0.4941	256	253	0.4941	0.5059	195	689	884	0.1301
0.55	0.5449	282	279	0.5449	0.4551	227	697	924	0.0665
0.60	0.5977	307	306	0.5977	0.4023	244	690	934	8.49×10^{-3}
0.70	0.6973	358	357	0.6973	0.3027	283	617	900	0
0.80	0.80	410	410	0.8008	0.1992	322	474	796	0
0.90	0.90	461	461	0.9004	0.0996	365	261	626	0
1.0	1.0	512	512	1.0	0	384	0	344	0

The latter requirement is fulfilled as follows. For the chosen initial concentration of microcubes g_0 , the procedure of obtaining a carbon cluster of the type shown in Fig. 1c, is repeated many times (tens and hundreds and thousands of variants). Herewith, each time, the new value of $S = S_2$ is compared to the previous one. If $S_2 > S_1$, the first configuration should be forgotten. If $S_2 < S_1$, the second implementation is discarded as useless and the next attempt is made to realize the carbon cluster structure.

The ultimately obtained cluster with the maximum reaction surface of its faces must be estimated on the basis of several parameters presented in Table 1. It contains:

g_0 being the initial bulk concentration of carbon microcubes in a support grain, g being the bulk concentration of carbon microcubes in the optimum cluster;

m_0 is the initial number of carbon microcubes randomly distributed in the support grain bulk, m is the number of microcubes in an optimum cluster;

$g_e = g$ is the porosity in microcubes in a support grain with an optimum cluster, g_{gas} is the porosity corresponding to voids in a support grain ($g_e + g_{\text{gas}} = 1$);

S_{out} is the number of faces of the optimum cluster located at the support grain surface, S_{in} is the number of carbon cluster faces inside the support grain, $S = S_{\text{out}} + S_{\text{in}}$ is the full number of the optimum cluster faces;

D^* is the effective gas diffusion coefficient in a support grain (the account for the role of the support grain microstructure, D^* is a dimensionless parameter). Let us point out that the D^* value for the optimum cluster was calculated repeatedly and in three variants (for the three coordinate axes). The final value is $D^* = (D_1 + D_2 + D_3)/3$. It was assumed in the calculation of D_1 that

the gas diffusion occurs through the voids only from top downward (or from the bottom upward). Herewith, the four side faces of the support grain are closed to diffusion.

The dependence of the parameters of S_{out} , S_{in} , and S on g is shown in Fig. 2 (curves 1–3) according to the data of Table 1. The number of faces of the optimum cluster on the support grain surface (curve 1 in Fig. 2) is much lower than the number of inner faces (curve 2 in Fig. 2). Therefore, it is so important to involve in the

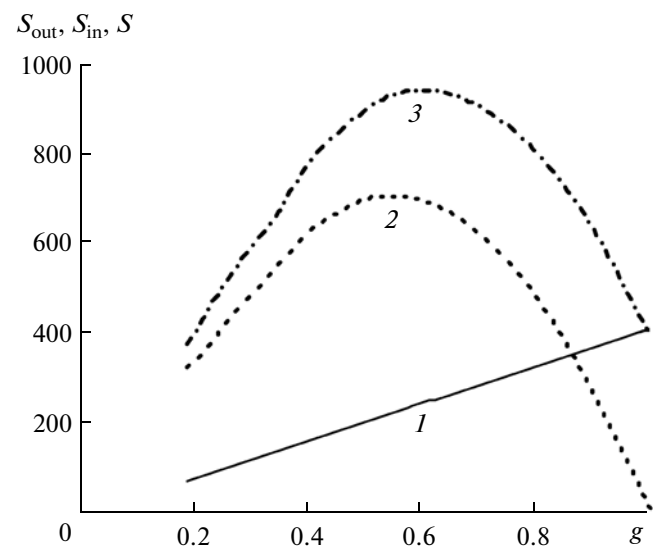


Fig. 2. Dependence of the number of carbon cluster faces on the carbon particle concentration g in a support grain: (1) the number of faces on the support grain surface, (2) the number of faces within a support grain, (3) the full number of carbon cluster faces.

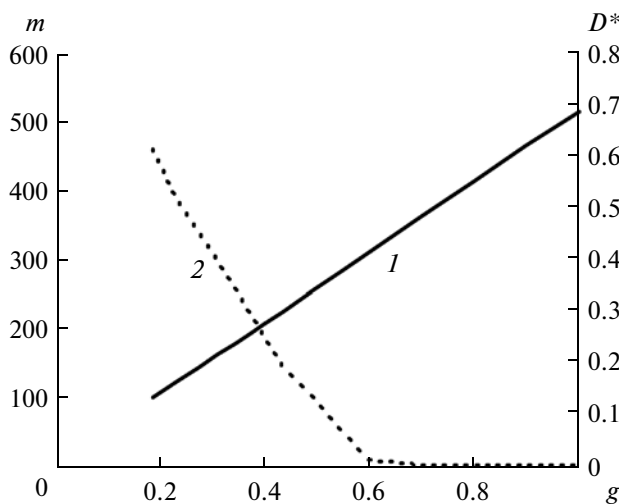


Fig. 3. Dependence of the carbon particle concentration g in a support grain: (1) number of carbon microcubes m in an optimum cluster in a support grain and (2) effective Knudsen diffusion coefficient D^* of the gas in a support grain (taking into account the role of the support grain microstructure).

electrochemical process not only the outer, but also the inner faces of the optimum cluster.

According to the data of Table 1, Fig. 3 is also constructed: the dependence of parameters m and D^* on g (curves 1, 2). At $g = 1$, when the support grain is completely filled by microcubes, as could be easily counted: $m = 8 \times 8 \times 8 = 512$. At $g \geq 0.7$, the value of the diffusion coefficient becomes zero: the connectivity between the voids in the support grain is interrupted.

3. TRANSPORT OF OXYGEN MOLECULES IN SUPPORT GRAIN

The last column of Table 1 contains the values of effective diffusion coefficient of oxygen D^* in the support grain calculated according to the method described in [12]. It was taken into account that the microstructure of the void space in the support grain is of a complex character, but it was assumed herewith that the diffusion coefficient is the same in all voids and is equal to an arbitrary unit. However, the gas pores in a support grain are very small and therefore Knudsen diffusion occurs in which the diffusion coefficient depends on the pore size.

An extremely complicated problem appeared. But for the purposes of this study, there is no necessity to attempt an absolutely precise calculation of the effective coefficient of Knudsen diffusion in support grains. In this paper, we will limit ourselves to approximate estimates that would simultaneously account both for the role of the void microstructure in the support grains and the Knudsen character of gas diffusion in them.

Let us assume that the effective Knudsen diffusion coefficient of the gas in support grains

$$D_e = D_{kn} D^*, \quad (1)$$

where D_{kn} is the coefficient of Knudsen diffusion for the ideal case when all gas pores in a support grain have the same minimum possible diameter equal to the size of carbon microcubes in support grains $d = 10 \text{ nm} = 10^{-6} \text{ cm}$.

Let us estimate Knudsen diffusion. The amount of gas passing through the cross-section of a capillary with diameter ρ and length l is provided by the following expression:

$$j = \pi \rho^3 (RT/2\pi M_g)^{1/2} (c_2 - c_1)/3l, \quad (2)$$

where M_g is the molecular weight of the gas (for oxygen $M_g = 32 \text{ g/mol}$), RT is the product of the gas constant by the absolute temperature $(c_2 - c_1)/l$ is the gas concentration gradient [13].

The density of the gas flux is proportional to the number of gas pores N per 1 cm^2 of the cross-section of the studied material. And this value is related to porosity τ of the material by the relationship of

$$\tau = \pi \rho^2 N/4. \quad (3)$$

Thus, we have for the Knudsen diffusion coefficient:

$$D_{kn} = 4\rho(RT/2\pi M_g)^{1/2} \tau/3. \quad (4)$$

Let us assume that $\rho = 10 \text{ nm}$ (the voids of the same size as carbon particles) and we shall use the value for $\tau = g_{gas}$ from Table 1. Then finally, we obtain the calculation formula for effective Knudsen diffusion coefficient of the gas in support grain pores D_{kn} , cm^2/s :

$$D_{kn} = (4 \times 10^{-3}) g_{gas}/1.5. \quad (5)$$

4. PROTON TRANSPORT IN ACTIVE LAYER

Now let us move from the "first" level of the cathode active layer to its "second" level: from studies of the structure and properties of the support grains to studies of the effective parameters of the whole active layer.

Let us turn to transport problems. The following equality is obviously true for concentrations of the three grain types:

$$g_s + g_i + g_g = 1, \quad (6)$$

where g_s is the support grain fraction, g_i is the Nafion grain fraction, and g_g is the void grain fraction.

It is shown in [1] that the optimum concentration of the support grains in the active layer is approximately in the range of $g_s = 0.5$. And let us also point out that such a spectrum of concentrations (fractions) of the three phases in the active layer is established, e.g., in [14]: the support with platinum, Nafion, and gas pores. It is shown that in our notations, the fraction of support grains is $g_s = 0.467$, the fraction of Nafion grains is $g_i = 0.257$, the fraction of void grains is $g_g = 0.274$.

Therefore, we will everywhere in our calculations assume that $g_s = 0.467$. And the fraction of Nafion grains g_i will be varied in order to provide the existence of a proton percolation cluster consisting wholly of Nafion grains.

The percolation proton cluster consisting only of Nafion grains appears after the percolation cluster of g_i^* is reached [15]:

$$g_i^* = \left[\left(1 + 2^{1/2}\right)^{1/3} + \left(1 - 2^{1/2}\right)^{1/3} \right] / 2 = 0.298 \approx 0.30. \quad (7)$$

Therefore, setting the value of $g_s = 0.467$, let us search through the values of Nafion grain fractions while increasing them, g_i : 0.35, 0.40, 0.45, etc. Then, according to relationship (6), the fraction of void grains will decrease as

$$g_g = 1 - 0.467 - g_i \quad (8)$$

up to the minimum limiting value of $g_g = 0.033$ (at $g_i = 0.50$).

Naturally, the value of effective proton conductivity in the cathode active layer κ^* (the protons move through the proton percolation cluster, κ^* is a dimensionless parameter) would grow at an increase in g_i . The dependence of κ^* on g_i in the model of equally sized grains of three types was calculated in [16]. The result of calculations is presented in Table 2.

Let us assume further that specific conductivity of Nafion under the optimum humidification is $\kappa = 1 \times 10^{-1} \text{ S cm}^{-1}$. Then, the product of

$$\kappa^{**} = \kappa \kappa^* \quad (9)$$

represents effective specific conductivity of the cathode active layer.

5. TRANSPORT OF OXYGEN MOLECULES IN ACTIVE LAYER

The transport of oxygen molecules in the active layer, as opposed to transport of protons, occurs in a complex way. Here, a combined gas percolation cluster consisting of support grains with a nonzero Knudsen diffusion coefficient D_e (formula (1)) and a certain amount of void grains (formula (8)) appears, as shown in [1]. Our problem in this section is to demonstrate the technique of calculation of D^{**} , cm^2/s , the effective Knudsen diffusion coefficient of the combined gas percolation cluster.

Above all, according to the data of Table 1, we will vary the g_e value in the range of $g_e = 0.1875$ to $g_e = 0.5977$. More precisely, let us choose from Table 1 five basic g_e values: 0.1875, 0.3086, 0.3730, 0.4941, 0.5977. It is necessary to know the g_e value, as we can use Table 1 (the last column) and formulas (1) and (5) to determine the value of D_e .

Further, fixing the g_e value (one of the above five values) and g_s ($g_s = 0.467$), we start searching through the values of Nafion concentration g_i : 0.35, 0.40 etc. until the maximum limiting value is reached. The

Table 2. Dependence of effective proton conductivity κ^* in the active cathode layer on the fraction of Nafion grains g_i

g_i	κ^*
0.35	0.0061
0.40	0.026
0.45	0.061
0.50	0.109
0.55	0.166
0.60	0.231
0.65	0.304
0.70	0.387
0.75	0.475
0.80	0.573
0.85	0.683
0.90	0.792
0.95	0.898
1.0	1.0

series of the g_i values corresponds to the series of values characteristic for void grain fractions g_g : $1 - 0.467 - 0.35 = 0.183$, $1 - 0.467 - 0.40 = 0.133$, $1 - 0.467 - 0.45 = 0.083$ etc. up to the value approximately equal to zero. This series must be associated with the values of effective gas diffusion coefficient D_e in support grains.

Then one must calculate the corresponding effective diffusion coefficients D^{**} characterizing combined gas percolation clusters with a given concentration g_i . Such clusters include all support grains with concentration $g_s = 0.467$ and diffusion coefficient D_e and the corresponding void grain fractions with the diffusion coefficient of $[(4 \times 10^{-3}) 80/30] \times 2 = 2.133 \times 10^{-2} \text{ cm}^2/\text{s}$ (formula (4): we assumed the void grain edge size to be 80 nm and porosity $\tau = 1$).

A specific example: Let $g_s = 0.467$, $g_e = 0.3086$, and $g_i = 0.35$; then $g_g = 1 - 0.467 - 0.35 = 0.183$. And the combined gas cluster consists of support grains with diffusion coefficient $D_e = [(4 \times 10^{-3}) g_{\text{gas}}/1.5]$ $D^* = [(4 \times 10^{-3}) \times 0.6914/1.5] 0.3934 = 7.253 \times 10^{-4} \text{ cm}^2/\text{s}$ (the data of Table 1) and of void grains with concentration $g_g = 0.183$ and with diffusion coefficient $D_g = 2.133 \times 10^{-2} \text{ cm}^2/\text{s}$. Let us point out that $D_e/D_g = 3.3 \times 10^{-2}$. The diffusion in support grains is much lower than diffusion in void grains. If $g_e = 0.1875$, then $D_e = 1.321 \times 10^{-3} \text{ cm}^2/\text{s}$ and $D_e/D_g = 6.193 \times 10^{-2}$.

Algorithms of computer calculation of effective Knudsen diffusion coefficient D^{**} in a combined gas cluster are related in the Annex (in the end of this paper). The results of calculation of the dependence of D^{**} on g_i are shown in Fig. 4 and in part in Table 3.

It is clear that concentration g_g of void grains decreases at an increase in Nafion concentration g_i in the active layer. Which would actually lead to a significant decrease in the value of effective Knudsen diffu-

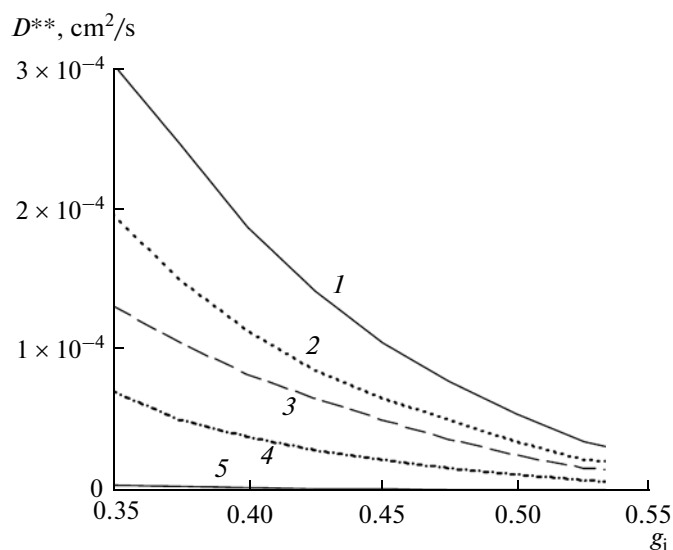


Fig. 4. Dependence of effective coefficient of Knudsen diffusion D^{**} in a combined gas cluster on the bulk concentration of Nafion grains g_i in the active cathode layer and on the fraction of carbon particle grains in the support grains. g_e : (1) 0.1875, (2) 0.3086, (3) 0.3730, (4) 0.4941, (5) 0.5977.

sion coefficient D^{**} of oxygen. According to Table 1, D^{**} decreases also at an increase in concentration g_e of the carbon component in support grains, as this results in a decrease of gas porosity g_{gas} in grains (formula (5) and the data of the last column of Table 1).

Table 3. Dependence of effective Knudsen diffusion coefficient D^{**} in a combined gas cluster on the concentration of Nafion grains g_i in the active cathode layer and on fraction g_e of carbon particle grains in the support grains

g_e	g_i	$D^{**} \times 10^4, \text{cm}^2/\text{s}$
0.1875	0.35	3
	0.40	1.9
	0.45	1.1
	0.50	0.55
0.3730	0.35	1.3
	0.40	0.84
	0.45	0.51
	0.50	0.26
0.5977	0.35	0.04
	0.40	0.025
	0.45	0.015
	0.50	0.0077

6. ESTIMATE OF SURFACE ON WHICH ELECTROCHEMICAL PROCESS OCCURS

In order to calculate the overall currents in the active layer of a cathode with polymer electrolyte and combined gas percolation cluster, it is necessary to determine, apart from the values of effective active layer coefficients (proton conductivity and diffusion coefficient), also the surface area on which the electrochemical process occurs.

There is no Nafion in support grains, so current generation can occur only on the outer surface of support grains. According to the data of Table 1, the fraction of electrochemically active surface of an individual support grain is $S_{\text{out}}/384$. And in order to determine the specific reaction surface area, one has to find the number of common faces in a model cube with the size of $100 \times 100 \times 100$ for electron and proton percolation clusters on which the actual electrochemical process occurs.

We have already solved such a problem in [16]. Now, we have to take into account that the fraction of support grains is $g_s = 0.467$ and fraction g_i of Nafion grains will be varied: from 0.35, 0.40 etc. to the maximum possible value. Herewith, the fraction of void grains being $1 - 0.467 - g_i$ will gradually decrease to the minimum value.

It remains to calculate each time with the help of a computer the number of common faces for electron and ion percolation clusters and then divide these numbers by 10^6 . These would be the specific reduced (multiplied by length L of grain edges) 3D contact surfaces between the ion and electron clusters: S_i . The dependence of S_i on g_i is shown in Fig. 5 and in part in Table 4.

Table 4. Dependence of reduced specific surface area S_i , on which the current generation process occurs, on bulk concentration g_i of Nafion grains in the active layer (the volume of support grains in the active layer $g_s = 0.467$)

g_i	S_i
0.350	0.5984
0.375	0.7539
0.400	0.8750
0.425	0.9786
0.450	1.0717
0.475	1.1579
0.500	1.2392
0.525	1.3170
0.533	1.3413

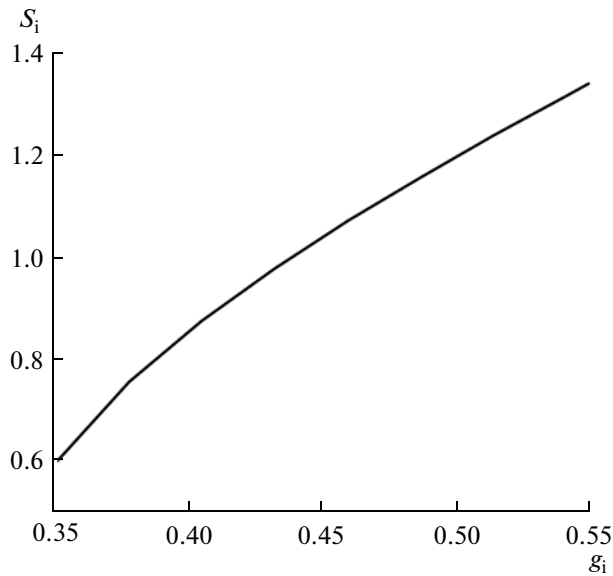


Fig. 5. Dependence of reduced specific surface area S_i , on which the current generation process occurs, on bulk concentration g_i of Nafion grains in the active layer (the volume of support grains in the active layer $g_s = 0.467$).

7. CALCULATION OF OVERALL CATHODE CURRENTS

Two polarization curve slopes are observed in the case of oxygen reduction on platinum in acidic media: 60 mV (high potential range) and 120 mV (low potential range) [17–20]. Regularities of calculation of overall cathode currents for the cases when the polarization curve has two sections with different slopes are considered in [21]. Let us perform calculations at the assumption that cathode potential $E_0 = 0.6$ V, active layer thickness $\Delta = 5 \times 10^{-4}$ cm; the remaining parameters required for calculations are given at the end of the paper in the List of Parameter Designations.

One should take into account that characteristic ohmic length L_{ohm} and characteristic ohmic current I_{ohm} in the high potential region take the form of:

$$L_{ohm} = [b_1 \kappa^{**} L / S_i (S_{out} / 384) i_0]^{1/2}, \quad (10)$$

$$I_{ohm} = [b_1 \kappa^{**} S_i (S_{out} / 384) i_0 / L]^{1/2}. \quad (11)$$

And characteristic diffusion length L_d and characteristic diffusion current I_d in the high potential range take the form of:

$$L_d = [n F D^{**} c_0 L / S_i (S_{out} / 384) i_0]^{1/2}, \quad (12)$$

$$I_d = [n F D^{**} c_0 S_i (S_{out} / 384) i_0 / L]^{1/2}, \quad (13)$$

where $L = 8 \times 10^{-6}$ cm is the grain size, the values for S_{out} must be taken from Table 1, $\kappa^{**} = \kappa \kappa^*$ is the effective specific proton conductivity of the active layer (Table 2), D^{**} is the effective Knudsen diffusion coefficient of the combined gas percolation cluster (Table 3), the S_i values are given in Table 4.

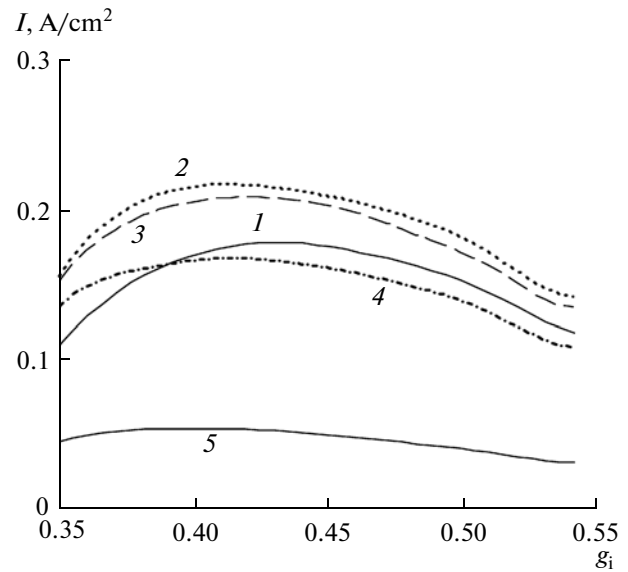


Fig. 6. Dependence of overall current I of the oxygen cathode of a fuel cell with polymer electrolyte on the bulk concentration of Nafion grains g_i in the cathode active layer and on the fraction of carbon particle grains on the support grains. g_e : (1) 0.1875, (2) 0.3086, (3) 0.3730, (4) 0.4941, (5) 0.5977. Cathode potential $E_0 = 0.6$ V, cathode active layer thickness $\Delta = 5 \mu\text{m}$.

The results of calculations of the dependence of overall currents on fraction g_i of Nafion grains are shown in Fig. 6 and in part in Table 5. The parameters of calculations in Fig. 6 were the five porosity values

Table 5. Dependence of overall current I of the cathode with polymer electrolyte on the fraction of carbon particle rains in support grains g_e and on Nafion concentration g_i in the active layer

g_e	g_i	I , mA/cm ²
0.1875	0.35	110.2
	0.40	172.5
	0.45	174.6
	0.50	145.9
0.3730	0.35	153.6
	0.40	207.5
	0.45	201.4
	0.50	164.0
0.5977	0.35	48.7
	0.40	55.1
	0.45	49.0
	0.50	38.7

Table 6. Maximum values of overall currents I and the corresponding values of Nafion concentrations g_i in the active layer of a cathode with polymer electrolyte with the support grains characterized by parameter g_e

g_e	g_i	I , mA/cm ²
0.1875	0.425	179.5
0.3086	0.410	218.4
0.3730	0.415	209.9
0.4941	0.410	168.5
0.5977	0.395	55.19

Table 7. Dependence of ohmic L_{ohm} and diffusion L_d characteristic lengths and ohmic I_{ohm} and diffusion I_d characteristic current on the fraction of carbon particle grains g_e and on Nafion concentration g_i in the active layer of the cathode with polymer electrolyte

g_i	g_e	L_{ohm} , cm	L_d , cm	I_{ohm} , mA/cm ²	I_d , mA/cm ²
	0.1875				
0.35	0.1875	0.127	0.386	0.125	0.380
0.40		0.217	0.251	0.312	0.361
0.45		0.300	0.170	0.529	0.299
0.50		0.373	0.114	0.760	0.232
	0.3730				
0.35	0.3730	0.077	0.154	0.207	0.414
0.40		0.131	0.101	0.516	0.399
0.45		0.181	0.071	0.875	0.343
0.50		0.225	0.047	1.258	0.264
	0.5977				
0.35	0.5977	0.057	0.020	0.276	0.097
0.40		0.098	0.013	0.689	0.092
0.45		0.136	0.009	1.168	0.079
0.50		0.169	0.006	1.678	0.061

corresponding to carbon microcubes in the support grain with the optimum cluster, g_e : 0.1875, 0.3086, 0.3730, 0.4941, 0.5977.

For example: let $g_e = 0.1875$. Then at $g_i = 0.35$, effective conductivity $\kappa^* = 0.0061$ (Table 2) and in formulas (10) and (11), $\kappa^{**} = \kappa^* \kappa = 0.0061 \times 0.1 \text{ S cm}^{-1}$. In formulas (10)–(13), $S_{out} = 50$ (Table 1). The D^{**} value is obtained from Table 3.

Let us determine the optimum current (electrochemical activity of the cathode) for each of the five curves in Fig. 6 and the values of parameters g_e and g_i corresponding to this optimum. These data are presented in Table 6. The generated currents proved to be

low: two hundreds of mA per cm² of the visible surface of the active cathode layer. The low current values can be explained.

Firstly, only the outer support grain surface participates in current generation, as it was assumed that there is no Nafion within the support grains and therefore no protons penetrate them. But as shown in Fig. 2 and by the data of Table 1, the number of active carbon cluster faces (Fig. 1c) on the support grain surface S_{out} is much lower than overall number S of outer faces of the carbon cluster. Therefore, the platinum utilization degree in the active layer must also be very small. And thus the current generated on the cathode must also be small.

Secondly, there are difficulties with transport of both protons and oxygen molecules towards support grains. An increase in concentration g_i of Nafion grains causes an increase in proton conductivity κ^{**} of the active layer (Table 2). But herewith, concentration g_g of void grains is simultaneously decreased. Thus, the value of effective Knudsen diffusion coefficient D^{**} in the combined gas cluster decreases (Table 3).

These regularities are also clearly seen in the data of Table 7. It contains the calculated characteristic ohmic and diffusion lengths and currents (formulas (10)–(13)). At an increase in g_i (the first column of Table 7), ohmic limitations decrease, but diffusion limitations increase. This circumstance is incidentally related to the character of curves in Fig. 6. The maximum in these is not very pronounced.

The thickness of active cathode layers was chosen rather arbitrarily. The issue of the change in the overall current under variation of the active layer thickness appears. The answer is in the data of Fig. 7. The values of the main parameters are chosen close to the optimum: $g_e = 0.3086$, $g_i = 0.4$ (Fig. 6, Table 6). Therefore $\kappa^{**} = 2.6 \times 10^{-3} \text{ S cm}^{-1}$, $S_{out} = 111$, $S_i = 0.875$, $D^{**} = 1.1 \times 10^{-4} \text{ cm}^2/\text{s}$, $L_{ohm} = 0.1455 \text{ cm}$, $L_d = 0.1312 \text{ cm}$, $I_{ohm} = 4.646 \times 10^{-4} \text{ A/cm}^2$, $I_d = 4.646 \times 10^{-4} \text{ A/cm}^2$. The dependence of cathode current I on active layer thickness Δ has a maximum at $\Delta = 5.5 \mu\text{m}$. The maximum overall current is $I_{max} = 264.7 \text{ mA/cm}^2$.

The dependence of I on Δ has an extremum. The explanation is as follows: the fact is that protons and oxygen are supplied from the opposite sides of the active layer. It is clear that an increase of the active layer thickness to infinity results in the current dropping to zero.

The role of diffusion and ohmic limitations, the choice of the working thickness of the active layer of the cathode with Nafion and platinum was studied in [22]. Calculation of the optimum thicknesses of the active layer of an oxygen and air fuel cell with Nafion and platinum was also carried out in [23].

8. CONCLUSIONS

The mechanism of current generation in the active layer of the cathode of a fuel cell with solid polymer electrolyte differs fundamentally from that in the cathodes with liquid electrolyte. There were no problems with transport of ions and gas molecules, such problems appeared in the active layer with polymer electrolyte.

Now, one has to apply not only agglomerates (grains) of Nafion molecules towards proton transport and not only void grains, but also support grains (agglomerates of carbon particles with supported platinum) must be involved in oxygen transport. Thus, support grains, apart from their usual functions (supply of electron transport in the active layer and promotion of electrochemical process, electrochemical current generation in them) must also promote to their best ability transport of protons and gas.

It is clear that transport options of support grains are small. However, their large amount (approximately 50% of the active layer volume must be filled by support grains [1]) results in the fact that transport of protons and oxygen molecules is now bound to occur through combined percolation clusters (grains of any type: Nafion grains and void grains plus the support grains). This also causes a more or less acceptable value of effective coefficients of the active cathode layer: tolerable values of specific proton conductivity and Knudsen diffusion coefficient of oxygen.

In this study, the support grain structure (a carbon cluster possessing electron conductivity along the three axes) was formed and their main parameters were calculated. All calculations were made under the assumption that there are no Nafion molecules within the support grain, so that such a grain possesses zero proton conductivity.

In conclusion, the overall current in the active layer of a cathode with a polymer electrolyte was calculated where proton conductivity is provided only by Nafion grains and the Knudsen diffusion of oxygen is created only by a combined percolation gas cluster consisting of void grains and support grains.

The overall currents at $t = 80^\circ\text{C}$ and the pressure of $p^* = 101 \text{ kPa}$ proved to be low: the maximum overall current at the active layer thickness of $\Delta = 5.5 \text{ }\mu\text{m}$ is $I_{\text{max}} = 264.7 \text{ mA/cm}^2$. Apparently, the value of currents can be increased significantly if the support grains are constructed that possess simultaneously both proton conductivity and the ability to support Knudsen diffusion of oxygen.

List of Notations of Parameters Characterizing the Fuel Cell with Nafion and Platinum and Their Values Used in Calculations

Active Layer Parameters:

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

$p^* = 101 \text{ kPa}$ is the pressure in the gas chamber

$\Delta = 5 \times 10^{-4} \text{ cm}$ is the active layer thickness

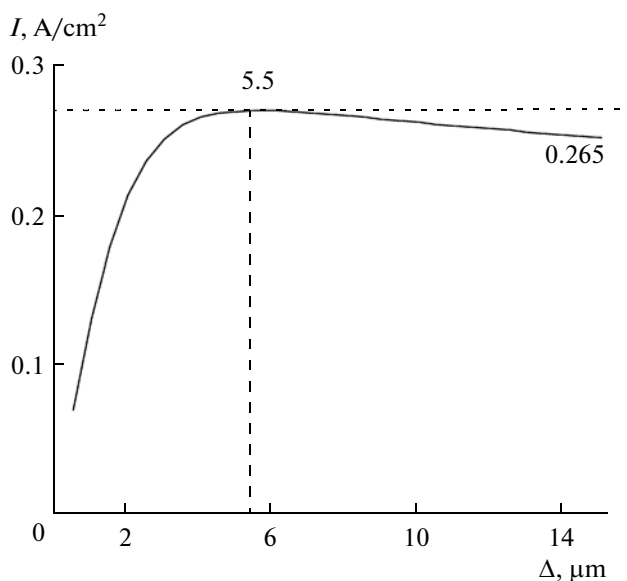


Fig. 7. Dependence of overall current I of the oxygen cathode of a fuel cell with polymer electrolyte on the active layer thickness Δ . The fraction of carbon particle grains in support grains is $g_e = 0.3086$, the bulk concentration of Nafion grains in the active layer is $g_i = 0.4$, the cathode potential is $E_0 = 0.6 \text{ V}$.

$E_{\text{st}} = 1.05 \text{ V}$ is the steady-state potential of the cathode

$E^* = 0.825 \text{ V}$ is the potential of the break point on the Tafel curve

$E_0 = 0.6 \text{ V}$ is the potential of the cathode

I , mA/cm^2 is the overall current

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

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

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

$F = 9.65 \times 10^4 \text{ C/mol}$ is the Faraday number

$i_0 = 1.01 \times 10^{-7} \text{ A/cm}^2$ is the exchange current in the high potential range at $t = 80^\circ\text{C}$

$c_0 = 5 \times 10^{-6} \text{ g-mol/cm}^3$ is oxygen solubility in Nafion at $p^* = 101 \text{ kPa}$

$\kappa = 0.1 \text{ S cm}^{-1}$ is the specific optimum proton conductivity of Nafion

κ^* (a dimensionless value) is the effective proton conductivity of the proton percolation cluster

$\kappa^{**} = \kappa^* \kappa$ is the effective specific proton conductivity of the active layer of a cathode with polymer electrolyte

g_s is the fraction of support grains in the active layer

g_i is the fraction of Nafion grains in the active layer

g_g is the fraction of void grains in the active layer

g_i^* is the percolation threshold for the proton percolation cluster

D^{**} is the effective diffusion coefficient of oxygen in the combined gas cluster

Parameters of an Individual Support Grain:

g_0 is the initial concentration of carbon microcubes
 g is the concentration of carbon microcubes in the optimum cluster

$S = S_{\text{out}} + S_{\text{in}}$ is the overall number of faces on the outer optimum cluster surface

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

S_{in} is the number of faces of the optimum cluster within a support grain

g_e is the porosity of microcubes in a support grain

g_{gas} is the porosity of voids in a support grain

m_0 is the initial number of microcubes in the optimum cluster

m is the number of microcubes in the optimum cluster

D_{kn} , cm²/s is the effective Knudsen diffusion coefficient of the gas in support grain pores (accounting for the average pore size value)

D^* is the effective Knudsen diffusion coefficient of the gas in a support grain (accounting for the support grain microstructure, a dimensionless parameter)

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

D_g is the Knudsen diffusion coefficient of the gas in void grains

$L = 80 \text{ nm} = 8 \times 10^{-6} \text{ cm}$ is the size of the edges of support, Nafion, and void grains

$d = 10 \text{ nm} = 10^{-6} \text{ cm}$ is the size of edges of carbon particles in support grains

if $M_{ijk} = 0$, then the cell contains a Nafion cell (we assign it index 0, as Nafion cells do not participate in gas diffusion). For convenience of description of the method of calculation of the diffusion coefficient, we will write further that the cell is either in “phase 1” or in “phase 2” or in any other one.

A random distribution of components across the cube volume was modeled using formation of array M of 10^6 elements with the help of a random-number generator. Herewith, the number of cells with phase “1” corresponded to g_s , the fraction of support grains, the number of cells with phase “2” corresponded to g_i , the fraction of Nafion grains.

Gas diffusion in the active layer is possible both through void grains and through support grains. Therefore, it is necessary to identify a combined gas cluster representing the set of continuous chains of void grains and support grains contacting each other and providing gas access from the active layer surface contacting the gas-diffusion layer. For this purpose, duplicate array M_{dub} is created that fixes the initial phase distribution. Then, the elements of matrix M corresponding to cells containing support or void grains are temporarily assigned the other (but similar!) phase, e.g., phase “7.” Let us fix cells with phase “7” on the upper cube surface (i.e., find elements M_{ijk} with $k = 1$) and consider them as sources of a “phase” wave that propagates along the chains of cells with phase “7” and converts them to a state with phase “8” (for example). Movement of the “wave front” occurs according to the Huygens–Fresnel principle for wave processes in optics [24]. Namely, each cell that has changed its phase becomes a source of a “secondary wave” that changes the phase of the neighboring cell if it is adjacent to it and is in phase “7.” If a wave reaches the lower cube face, this points to the presence of a conducting cluster. The cells that a wave could not penetrate do not change their phase and therefore are not included into the cluster. Having determined the cells on the lower cube boundary (elements M_{ijk} with index $k = 100$) that changed phase “7” to phase “8,” we consider them as primary sources of a new wave propagating in the direction from the lower boundary to the upper one and changing cell phases to new phase “9.” Thus, dead-end channels beginning on the upper layer boundary but never emerging to the lower layer boundary are cut off from the cluster.

The obtained cluster has a rather branched shape. Certain branches represent dead-end channels. This means that one of the ends of the chain of cells forming a channel turns out to be isolated from other cells conducting gas. It is clear that such channels cannot participate in gas transport from the outer layer boundaries and must be excluded from consideration of the gas diffusion process in the modeled medium. Removal of dead-end channels (“cutting” of the cluster) was performed using a separate subprogram; its algorithm is also based on the “wave approach” towards the search

APPENDIX

ALGORITHMS OF COMPUTER CALCULATIONS OF EFFECTIVE KNUDSEN DIFFUSION COEFFICIENT IN COMBINED GAS CLUSTER

The volume of a support grain was divided into equally sized cells: microcubes with carbon (catalyst support), microcubes of Nafion, and void microcubes (we will further denote them as grains). The distribution of these components across the cells was random.

The values of reduced effective specific Knudsen diffusion coefficient D^{**} were calculated as follows:

1. It was assumed that a cube consists of $100 \times 100 \times 100$ cells. The corresponding 3D array M (100, 100, 100) of 10^6 numbers was considered for description of the structure. Indices (i, j, k) of each element M_{ijk} determine the geometric position of a cell in the cube and the numerical value of the element corresponds to the active layer component located in this cell. If $M_{ijk} = 1$, this means that the cell is occupied by a carbon black particle, if $M_{ijk} = 2$, this is a void cell,

for such channels. Cells of dead"; the cells of the "cleaned" cluster are marked as phase "3."

Thus, a cluster is obtained, in which each cell can participate in gas transport from one active layer boundary to the opposite boundary. To find out what components were included into the cluster, elements of transformed matrix M and matrix M_{dub} storing information on distribution of components across the cells are compared. If any element $M_{ijk} = '3'$ and $M_{\text{dub}ijk} = '1'$, this means that a support grain is located in a cell within a cluster with indices $\{i, j, k\}$. Therefore, the value of $M_{ijk} = '1'$ is assigned now to this element of matrix M . Similarly, if $M_{\text{dub}ijk} = '2'$, then accordingly $M_{ijk} = '2'$.

A combined gas cluster consists of support grains with diffusion coefficient $D_{\text{kn}}D^*$ and void grains with diffusion coefficient $D_g = 2.133 \times 10^{-2} \text{ cm}^2/\text{s}$. The effective diffusion coefficient of D^{**} of a combined gas cluster was calculated in the same way as in calculations of conductivity of an electric circuit [12] by numeric simulation using the Monte-Carlo method [25, 26].

Each gas cluster cell was represented as a node with six gas channels. It was naturally assumed that gas diffusion in a separate cell is similar both in the vertical and horizontal direction. The lattice nodes are numbered using whole numbers. Each channel connecting nodes i and k is characterized by diffusion coefficient $D_{i,k}$. Herewith, the composite channel connecting neighboring void cells is characterized by coefficient D_g ; a composite channel connecting neighboring support cells is characterized by coefficient D_e . The gas diffusion coefficient in a channel connecting support cells with void cells was assumed equal to

$$D_{\text{eg}} = 2D_e D_g / (D_g + D_e). \quad (\text{A})$$

According to the Fick law, the flux in each channel can be written as:

$$J_{ik} = -D_{ik}(C_i - C_k), \quad (\text{B})$$

where C_i is the gas concentration in node i (cell).

The sum of fluxes converging in each node is zero:

$$\sum D_{ik}(C_i - C_k) = 0, \quad (\text{C})$$

where summation is carried out over all neighboring nodes, to which node i is connected to conducting channel. As follows from equation (C), if fluxes are steady-state, concentrations of the neighboring nodes are related through the relationship of:

$$C_i = \left\{ \sum_{k=1}^m D_{ik} C_k \right\} / \sum_{k=1}^m D_{ik}, \quad (\text{D})$$

where m is the number of neighboring nodes, to which this node is connected through a conducting channel.

The value of concentration C in each node of the upper ("front") layer is assumed to be unity and the concentration in the nodes of the opposite ("rear") layer is equated to zero (these values remain

unchanged in the course of numeric iterations). The values of concentrations of inner nodes C_i at the beginning of calculations are provided arbitrarily in the range of 0 to 1.

For each node located in the conducting cell center, equation (D) is solved numerically, namely: the concentration in the node is calculated as the average concentration of all the surrounding neighboring nodes in conducting cells. The nodes are considered consequently across the layers in the direction from the front active layer surface to its rear boundary.

After the first run overall all the cells, significant concentration redistribution is possible. However, the concentration distribution acquires a steady-state character under the further iterations. Iterations are over when the difference in the flux values on the front and rear boundaries of the studied sample becomes vanishingly small. The flux on the front surface is calculated as a sum of fluxes from the node with concentration $C = 1$ to a conducting node to the next closest layer:

$$I_F = \sum_n D_n(1 - C_n), \quad (\text{E})$$

where summation is carried out over all nodes with a channel emerging to the front boundary.

Similarly, the flux through the rear lattice surface is determined by the equality:

$$I_T = \sum_m D_m C_m, \quad (\text{F})$$

where summation is carried out over all nodes emerging to the rear boundary with concentration $C = 0$.

The effective diffusion coefficient of gas diffusion in a combined cluster for each specific model lattice configuration is determined as the ratio of the flux in the system to the difference in the concentrations on the outer boundaries: $D^{**} = I/\Delta C = I$, as we assume that $\Delta C = 1$.

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