

Active Layer of an Electrode with Polymer Electrolyte: Estimation of Platinum Utilization Degree

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Abstract—A specific feature of the electrode active layer with polymer electrolyte consists in the fact that the current generation process can occur only on the condition of the direct contact of the catalyst support (carbon black) particles with Nafion. However, in reality, the support particle agglomerates (grains) contact the Nafion particle agglomerates (grains). Therefore, one must expect a low catalyst (platinum) utilization degree. A hypothesis is offered that a fractal film of Nafion is formed on the surface of the support grain pores in the case of manufacturing the “catalytic ink” used to form the active layer. It can significantly increase the platinum utilization degree. A detailed computer simulation of the process of Nafion penetration into the support grain pores is performed. Factors are established allowing reaching a high platinum utilization degree. The data of computer simulation agree with the experimental estimates of platinum utilization degree.

Key words: fuel cell with polymer electrolyte, active layer, platinum utilization degree, diffuseness factor of the contact surface of ionic and gas percolation clusters, fractal film, Brownian motion

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INTRODUCTION

A fuel cell with polymer electrolyte (in the first place, with Nafion) still remains at the beginning of the XXI century one of the most promising sources of environmentally clean electric energy obtained at a high efficiency. But it is not devoid of obvious faults. One of them is an incomplete platinum utilization degree: not all platinum applied on the support (carbon black) can participate in the current generation process.

In the active layer of hydrophobically modified porous electrolytes, the whole catalyst surface wetted with an acidic electrolyte solution can potentially participate in an electrochemical process, as protons migrate and diffuse freely in a liquid. It is not so in the case of the active electrode layers with Nafion. Here, protons are “connected” to the Nafion molecules, so that the current generation process occurs only where Nafion contacts directly the catalyst applied on the support, as shown in Fig. 1a. It is not easy to provide such a contact by organizing a high specific surface of the support/Nafion contact. Therefore, the active platinum fraction accessible for the electrons (e), gas molecules (O_2 , if it is the cathode), and protons (H^+), can appear low. Platinum utilization degree ψ corresponding to the ratio of the catalyst active surface to its overall surface per active layer volume unit would also be low.

The low platinum utilization degree is evidenced by the results of studying the microstructure of the active

layer of the electrodes with Nafion and platinum on a carbon support using the methods of transmission microscopy: TEM (transmission electron microscopy) and SEM (scanning electron microscopy). Such studies were performed, e.g., in [1, 2]. It is shown that the corresponding agglomerates are formed of carbon particles (carbon black) and Nafion particles (we will further designate them as the support grains and Nafion grains). It is obvious herewith that the contact surface of these grains must correspond to a very low fraction of the whole support grain surface coated by platinum particles. Therefore, it would seem that the platinum utilization degree must be low.

The aim of this communication is to assess the platinum utilization degree for the electrodes with polymer electrolyte, identify the mechanisms and factors affecting the values of this important performance indicator of the electrodes of this type and try to discover the conditions assisting the high platinum utilization degree.

ESTIMATION OF PLATINUM UTILIZATION DEGREE ON THE HYPOTHESIS THAT ONLY THE EXTERNAL SUPPORT GRAIN SURFACE IS ELECTROCHEMICALLY ACTIVE

Let us now quantitatively estimate the platinum utilization degree assuming that the electrochemical process occurs only at the external support grain surface, where it contacts Nafion grains.

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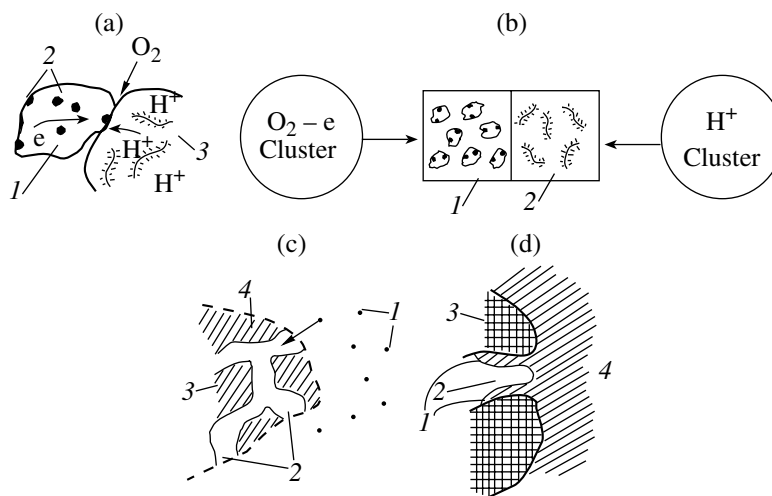


Fig. 1. Schematic drawing of the interface of the platinum support (carbon black)/solid polymer electrolyte: (a) contact of (1) the carbon black particle, (2) platinum crystallite on it, and (3) Nafion particles transferring protons; (b) contacts of (1) platinum support grains and (2) Nafion within the corresponding percolation gas and ionic clusters ("model of equal-size grains"); (c) deposition of (1) Nafion particles within the solution on (2) the pore surface of (3) the platinum support grain consisting of (4) an agglomerate of carbon black particles; (d) formation of a (1) fractal Nafion film on the (2) pore walls in the support grain at the contact interface of (3) platinum support grain/(4) Nafion grain.

Computer simulation of the structure of active layers of the electrodes with Nafion and platinum was carried out in [3, 4]. A "model of equal-sized" grains was suggested that is convenient for calculation of the overall electrode parameters (currents and power densities). In it, the support grains and Nafion grains correspond to microcubes of similar size with edge length L distributed randomly in the active layer. Such a "primary" active layer structure can generate a significant current only in the case when two percolation clusters are formed in the active layer: a ionic cluster (an ensemble of interconnected Nafion grains; it is a channel for supplying protons into the current generation region) and gas cluster (an ensemble of interconnected porous support grains; it is the small pores in the support grains that form a channel for oxygen supply into the current generation region).

The processes of current generation in the electrode with polymer electrolyte are concentrated in the "secondary" active layer structure. It represents an interface of the ionic and gas percolation clusters (let us designate its specific surface as S^*). In the calculations of the S^* value, it was assumed that the contact interfaces of the support grains and Nafion grains (Fig. 1b) being a part of the corresponding clusters represent geometrically smooth surfaces: squares with surface area L^2 .

The generated current value determines the composition of the components forming the active layer: bulk concentrations of Nafion grains g_e , support grains g_s , and "grains" inevitably present in one way or another: voids, g_0 . As the sum of these concentrations is 1, in order to register the composition of the active layer components unambiguously, it is sufficient, e.g., to fix the g_0 value and consider it a parameter and start vary-

ing the g_e value. Then the g_s value will be determined by the following expression:

$$g_s = 1 - g_e - g_0. \quad (1)$$

Calculation of the dependence of the reduced specific surface area of the contact between the ionic and gas percolation clusters ϵ determined as $\epsilon = S^*L$ on the polymer electrolyte bulk concentration g_e was performed in [3, 4]. The calculation results are presented in Table 1. It can be seen that at the given value of the grain edge length L , specific surface area S^* depends significantly on the amount of voids in the active layer g_0 . The probability of the support grain contact with a Nafion grain must obviously decrease fast at an increase in the void fraction. As shown in Table 1, S^* reaches maximum values at $g_0 = 0$

Table 1. Dependence of reduced specific surface, on which the current generation process occurs, on the bulk solid polymer electrolyte concentration

g_e	$\epsilon = S^*L$	
	$g_0 = 0.0$	$g_0 = 0.1$
0.35	0.908	0.755
0.40	1.198	0.966
0.45	1.325	1.021
0.50	1.362	0.965
0.55	1.325	0.759
0.60	1.196	0.0
0.65	0.906	0.0

(the voids are absent). Under variation of the Nafion grain bulk concentration g_e , specific surface area S^* reaches its maximum (which is again quite obvious, assuming that $g_0 = 0$), if the following equality is fulfilled:

$$g_s = g_e. \quad (2)$$

This condition must be considered optimum for the current generation process in an electrode with polymer electrolyte.

Thus, we have finally that in the case of the optimum composition of the components ($g_0 = 0$ and $g_s = g_e$) in the active layer, according to the data of Table 1,

$$S^* = S_{\max}^* = 1.362/L. \quad (3)$$

Naturally, the specific contact surface area of the ionic and gas clusters represents only a part of the overall specific surface area of equal-size cubes of two types (Nafion cube grains and platinum support cube grains with pores throughout and porosity ν). It can be shown that this overall specific surface area Σ composed of all the cube grain faces (without discrimination of their nature) is equal to:

$$\Sigma = 3/L. \quad (4)$$

The fact is that the amount of cube grains per active later volume unit is $1/L^3$, the face surface area of each cube grain is $6L^2$. It would seem that the specific surface area of all the faces is $6L^2(1/L^3) = 6/L$. However, in this calculation, each of the cube faces is obviously considered twice. Therefore, the exact result is provided by formula (4).

Comparison of expressions (3) and (4) allows making an important conclusion. In the "model of equal-size grains" at an optimum choice of the concentrations of the active layer components, approximately only a half of all the faces (more precisely, $1.362/3 = 45.4\%$) corresponds to the contact interface of the ionic and gas clusters. Thus, choosing an arbitrary support cube grain belonging to the gas cluster and assuming that the porosity of this grain is $\nu = 0.5$, one can state that the external surface of such a cube s bordering on the surface of the Nafion grains belonging to the ionic cluster turns out to be, on the average:

$$s = 1.362L^2\nu = 1.362L^2/2. \quad (5)$$

It is useful to compare this surface area with the overall inner and outer surface of the same support cube grain. The data of Table 1 also allow doing this.

Let us imagine that the whole active layer volume is filled only by the support grains. Let us further assume that the carbon black particles forming these grains are all similar and have a form of the cubes with edge d . All of them together with the voids separating them (the latter can also obviously be rendered as separated into similar microcubes with edge d) are packed into a cubic mode lattice (according to the percolation theory terminology [5]). Then, according to the data of Table 1 (let us substitute the support grain/Nafion grain pair by the

pair of carbon black particles/void "particles"), the specific surface of such an imaginary support grain of infinite size that is open for electrocatalysis reaches a maximum provided that the support grain porosity $\nu = 0.5$. The formula for estimation of the specific surface area of the carbon black particles herewith is similar to relationship (3) and the surface area value is $1.362/d$.

However, our concern is not the overall specific surface, $1.362/d$, but the overall surface s_L of a separate support grain available for electrocatalysis, which is a finite-size object limited by volume L^3 . In this case, we have the expression of:

$$s_L = L^3(1.362/d). \quad (6)$$

Thus, the possibility of estimating the platinum utilization degree in the active layer ψ appears, provided that only the contact surface of the ionic and gas clusters participates in the current generation process. Finally, with account for relationships (5) and (6), we obtain:

$$\psi = s/s_L = 1.362L^2\nu/L^3(1.362/d) = d\nu/L = d/2L. \quad (7)$$

Let us now perform the numeric evaluation of quantity ψ . As shown by the studies of the microstructure of the electrode active layer with polymer electrolyte [6], the size of separate support (carbon black) particles is approximately 20–40 nm; the size of the carbon black particle agglomerates (support grains) is 200–300 nm. The pores between the support grains are in the same range of sizes and they are either partially or completely filled by agglomerates of the polymer electrolyte molecules (Nafion grains). Let us assume the size of the carbon black microcubes in the support grains $d = 30$ nm and the support grain size $L = 8d = 240$ nm. Then, according to relationship (7), the platinum utilization degree, as could be expected, turns out to be very low, $\psi = (1/16) \times 100 = 6\%$.

Let us now turn to the literature data. They indicate that the platinum utilization degree (its surface fraction participating in the electrochemical process) in the fuel cell cathodes with Nafion is at present increased to the record values: up to 75–98% [7, 8] (in [9], the platinum utilization degree is estimated within the limits of 60–70%; in [10], it is within 80–90%). Earlier, the ψ value was estimated to be within 20–25% [11].

What is the cause of deviation of the theoretical estimates and the obtained experimental data? In our opinion, the assumption forming the basis of the above estimates that only the outer surface of the support grains participates in the current generation process is incorrect in principle. In fact, the contact interface of the electronic and ionic clusters (Fig. 1b) does not represent a geometrically smooth surface; in practice, a certain transition range exists, in which the carbon black particles are mixed with Nafion. But how is the contact of the two phases realized? How is a sufficiently extended contact interface of carbon black and Nafion constructed, as required by Fig. 1a? It remains to assume that the following takes place.

One of the necessary stages of the process of preparing the “catalytic ink” (a solution of the mixture of agglomerates of carbon black and Nafion particles), a substance of which later the active layer is formed, is a prolonged ultrasonic treatment of the solution. At this stage, not only intensive stirring of the carbon black and Nafion particles can occur, but also decomposition of Nafion agglomerates to fragments. The smallest of these can penetrate (Fig. 1c) the support grain pores. Herewith, the process of Nafion molecule adhesion on the carbon surface can occur within the support grain. As a result, the surface of the pores within the support grain coated by a catalyst can be partially or even wholly covered by a fractal Nafion film (Fig. 1d). Then, not only the outer surface, but also some of the inner surface of the support grains can participate in the current generation process. And in this case, the platinum utilization degree turns out to be higher and corresponding to the values registered in the experiments.

COMPUTER SIMULATION OF THE NAFION ADSORPTION PROCESS ON THE INNER SURFACE OF THE SUPPORT GRAINS

Thin porous layers of nanoparticles with a fractal structure (in short, fractal films) are required in many devices. They are used in sensors [12], supercapacitors [13], in power sources [14] and, above all, in fuel cells [15, 16]. The methods of fractal film manufacturing are diverse. The processes used are reduction, thermal decomposition, deposition in vacuum of the corresponding precursors, deposition of noble metals on the support, deposition from the salt solutions etc.

The fractal clusters and films are usually “grown” on point objects, various surfaces or in bulk. In our case, it is necessary to create fractal films within a porous structure. Review of the literature data shows that this is a wholly new subject of research that has apparently not been studied before by anyone.

Here is another general remark. The information on the properties of fractal films and, broader, fractal clusters can in principle be obtained experimentally. However, this is a very complicated problem. It is much easier to study fractal structures using computer simulation. It was this approach that lay foundations for the knowledge on fractal clusters. Advantages of computer experiments are obvious: one can swiftly obtain results and use models with varied parameters. The latter allows approximating the character of a fractal cluster formation, reconstructing the object with all its regularities and also analyzing its properties and character of growth. The possibility of computer modeling will also be used in the present work.

There is a large set of computer modeling tools [17–22] that are used for simulating the processes of particle aggregation and, in particular, for studying the process of fractal film formation. Usually, two essentially different models of fractal cluster models are used. The first model

was named the diffusion limited aggregation or DLA model [23]. It is assumed in this model that the fractal cluster growth occurs as a result of association, agglomeration of the cluster with the particles engaged in Brownian motion. The second model is known as the CCA model (cluster–cluster aggregation) [24]. This model implies the stage scheme of the fractal cluster formation. At the first stage, the particles moving along certain paths collide, herewith agglomerating and forming a large number of small–size clusters. These clusters are further (second stage of the process) already agglomerated into large–size clusters.

Naturally, for the process that occurs in our case of the fractal film formation in the pores, one should use the DLA model. Applicability of the CCA model is here dubious, as it is much easier for separate small–size Nafion particles to penetrate narrow pores than for the clusters, of which the size can even exceed the pore size.

It is usually assumed in both models that the probability of contact agglomeration of construction fragments (particles or clusters) is high, about a unity. Now, if we return to the process under consideration (penetration of Nafion molecules into the pore space of the support grain), here, we can in no way make shift with a single probability. Here, it is necessary to distinguish clearly two acts: adhesion of Nafion on the carbon black particle surface (let us designate this probability as p_s) and autohesion, agglomeration of Nafion particles (let us designate this probability as p_n).

The following can be stated regarding the value of probabilities p_s and p_n . Apparently, it is desirable that the inequality of $p_s \gg p_n$ is observed. That is because it is impossible to provide the formation of a fractal film of Nafion and therefore a significant platinum utilization degree in the support grains without detectable adsorption of Nafion on carbon black. And the autohesion of Nafion particles must be weak, not least because the Nafion particles will otherwise start actively agglomerating in the solution outside the pores, forming clusters that simply cannot penetrate the support grain pores.

More specific estimates of the optimum values for probability p_n will be provided later.

In order to escape complicating for no particular reason the computer simulation procedure, let us assume that $p_s = 1$. That is, let us assume that as soon as the Nafion particle reaches the carbon black surface in the Brownian motion process in the solution, it is immediately deposited (an adhesion act occurs).

Let us now introduce the designations of all parameters of the model we study. Let us make the following assumptions.

(1) The concentration of Nafion particles (fragments) in the solution is not high and they are supplied into the solution in small amounts, i.e., we always deal with the dilute polymer solution.

(2) Nafion particles in the solution have a form close to globular (coil configuration) and they can be rather

conventionally presented in the form of a population of equal-size microcubes with edge d_n ; their length is conventionally equal to unity. As will be shown further, one need not determine the absolute Nafion particle size.

(3) The carbon black particles that form the platinum support grain also have a form of similar microcubes with edge size d . Let us assume that the ratio of $d/d_n = m$ can be 4, 8, or 16.

(4) The (porous) support grain also has the form of a cube; let us designate its edge as L (it represents a set of equal-size carbon black microcubes and void "microcubes"). Let us assume that the ratio of $L/d = n$ can also be 4, 8, or 16.

(5) The value of the maximum possible amount of Nafion particles that can be located on the overall outer surface of the bulk support grain, $N^* = 6(L/d_n)^2 = 6(L/d)^2(d/d_n)^2 = 6n^2m^2$. For example: if the edge of a carbon black microcube is 8 times higher than the edge of a Nafion microcube ($m = 8$) and if a support cube edge is herewith 16 times higher than the carbon black microcube edge ($n = 16$), then $N^* = 6 \times 256 \times 64 = 98304$.

(6) Let us now introduce the concept of an "electrochemically active" Nafion particle. This is, firstly, a Nafion particle deposited on the carbon black surface that is in direct contact with carbon black (located in the first monolayer). Secondly, the active particle must be connected in the support grain pore space (through the Nafion particle chains, with the exclusion of active particles) with the outer support grain surface, behind which a Nafion grain included into the ionic cluster can be located ("the model of equal-size grains"). Only if this condition is fulfilled, one can provide a continuous supply of both electrons and protons towards the contact point of carbon black with a catalyst/Nafion active particle, which enables an electrochemical process at the given site of the support grain inner surface. (Let us note that the concept of an "electrochemically active" Nafion particle makes the problem under consideration (the process of the Nafion fractal film formation in a porous support grain) assume not only fractal, but also percolation character.)

(7) If the pores of a bulk support grain are filled from all 6 sides by Nafion particles and if the overall number of active Nafion particles N is calculated, then one can introduce a parameter important for calculation of the current generation in the electrode active layer. Let us denote it as the "diffuseness" factor of the contact surface of the ionic and gas percolation clusters ξ . This parameter indicates how much the real surface area S on which the electrochemical process occurs is higher than the contact surface of the ionic and gas percolation clusters S^* .

Parameter ξ allows determining the value of the most important indicator of the current generation intensity in the active layer, characteristic bulk current density i^* . It is equal to the product of exchange current i_0 and the fraction of specific surface S available for

electrocatalysis of the catalyst (platinum) particles participating in the electrochemical process. Thus,

$$i^* = i_0 S. \quad (8)$$

In the "equal-size grain model", the S value is proportional to the specific surface area of the contact of ionic and gas percolation clusters S^* , but specific surface areas S and S^* are naturally not identical. The true specific surface area of platinum participating in electrocatalysis under normal conditions must be higher than S^* . The contact surface of ionic and gas clusters is somewhat "diffused" to a certain "depth" and it must be taken into account when calculating the S value. Therefore,

$$S = S^* \xi, \quad (9)$$

where $\xi > 1$ under normal conditions. In the computer model that we consider,

$$\xi = N/N^*, \quad (10)$$

where N^* is, as shown above, the maximum possible number of Nafion particles that can be located on the overall outer support grain surface.

(8) Now, as regards the platinum utilization degree ψ . Let us determine this value as ratio $\psi = N/M$, where M is the maximum amount of Nafion particles that can be located on the overall (outer and inner) support grain surface. An exact calculation of value M must be performed using computer techniques. The M value can be approximately estimated using formula (6).

$$M = L^3(1.362/d) = (1/362)(mn)^3/m = 1.362m^2n^3.$$

For example: if $m = 4$ and $n = 8$, then $M = 1.362 \times 16 \times 512 \approx 11158$ Nafion particles. It is clear that the inequality of $\psi \leq 1$ must always be observed.

(9) Parameters of the studied model are also the probability of the Nafion particle adhesion on the carbon black surface p_s and probability of agglomeration (autohesion) of two Nafion particles p_n .

ALGORITHMS OF COMPUTER SIMULATION

Computer simulation and calculations were performed in the programming language of Visual Basic 6.0 for Application [25] allowing obtaining a visual idea of the model and featuring a sufficient operation speed at the arithmetic operations with large numeric arrays. The algorithm of realization in a 3D space consists in the following sequential operations.

(1) The initial parameters are provided: size of carbon black particle edge m , size of support grain edge n , grain porosity v , linear size of the free space outer boundary N^{**} (arbitrary but within due limits), probability of autohesion of Nafion particles p_n , and free path of particles in the Brownian motion l .

(2) Let us fill the 3D numeric array by the values of $A(x, y, z) = 0$, where x, y, z are the coordinates of the points (unit volume elementary cells) in the selected space, "0" is the "phase" of the microcell points free of any particles. Let us establish the space boundaries by

setting the values at the phase boundary points to be $A(x^*, y^*, z^*) = "-3"$.

(3) Let us divide the support grain into large cells with the carbon black particle size of m^3 . The amount of such cells in the cube is $K = n^3$. Let us calculate the amount of large cells that must form the porous space in the support: $K_p = \nu n^3$. Let us assign phase $"-1"$ to the cells occupied by carbon black and phase $"0"$ to the pore cells. Let us then create a linear array with size K , in which the first K_p positions are occupied by numbers $"0"$ and the further $K - K_p$ positions are filled by numbers $"-1"$. Let us perform the randomization of this array using the subprocedure function of "Function dhRandomShuffle" [26]. Let us then fill large cells, layer by layer, by phases extracting them from a randomized array. We obtain a structure with a random distribution of carbon black and pores along the support grain volume.

(4) We create an array with the size of $6 \times N^{**} \times N^{**}$ using the coordinates of points limiting the motion space of Nafion particles. Let us randomly select from this array coordinates of points determining the origin of movement of a Nafion particle, assign phase $"1"$ to a particle and trace its movement further. (The only limitation imposed on the motion of particles is the prohibition on crossing the outer boundary in the direction of the support grain.) Before each successive movement, one of the 6 directions considered equally probable is determined. In this direction, the Nafion particle can make maximum l steps (free path). The state of the surrounding cells is verified after each step. If the particle contacts a carbon black cell filled by phase $"-1"$, its movement stops, the particle coordinates are registered and the phase is changed to phase $"2"$. In the case of a contact of a moving particle with the already deposited particle, it can stop its movement and change its phase with the probability of p_n .

(5) After deposition of a certain amount of Nafion particles on carbon black (the $N^* = 6 \times (n \times m)^2$ number is chosen as a criterion), we check the presence of free inlets into the support grain pores. For this purpose, we start a "wave" from the outer boundaries towards the support grain that successively (according to the Huygens–Fresnel principle) changes phase $"0"$, e.g., to phase $"4"$ in all free points both outside the support grain and inside its pores. If the pore throats are blocked by adsorbed Nafion particles, then the "wave" does not reach them and in these points phase $"0"$ remains unchanged. Let us determine the number of inlets into the pores having changed the phase, i.e., remaining still free for penetration of Nafion particles.

(6) If this number is 0, the process of introducing the Nafion particles is terminated. If it is higher than 0, a "wave" restoring the initial free space phase (state) is introduced into the reverse direction: from the pore throats with phase $"4"$ to the outer boundaries. Herewith, the space region, in which the first "wave" could not push through to the pore throats, remains in phase $"4"$ and is further excluded from consideration.

(7) After the process of deposition of Nafion particles is over, it is necessary to establish, which of the particles deposited directly on carbon black must be considered "active", i.e., connected to Nafion particles outside the support grain through the Nafion particle chains in the layers adjacent to these particles. For this purpose, let us first mark all Nafion particles directly contacting the carbon black cells by changing their phase $"2"$ to phase $"6"$. Then we let the "wave" pass across the cells occupied by Nafion, from the support grain boundaries towards its center. This wave will change phase $"2"$ of these cells to new phase $"5"$.

(8) Sorting out all cells with phase $"6"$, let us determine if they have a general face with cells in phase $"5"$: if so, then we include them into the "active" set; if not, we include them into the "passive" set.

To determine M , the maximum number of Nafion particles that can be placed on the overall (outer and inner) support grain surface, let us use a separate algorithm. Let us choose a support grain together with the free surrounding space. Let us create a convergent "wave" from the outer space boundaries to the support grain center that changes phase $"0"$ of all particles free of carbon black to phase $"4"$. Herewith, if the pore cell is isolated by the surrounding carbon black cells, then the "wave" does not enter these cells and their phase remains unchanged. After that, let us calculate all cells with phase $"4"$ that have a common boundary with the carbon black cell with phase $"-1"$. In the case of two and three common boundaries, they are considered only once.

RESULTS OF COMPUTER SIMULATION

For visualization of the results of computer simulation, let us first consider not 3D, but 2D models of the support grains: square structures surrounded by solution from all sides. Fig. 2a presents the support grain with parameters $8 \times 4 \times 1$ ($n = 8, m = 4$). This means that the Nafion particles (small gray squares) that have arbitrary unit size, the carbon black particles (larger gray squares) are 4 times higher and the support grain edge (its outer outlines are delineated with dashes) is 8 times larger than the carbon black particles. The support grain porosity $\nu = 0.62$, the probability of Nafion particle autohesion $p_n = 0.001$, the number of Nafion particles already deposited on the grain is 226. The amount of active Nafion particles (they are designated by small black squares) is 48.

Nafion in Fig. 2a is located in all available sites on the surface of carbon black particles. But according to determination of an "electrochemically active" particle, as yet, only those of them that are located at the outer support grain surface can participate in the proton transfer. The rest of Nafion particles located on carbon black within the support grain have no such possibility (for this reason, they are colored gray in Fig. 2a).

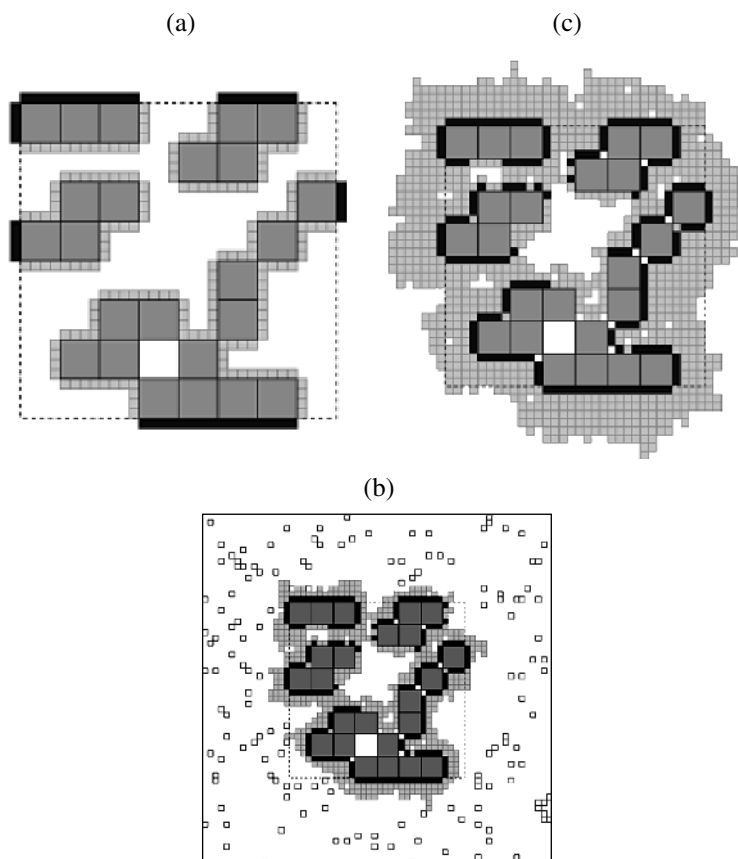


Fig. 2. Stages of filling the support grain pores by Nafion (the region delineated by dashes; the carbon black particles are marked in gray; grain porosity $\nu = 0.62$): (a) the amount of Nafion particles deposited on a support grain is 226 (small gray squares correspond to particles not participating in the proton transfer; small black squares are particles providing the proton transfer), the amount of active Nafion particles is 48; (b) the amount of Nafion particles deposited on a support grain is 599, the amount of active Nafion particles is 170; (c) the final stage: the amount of Nafion particles deposited on a support grain is 1029, the amount of active Nafion particles is 172, platinum utilization degree $\psi = 0.76$, the “diffuseness” factor of the contact surface of ionic and gas percolation clusters $\xi = 1.34$. $L/d = n = 8$, $d/d_n = m = 4$, $p_s = 1$, $p_n = 0.001$, free particle path is 16, the amount of Nafion particles that can be located along the support grain perimeter is $4 \times 8 \times 4 = 128$, the amount of Nafion particles that can be located along the carbon black particle surface forming the support grain is 226.

However, at an increase in the amount of Nafion particles deposited on the support grain, their fraction within the support grain also gradually turns into active particles. Fig. 2b shows the moment when the amount Nafion particles deposited on the support grain reached 599. Herewith, the amount of active particles is 170. Now, it is seen more clearly that all Nafion molecules deposited on the support grain can be divided into two classes. The active particles are marked in black (small squares). They are either at the outer support grain surface, or within; the latter are connected with the outer support grain environment, where an agglomerate of Nafion particles is formed in time (a Nafion grain). Thus, these active particles can transfer protons and participate in the electrochemical process. However, there are also inactive Nafion particles on the surface of the carbon black particles (they are designated by small gray squares). These particles are also of two sorts: either they are not located directly on the surface of carbon black particles

(they are situated in the second, third etc. Nafion layers), or they are on the carbon black surface, but they are isolated from the support grain surface. Therefore, both cannot participate in the current generation and they are not active particles.

The support grain also has isolated pores (a light large square in the lower part of the support grain), which Nafion can even not happen to penetrate. Vacancies remaining unoccupied can also exist (small white squares in Fig. 2b), into which Nafion could get for some reason.

And finally, let us consider Fig. 2c. Here, Nafion particles connected to the support grain surround its outer surface by a compact ring. The further support grain filling by Nafion is impossible. Therefore, an increase in the amount of active particles is also impossible. Further, a more and more compact “shell” of Nafion particles will gradually grow around the support grain. Thus, Nafion agglomerates will be finally

formed within the ionic percolation cluster that provides proton transfer into the electrode active layer.

In Fig. 2c, the amount of Nafion active particles is 172 and the overall amount of the initially vacant sites on the carbon black surface forming the support grain, as can be easily counted (Fig. 2a), is 226. Therefore, the platinum utilization degree in the grain with the parameters of $8 \times 4 \times 1$ $\psi = 172/226 = 0.761$. One can also calculate parameter ξ . The overall support grain perimeter outlined by dashed line in Fig. 2 is $4 \times 8 \times 4 = 128$. Therefore, $\xi = 172/128 = 1.344$.

Let us now analyze how the support grain size affects the value of parameters ψ and ξ . Let us consider a support grain (Fig. 3) with parameters $16 \times 4 \times 1$. In comparison with Fig. 2, the support grain surface area increased by 4 times (it was 4×4 and it became 16×16), while the carbon black particle size remained the same ($m = 4$), and the grain porosity (0.62) and autohesion probability (0.001) remained unchanged.

In Fig. 3, the overall amount of sites available for Nafion particles is 854. Here, the final stage of the support grain surface filling by Nafion particles is shown. The further variation of the amount of active and inactive Nafion particles on the carbon black particle surface in the support grain is impossible. A Nafion "shell" can be grown only at the outer support grain surface. In Fig. 3, the overall amount of active particles is 401. The platinum utilization degree in the grain with the parameters of $16 \times 4 \times 1$ $\psi = 401/854 = 0.470$ and parameter $\xi = 401/(4 \times 16 \times 4) = 1.566$. Thus, as could be expected, the platinum utilization degree decreases at an increase in the support grain size at a constant size of the constituent carbon black particles (in Fig. 2c, $\psi = 0.761$), though the "diffuseness" factor value of the contact surface of ionic and gas percolation clusters grows (in Fig. 2c, $\xi = 1.344$).

Until now, in our calculations of ψ and ξ , we assumed the probability of Nafion particle autohesion to be 0.001. Let us show that this is the optimum value corresponding to the maximum values of ψ and ξ . Let us consider a support grain with the size of 16×16 and let us assume that the carbon black particle edge is 16 times higher than the size of Nafion particles. Thus, the support grain perimeter in arbitrary units is now $4 \times 16 \times 16 = 1024$.

Let us start varying the probability of autohesion of Nafion particles in the solution. Let the autohesion probability be high at first; let us assume $p_n = 1$. Then (Fig. 4a), Nafion will penetrate the support grain pores with great difficulty. The fact is that a shell of intensively agglomerating (probability p_n is high) Nafion particles grows fast on the support grain surface. It is practically impossible for Nafion to penetrate such an obstacle and be deposited on the inner surface of the support grain. Therefore, the platinum utilization degree is low, $\psi = 0.169$, and the "diffuseness" factor of the contact surface of ionic and gas percolation clusters is low, $\xi = 0.598$.



Fig. 3. Final stage of Nafion filling the support grain pores. The amount of Nafion particles that can be located on the surface of carbon black particles forming the support grain is 854, the amount of Nafion active particles is 401, platinum utilization degree $\psi = 0.47$. The amount of particles that can be located along the support grain perimeter is $4 \times 16 \times 4 = 256$, "diffuseness" factor of the contact surface of the ionic and gas percolation clusters $\xi = 1.57$. $\nu = 0.62$, $L/d = 16$, $d/d_n = 4$, $p_s = 1$, $p_n = 0.001$, particle free path = 16.

Let us now consider the other limiting case. Let the autohesion probability of Nafion particles be zero. Let us assume $p_n = 0$ (Fig. 4b). Nafion particles cannot agglomerate with each other, cannot form any "shell". And though all carbon black particles in the support grain are covered by a Nafion monolayer, no other layer of Nafion can be formed. Therefore, the active Nafion particles among those on carbon black will only be the particles located at the outer surface of the support grain that can obtain protons from the Nafion grains surrounding the support grain (the process of active layer preparation implies drying the "catalytic ink" and baking the carbon black mixture and Nafion at elevated temperatures). Therefore, indicators ψ and ξ are again low. Calculations show that Fig. 4b can be characterized by the indicators of $\psi = 0.097$, $\xi = 0.344$.

Dependence of platinum utilization degree ψ (curve 1) and "diffuseness" factor of the contact surface of the ionic and gas percolation clusters ξ (curve 2) on the value of probability of Nafion particle autohesion in the solution is presented in Fig. 5. The range of probability p_n variation is from 0 to 1.0. Fig. 5 evidences graphically that parameters ψ and ξ increase at a decrease in p_n and reach a maximum at very low values of the autohesion probability of Nafion particles.

The true pattern of variation of parameters ψ and ξ near point $p_n = 0$ can be established using the data of Table 2. At very low values of probability p_n , parameters ψ and ξ reach a maximum and cease to depend on the value of the autohesion probability. A drastic decrease in parameters ψ and ξ is observed only at a strict observation of the condition of $p_n = 0$ (Fig. 4b). But if probability p_n differs from zero even by a negligibly small value, then a Nafion "shell" grows inevitably and the same maximum of parameters ψ and ξ is reached (the data of Table 2).

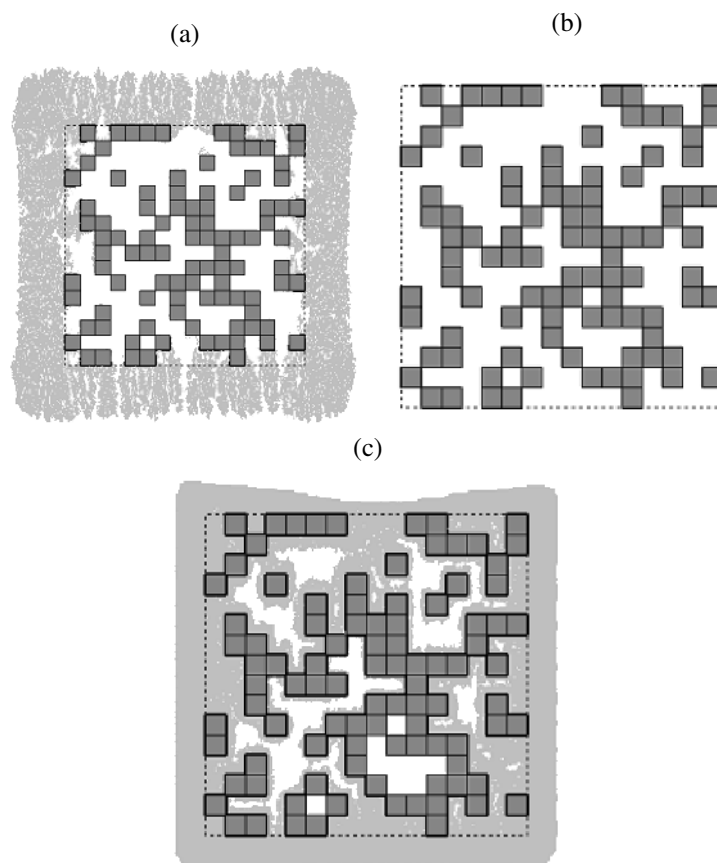


Fig. 4. Variation of the Nafion distribution pattern across the surface of carbon black particles forming a support grain, as dependent on the value of autohesion probability of Nafion particles in the solution. $v = 0.62$, $L/d = 16$, $d/d_n = 16$, $p_s = 1$, particle free path = 16. p_n : (a) 1.0 ($\psi = 0.17$, $\xi = 0.60$), (b) 0.0 ($\psi = 0.10$, $\xi = 0.34$), (c) 0.001 ($\psi = 0.97$, $\xi = 3.43$).

Let us point out another important moment. Let us compare Fig. 3 with Fig. 4c (the same figure presents the final state of the process of Nafion deposition on the support grain). The support grains in Fig. 3 and in Fig. 4c have an exactly similar structure, but in Fig. 3,

Table 2. Dependence of platinum utilization degree ψ and “diffuseness” factor ξ of the contact surface of the ionic and gas percolation clusters on the value of probability of Nafion particle autohesion in the solution p_n

p_n	ψ	ξ
0	0.097	0.344
0.0001	0.971	3.429
0.005	0.970	3.424
0.001	0.971	3.426
0.01	0.672	2.371
0.05	0.485	1.713
0.1	0.419	1.478
0.5	0.260	0.916
1.0	0.169	0.598

the carbon black particle size is 4 times higher than the size of Nafion particles, while in Fig. 4c, it is 16 times higher. It is clear that it is easier for small Nafion particles to penetrate into the support grain pore space, so that one must expect that the platinum utilization degree in Fig. 4c must be higher than in Fig. 3. Indeed: Fig. 3 corresponds to the value of $\psi = 0.47$, while in Fig. 4c, as shown by the data of Table 2 (at $p_n = 0.001$), the value of this parameter is significantly high: $\psi = 0.97$. The “diffuseness” factor of the contact surface of the ionic and gas percolation clusters also grows significantly. In Fig. 3, $\xi = 1.57$; in Fig. 4c, $\xi = 1.344$.

Until now, we studied 2D models of the support grains. Now, we will consider 3D models. The results of computer simulation in this case are presented in Table 3. There, N^* is the amount of Nafion particles that can be potentially placed on the whole outer surface of the support grain, M is the maximum amount of Nafion particles that can be located on the overall (outer and inner) support grain surface, N is the amount of “electrochemically active” Nafion particles. It was assumed in computer simulations that the probability of Nafion particle autohesion (agglomeration) $p_n = 0.001$ and their free path is 16.

The conclusions to which we came after consideration of the 2D support grain models are confirmed. Namely, at a decrease in the Nafion particle size (parameter m increases at the constant n parameter, the set of data of the first to third and fourth to sixth rows in Table 3), parameters ψ and ξ increase reaching limiting values. However, if the support grain size increases (parameter n grows at a constant parameter m , the set of data of the first and fourth, second and fifth, third and sixth rows in Table 3), then platinum utilization degree ψ starts decreasing, while the “diffuseness” factor of the contact surface of ionic and gas percolation clusters ξ grows.

Let us now assume that the size of Nafion fragments is $d_n = 4$ nm, the size of carbon black particles $d = 30$ nm, the support grain size $L = 240$ nm (the latter two quantities are provided with account for the data presented in paper [6]). Then the hypothetic support grain with such indicators will be characterized by the following parameters: $m = d/d_n = 8$ and $n = L/d = 8$. These parameter values correspond to the values in the fifth row of Table 3. Namely, platinum utilization degree $\psi = 0.752$ and “diffuseness” factor of the contact surface of the ionic and gas percolation clusters $\xi = 1.520$.

CONCLUSION

The specific character of current generation in the electrodes with polymer electrolyte consists in the fact that the electrochemical process can occur only where Nafion directly contacts the catalyst (platinum) support (carbon black). It is not easy to develop highly dispersed support/Nafion contact surface. According to the data of transmission microscopy (TEM and SEM methods), the electrode active layer consists of a mixture of agglomerates (grains) of support particles and agglomerates (grains) of Nafion particles. However, the specific surface of contact between the support grains and Nafion grains can correspond only to a low fraction of the overall surface of the catalyst within the support grains, so that the platinum utilization degree can be low.

The performed experiments show that the platinum utilization degree in the electrodes with Nafion is at present boosted to high (sometimes, close to 100%) values. The cause for discrepancy between the theoretical estimates and experimental data probably consists in the fact that the possibility of participation of the inner surface of the support grains in electrocatalysis of the inner surface of the support grains (they are porous) is not taken into account in the calculations. We surmised that separate Nafion fragments can penetrate the pores of carbon black agglomerates in the process of “catalytic ink” production. Also, a fractal film of Nafion particles can be formed on the carbon surface inside the support grain. Therefore, the platinum utilization degree can also turn out to be sufficiently high.

This hypothesis was verified using computer simulation. The DLA model (“diffusion limited aggrega-

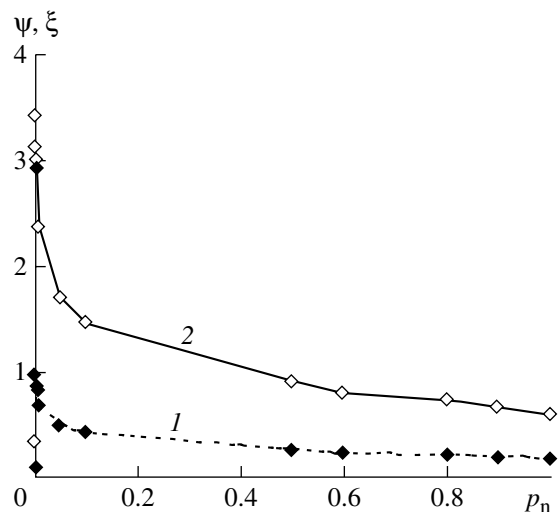


Fig. 5. Dependence of (1) platinum utilization degree and (2) “diffuseness” factor of the contact surface of the ionic and gas percolation clusters on the value of probability of Nafion particle autohesion in the solution.

tion”) was chosen out of a set of models of the particle aggregation processes. The run of the process of the fractal film formation depends on the values of the probability of Nafion adhesion to carbon black particles p_s and autohesion of the same particles between themselves p_n . As shown by the calculations, assuming that $p_s = 1$, the platinum utilization degree reaches its maximum at $p_n = 0.001$.

The character of the surface contact of the support grain pores/Nafion particles depends on the values of parameters characterizing the support grain forming its components and Nafion particles. It is assumed in the model that Nafion particles, carbon black particles, and the very support grain have the form of a cube (square, it is a 2D molecule). The size of Nafion particles was assumed to be an arbitrary unit ($d_n = 1$), the size of car-

Table 3. Dependence of platinum utilization degree ψ and “diffuseness” factor ξ of the contact surface of the ionic and gas percolation clusters on parameters characterizing the bulk support grain

n	m	N^*	M	N	$\psi = N/M$	$\xi = N/N^*$
4	4	1536	1750	1267	0.724	0.825
4	8	6144	7454	6288	0.844	1.023
4	16	24576	30766	26000	0.845	1.058
8	4	6144	11483	6546	0.570	1.065
8	8	24576	49663	37360	0.752	1.520
8	16	98304	206471	154596	0.749	1.573

bon black particles is m times higher ($d = m$) and the support grain size is n times higher than the carbon black particle size ($L = nd = nm$). Thus, the support grain characterizes unambiguously the set of n and m values.

The concept of “electrochemically active” Nafion particles is introduced. These are the particles that are adsorbed directly on the surface of carbon black particles (transporting electrons) and are connected to the outer grain surface through the Nafion particles in the pores of this grain transporting protons. The ratio of the amount of active particles to the overall amount of particles that can be located on the surface of carbon black particles forming the support grain is platinum utilization degree ψ .

Computer simulation allows not only determining the platinum utilization rate, but also calculating the “diffuseness” factor of the contact surface of ionic and gas percolation clusters ξ . Parameter ξ allows calculating the value of the most important indicator of the current generation intensity in the cathode active layer, characteristic bulk current density i^* .

Computer simulation was performed both for 2D (for the purpose of visualization exposition of general calculation concepts) and 3D models of the support grain. It is shown that ψ and ξ increase at a set value of parameter n at a decrease in the Nafion particle size (herewith, parameter m increases). This is not surprising, as it is easier for the smallest Nafion particles to penetrate the support grain pores. However, if parameter m is fixed, then ψ starts decreasing, while ξ grows at an increase in the support grain size (parameter n grows). The tendency for a decrease in the platinum utilization degree at an increase in the support grain size is obvious, as the ratio of the grain surface to its volume decreases and the possibilities for Nafion penetration into the support grain pores decrease.

The studies of microstructure of the electrode active layer with polymer electrolyte showed that the average size of carbon black particles in the support grains $d = 30$ nm and the support grain size is approximately $L = 8d = 240$ nm. Therefore, parameter $n = 8$. If $m = 4$ (the Nafion particle size is 4 times lower than the carbon black particle size), then, as evidenced by the data of Table 3 (the third line), platinum utilization degree $\psi = 0.76$. This indicator increases even more if the actual size of Nafion particles is yet more decreased. Thus, the data of the calculations performed agree well with the estimates of the ψ value found in the literature sources.

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