

Computer-Aided Simulation of the Cathodic Active Layer in Fuel Cells with Solid Polymer Electrolyte: the Nature of Overall Current Transient

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Received October 29, 2014

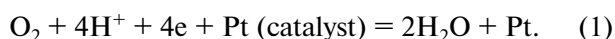
Abstract—Total computer-aided simulation of the structure and current-generation processes in the cathodic active layer of a fuel cell with solid polymer electrolyte is carried out. Not only the transport structure of the active layer but also the structure of support grains (agglomerates of carbon particles with platinum-covered surface) are modeled. The process of active layer functioning under potentiostatic conditions is studied. It is demonstrated for the first time how the moisture exchange in the pores of support grains affects the cathode overall characteristics. The time variations of the overall current, the average temperature of the active layer, and the total degree of water-flooding of support-grain pores within the active layer are calculated by numerical methods. It is shown that for the fuel cell voltage of 0.6 V and its working temperature of 80 °C, the flooding process dominates over the process of drying of pores in support grains. In 10–15 s, all support-grain pores turn out to be entirely filled with water. Then they begin functioning not in the kinetic mode (in the moment of switching-on the current, the Knudsen diffusion of oxygen in the support grains is observed) but in the inner-diffusion mode. As a result, the overall cathodic current decreases from its initial value of 4.323 A/cm² to its final value of 0.526 A/cm² and the active layer temperature decreases from the initial value of 102 °C to the final value of 82.5 °C. The overall current transient is studied also experimentally, the qualitative coincidence of theoretical and experimental data is demonstrated.

Keywords: cathode active layer in a fuel cell with polymer electrolyte, computer-aided simulation, potentiostatic mode, overall current transient, phenomenon of active layer heating, moisture exchange in support grains, calculation of overall characteristics

DOI: 10.1134/S1023193516020026

FORMULATION OF THE PROBLEM

Low-temperature hydrogen-oxygen (air) fuel cells with solid polymer electrolyte and platinum as the catalyst (PEMFC) are still among the main candidates for autonomous and environmentally clean electric power sources to be used in space and terrestrial devices. Their most dubious part is still the cathodic active layer in which the sluggish process of oxygen electroreduction proceeds in the acidic medium to produce water



An important factor affecting the functioning and the service life of PEMFC is provision of the optimal moisture exchange in the membrane-electrode assembly (MEA). This problem was analyzed in detail in many publications [1–9]. Unfortunately, the thorough

analysis of the moisture exchange processes in the MEA as a whole, namely, in its Nafion membrane, microporous layers, gas-diffusion layers, and gas-supplying chambers usually pays little attention to the problems of moisture exchange in the cathode active layer, more exactly, in the pores of support grains (agglomerates of carbon particles with the platinum-covered surface) where the main processes occur: the current generation and the formation of the electrochemical reaction product – water.

With the use of the computer simulation methods [12], the most important fact was demonstrated for the first time [10, 11], namely, the overall current generated in the cathode active layer substantially depends on the extent to which gas pores in the support grains are filled with water. Moreover, it should be noted that the problem of the removal of water formed in a fuel

cell was completely nonexistent in the first two generations of fuel cells with aqueous electrolyte solutions [13, 14]. It emerged to be one of the chief problems only for the third generation of fuel cells, the systems with solid polymer electrolyte.

The questions of how the water formation in support grains under potentiostatic conditions of current generation in the cathode with Nafion can change the overall current (the appearance of its transient), how the process of flooding of not only individual support grains but also the grains of the whole active layer proceed in time were discussed in detail earlier [15]. The difference of the present study lies in the fact that this time the moisture exchange in pores of support grains is assumed to involve not only the process of flooding [15] but also the process of water removal. The second most important deviation consists of the fact that for the first time, the heating of the cathode active layer is taken into account: now its temperature exceeds the fuel cell working temperature.

COMPUTER MODEL OF THE ACTIVE LAYER STRUCTURE

Many aspects of the current generation mechanism in the cathodic active layers of fuel cells with Nafion still remain unclear. The structure of cathodic active layers containing Nafion and carbon-supported platinum is multicomponent and extremely complicated (characterized by 10 parameters). Its complete computer simulation could be carried out only after performing a large complex of studies by the TEM and SEM methods [16–20].

In the active layer of a cathode with Nafion, first of all, the channels should be created for the delivery of all substances involved in the electrochemical process (Eq. (1)) (oxygen molecules, protons, and electrons), and also for the removal of the reaction product (water). All this in aggregate forms the transport structure of the active layer. It can be modeled as a composition of support grains, Nafion grains (agglomerates of Nafion molecules), and grains-voids. Thus we have the “model of equal-sized cubic grains of three types” [21].

The model cube selected for calculations should have macroscopic dimensions, because the edge of cubic grains $L \sim 100 \text{ nm} = 10^{-5} \text{ cm}$ and the active layer thickness $\Delta \sim 10 \text{ }\mu\text{m} = 10^{-3} \text{ cm}$. Hence, the model cube that imitates the active layer of a cathode with Nafion should be sufficiently large. In calculations, it is assumed that the model-cube volume $100 \times 100 \times 100 = 10^6$ is formed by one million of grains of three types.

Let us introduce designations. Let g be the volume concentration (fraction) of support grains in the model cube, g_i be the fraction of Nafion grains, g_{gas} be

the fraction of grains-voids. Evidently, we have the following relationship:

$$g + g_i + g_{\text{gas}} = 1. \quad (2)$$

In the model cube, clusters (aggregates of mutually bound grains of one or another type) appear spontaneously. Such percolation clusters extending over the whole thickness of the active layer provide the proper electrochemical process (Eq. (1)) in any section of the active layer. The conditions that allow the formation of such clusters or the channels for the delivery of electrons, protons, and dioxygen to the active layer should be discussed within the framework of a special division of mathematics and theoretical physics – the percolation theory [22].

Now we characterize the parameters of the active layer as a whole. It is assumed that $g = 0.5$ (this is the active layer fraction accounted for support grains), $g_{\text{gas}} = 0.5$ (the volume fraction accounted for grains-voids), and $g_i = 0$ (Nafion grains in the active layer are absent but Nafion is present in support grains; hence, the active layer as a whole is proton-conductive). Because we have chosen this structure for the cathode active layer, in virtually every support grain, the diffusion of oxygen molecules inside this grain proceeds only from one of its 6 faces and is accompanied by the absorption of oxygen on the electrocatalysis-accessible surface regions of carbon cluster inside the support grain. Thus, we can restrict our consideration to calculating the one-dimensional diffusion of oxygen in an individual support grain.

The second advantage of the parameters chosen is that according to estimates, the diffusion coefficients of oxygen molecules and water vapor are high in the active layer. Hence, the diffusion limitations in the active layer are virtually absent.

Support grains are the active layer loci in which the oxygen reduction as such occurs. The model of the support grain structure (all such grains in the active layer are assumed to be identical) was put forward in [23–25]. Let g_e be the volume concentration of carbon cubes in the support grain, g_{ii} be the volume concentration of Nafion particles involved in the proton-exchange cluster, and g_{gg} be the porosity accounted for voids. It is evident that the sum of volume fractions of the carbon material, Nafion, and voids in the support grain satisfies the relationship

$$g_e + g_{ii} + g_{\text{gg}} = 1. \quad (3)$$

The amount of the carbon material in the support grain g_e can vary sufficiently widely: from minimum possible values to the largest permitted ones. The carbon clusters in grains should interconnect all three pairs of opposite faces of support grains, which does provide a proper electronic cluster in the active layer. This is the factor that minimizes parameter g_e . On the other hand, as g_e increases further, approximately to $g_e = 0.5$, the carbon cluster surface begins to decrease;

hence, the possibility of carrying out the electrochemical process in this support grain decreases.

In the below calculations, for g_e we take its intermediate value [25] $g_e = 0.279$. Next, we assume that the concentration of Nafion grains $g_{ii} = 0.420$, the concentration of voids $g_{gg} = 0.301$. For the model support grain cube, it is assumed that $L = 100 \text{ nm} = 10^{-5} \text{ cm}$ is the edge of the support-grain cube (and also the edge of the Nafion grain and the grain-void).

According to calculations, with the above assumptions, the total surface of a carbon cluster in the support grain $S_0 = 9.72 \times 10^{-10} \text{ cm}^2$. However, it deserves mention that the current generation in support grains is only possible in those loci of the carbon cluster surface which are in contact with the proton-exchange cluster. In other words, the real electrochemical processes proceed not on the whole surface of the carbon cluster $S_0 = 9.72 \times 10^{-10} \text{ cm}^2$ but only on its part $S_{in} = 5.20 \times 10^{-10} \text{ cm}^2$.

It was shown [25] that in such a support grain, the effective coefficient of Knudsen diffusion of gas in support-grain pores (provided all pores are free of moisture) is $D_{kn} = 1.50 \times 10^{-5} \text{ cm}^2/\text{s}$. For gas pores in a support grain completely filled with water, the coefficient D_w considerably decreases and reaches the value $D_w = 4.1 \times 10^{-9} \text{ cm}^2/\text{s}$.

THE PROCESS OF FILLING OF A SUPPORT GRAIN WITH WATER

The moisture exchange in support grains involves two processes: flooding of support-grain pores with water formed in the current generation and their liberation from water due to evaporation. First, we consider in detail the process of flooding [10].

The diffusion process accompanied by absorption of oxygen molecules in the support grain is described, as was assumed, by the one-dimensional equation shown below in dimensionless coordinates:

$$dc^{**2}/dy^{*2} = i_0 e^{\eta} S_{in} / nFDc_0 L c^{**}. \quad (4)$$

Here, $c^{**} = c^*/c_0$ is the normalized average concentration of oxygen in an arbitrary section of pores in a support grain (c^* is the current value of oxygen concentration in Nafion, c_0 is the oxygen solubility in Nafion), $y^* = y/L$ is the normalized coordinate (L is the edge in the support-grain cube) reckoned from the frontal surface of the grain (where $y = 0$), i_0 is the exchange current, η is the normalized overvoltage in the active-layer section accommodating the support grain, $n = 4$ is the number of electrons involved in the oxygen electrooxidation reaction, F is the Faraday number, D is the diffusion coefficient of oxygen in the support grain.

The boundary conditions of Eq. (4) are as follows:

$$y = 0 \quad c^* = c, \quad (5)$$

$$y^* = 1 \quad dc^{**}/dy^* = 0, \quad (6)$$

where c in boundary condition (5) is the oxygen concentration at the inlet to the support grain (at $y = 0$) in that cathode active layer section where this support grain is localized.

Then, the solution of Eq. (4) is as follows:

$$c^{**} = (c/c_0) [\cosh[\alpha^{1/2}(1 - y^*)] / \cosh(\alpha^{1/2})]. \quad (7)$$

Hence, the current i generated in the grain (at $y = 0$)

$$i = -i^* dc^{**}/dy^*, \quad (8)$$

where $i^* = nFDc_0L$ [A] is the characteristic current. Taking into account solution (7) and formula (8), we obtain the ultimate expression for the current generated in the support grain

$$i = [nFD^* D_{kn} c_0 L i_0 S_{in}]^{1/2} (c/c_0) e^{\eta/2} \times \tanh \left[(i_0 S_{in} / nFD^* D_{kn} c_0 L)^{1/2} e^{\eta/2} \right], \quad (9)$$

where the dependence of the exchange current i_0 on the active-layer temperature T_s is as follows [26]:

$$i_0 = 10^{-8} \exp[8804(1/323 - 1/T_s)], \text{ A/cm}^2. \quad (10)$$

In formula (9), the number of electrons involved in the electrochemical process of oxygen reduction $n = 4$, the Faraday number $F = 9.65 \times 10^4 \text{ C/mol}$, the effective Knudsen diffusion coefficient, as noted above, $D_{kn} = 1.50 \times 10^{-5} \text{ cm}^2/\text{s}$, the oxygen solubility in Nafion $c_0 = 5 \times 10^{-6} \text{ g-mol/cm}^3$ for pressure $p^* = 101 \text{ kPa}$, the edge of the model support-grain cube $L = 10^{-5} \text{ cm}$, the surface on which the electrochemical process occurs $S_{in} = 5.20 \times 10^{-10} \text{ cm}^2$; the values of the normalized solubility of oxygen in Nafion c/c_0 and the cathodic polarization η are to be found in subsequent calculations. The effective diffusion coefficient D^* involved in formula (9), which is also time-dependent (because we consider the process of gradual filling of support-grain pores with water), is to be found too. Furthermore,

$$D^* = D/D_{kn}. \quad (11)$$

The quantity D^* varies in the range from 1.0 (when the support grain contains no water) to $D^* = (4/1.5) \times 10^{-4}$ (when the support grain is completely water flooded). The dependence of the true diffusion coefficient D on the degree of water-flooding of support-grain pores g_w was calculated in [15] and is shown in Table 1.

Note also that in Eq. (9), the potentials E involved in calculations should be converted into polarization η as follows:

$$\text{For } E_{st} \geq E \geq E^*, \quad \eta = (1.05 - E)/2.6 \times 10^{-2}, \quad (12)$$

$$\text{For } E \leq E^*, \quad \eta = (1.05 - 0.825)/2.6 \times 10^{-2} + (0.825 - E)/5.2 \times 10^{-2}. \quad (13)$$

(For example: if $E = 0.6$ on the frontal surface of the active layer, then $\eta = 225/26 + 225/52 = 12.98$.)

Table 1. Dependence of the effective diffusion coefficient of oxygen D (cm^2/s) on the degree of filling of pores in a support grain with water g_w

g_w	$D \times 10^5$
0	1.5
0.0117	5.96×10^{-1}
0.0235	3.90×10^{-1}
0.0578	2.02×10^{-1}
0.0775	1.51×10^{-1}
0.1174	7.39×10^{-2}
0.1761	3.44×10^{-2}
0.1878	2.50×10^{-2}
0.1995	1.90×10^{-2}
0.2347	4.10×10^{-4}

PROCESS OF WATER REMOVAL FROM THE SUPPORT GRAIN

Now, let us consider the diffusion process of extraction of water vapor from the support grain [27]. The three-component system under consideration (graphite grains with platinum, Nafion, pores open to the diffusion of oxygen and water vapor) is extremely complicated for analysis; hence, several simplifications should be introduced.

As a result of current generation in the cathode (oxygen reduction to water proceeds in support grains), the cathode is heated. The temperature of the carbon cluster in support grains T_s turns out to be higher than the temperature T at which the fuel cell operates. Taking account of the high thermal conductivity of water and the low thermal conductivity of gas (oxygen + water vapor molecules) supplied continuously to the support grain, we can assume with the high degree of confidence that water in support grains has also temperature T_s , whereas the temperature in gas pores is lower than T_s . Thus there appears the possibility of water evaporation from the surface of liquid in contact with the gas phase, which is the reason for the subsequent removal of water vapors from gas pores in support grains by means of diffusion.

The diffusion escape of water vapors from support-grain pores is assumed to be a one-dimensional process (from the support-grain face open for the delivery of oxygen and the removal of water-vapor to its opposite closed face). This process is described by the following equation:

$$D_s dc^2/dy^2 + (2SD_s/\delta)(c_{ss} - c) = 0, \quad (14)$$

where D_s is the effective diffusion coefficient of water vapor in water-free support grains, c [mol/cm^3] is the average concentration of water vapors in an arbitrary section of the support grain, $c_{ss} = P_{ss}/T_s$ is the concen-

tration of saturated water vapor at the liquid/gas interface (c_{ss} is determined by the temperature of the support grain T_s and the saturated vapor pressure P_{ss} corresponding to this temperature T_s), $0 \leq y \leq L$ is the coordinate from the frontal ($y = 0$) to back ($y = L$) surface of the support grain.

It remains only to explain the meaning of parameters S and β entering into Eq. (14). The part of the support grain volume free from the carbon material and Nafion represents a set of fine pores of the nanometer size. Assume that these pores are the capillary partly filled with water and "spread" uniformly throughout the grain volume. Thus, in Eq. (14), S is the specific surface of the contact between the water-filled space and the gas phase, δ is the average diameter of gas pores minus water-filled pores. The latter quantity can be found using formula (15)

$$\delta = (0.235 - g_w)^{1/3}/g_w^{1/3}, \quad (15)$$

where g_w is the surface coverage of support grains with water.

In dimensionless coordinates, Eq. (14) takes the form

$$dc^2/dy_s^2 + \beta(c_{ss} - c) = 0, \quad (16)$$

where $y_s = y/L$ is the normalized coordinate reckoned from the frontal surface of the grain and β is the dimensionless parameter entering into Eq. (16)

$$\beta = 2L^2S/\delta. \quad (17)$$

The boundary conditions for Eq. (16) are as follows:

$$y = 0, c = c_s \quad (18)$$

$$y_s = 1 (y = L) dc/dy_s = 0 \quad (19)$$

where c_s in condition (18) is the concentration of saturated water vapor on the frontal surface of the support grain.

The solution of Eq. (16) has the form

$$c = c_{ss} + (c_s + c_{ss}) \left[\frac{\exp\{\beta^{1/2}(y-2)\} + \exp\{-\beta^{1/2}y\}}{1 + \exp\{-2\beta^{1/2}\}} \right] \quad (20)$$

and the current density generated in a support grain (the flow of water vapor j_s at $y = 0$) is

$$j_s = -(2FD_s/L)dc/dy_s \quad (21)$$

Taking into account solution (20) and formula (21), we have the following ultimate expression for the current j [A] generated in the support grain:

$$j = j_s L^2 = (2FD_s L)(P_{ss}/T_s - c_s)(\beta)^{1/2} \tanh[(\beta)^{1/2}]. \quad (22)$$

Parameter β entering into Eq. (16) and dependent on the degree of filling of grain pores with water g_w can be determined based on the data of Table 2 [25].

Table 2. Dependence of the parameter β on the degree of filling of support-grain pores with water g_w

g_w	0	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.2	0.22	0.235
β	0	0.421	0.999	1.594	2.159	2.65	3.036	3.282	3.348	3.18	2.708	1.709	0

Table 3. Dependence of the effective diffusion coefficient of water vapor $D_s \times 10^5 \text{ cm}^2/\text{s}$ on the degree of filling of support-grain pores with water g_w

g_w	0	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
$D_s \times 10^5$	2.24	1.712	1.253	0.8144	0.4655	0.2493	0.1318	0.07855	0.03346	0

Table 3 shows the dependence of the diffusion coefficient of water vapor D_s on the degree of filling of pores in the support grain with water g_w [27].

Now it is necessary to determine the parameter entering into boundary condition (18). The active layer structure was chosen above in such a fashion ($g = 0.5$, $g_{\text{gas}} = 0.5$, $g_i = 0$) that, according to estimates and calculations shown below, the diffusion limitations for oxygen and water vapor in the active layer can be considered negligible.

For the sake of definiteness and maximum simplification of complicated calculations, we assume that the Stefan diffusion proceeds without limitations not only in the active layer but also in the gas-diffusion layer. This is why the concentration c_s (Eq. (18)) is determined by the degree of humidification of oxygen at the inlet to the cathode gas-diffusion layer. Thus, for dry oxygen, $c_s = 0$ and for oxygen maximally humidified $c_s = P_s/T$. Below, the calculations of overall characteristics of the cathode will be carried out by selecting the maximum possible value for c_s . Then, in place of Eq. (22), we have

$$j = \left(2 \times 10^{-3} \times FD_s L / R\right) \left[\left(P_{ss} / T_s\right) - \left(P_s / T\right) \right] (\beta)^{1/2} \tanh \left[\beta^{1/2} \right], \quad (23)$$

where $T_s > T$ (active layer is heated) and P_{ss} and P_s are the values of pressure of saturated water vapor corresponding to these temperatures. When calculating, the pressure should be expressed in kPa.

THE PROGRAM FOR CALCULATING THE CATHODE CHARACTERISTICS

First of all, let us consider how the phenomenon of heating of the cathode active layer in a fuel cell with Nafion can be described in a simple form.

In its simplest form, the law of conservation of thermal energy (heat liberation in the active layer – heat removal in the gas-diffusion layer (GDL)) can be described as follows:

$$(1 - \varepsilon)IE_0 = \lambda(T_s - T) / \Delta_s, \quad (24)$$

where $\varepsilon = 60\%$ is the efficiency coefficient of the cathode, I is the overall current density (A/cm^2) generated in the cathode active layer, E_0 is the cathode potential, $\lambda = (0.2/100) \text{ W}/\text{cm K}$ is the thermal conductivity of the GDL, T_s is the absolute temperature of the active layer, $T = 353$ (80 C) is the working temperature of the fuel cell ($T < T_s$), $\Delta_s = 400 \mu\text{m}$ ($4 \times 10^{-2} \text{ cm}$) is the GDL thickness.

Considering the problem how the whole active layer is filled with water as compared with an individual grain, one has to take into account the factor of unequal accessibility in the system studied: different sections of the active layer have different potential values and thus the flooding of support grains should vary along the active layer thickness.

Below, we show the program for calculating how the active layer is gradually filled with water.

1. Selecting the cathode potential; let $E_0 = 0.6 \text{ V}$.
2. Selecting the structure support grains (all the grains in the active layer are identical as regards their properties): $g_e = 0.279$, $g_{ii} = 0.420$, $g_{gg} = 0.301$, $S_{in} = 5.20 \times 10^{-10} \text{ cm}^2$, $S_0 = 9.72 \times 10^{-10} \text{ cm}^2$.
3. Selecting the active layer thickness, let $\Delta = 10 \mu\text{m}$. For the grain size $L = 100 \text{ nm}$, 100 grain layers fit in the active layer thickness.
4. Selecting the active layer composition: the fraction of support grains $g = 0.5$, the fraction of grains-voids $g_{\text{gas}} = 0.5$ (Nafion is present only in support grains). According to calculations, under these assumptions, the effective protonic conductivity of the active layer $k^{**} = 4.58 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ and the effective diffusion coefficient of oxygen in the active layer $D^{**} = 2.18 \times 10^{-2} \text{ cm}^2/\text{s}$.
5. The calculations are started with assuming that all the support grains in the active layer are free of moisture; hence, the effective diffusion coefficient of oxygen in the expression for current i (Eq. (4)) in support grains is everywhere $D = D_{\text{kn}} = 1.50 \times 10^{-5} \text{ cm}^2/\text{s}$.
6. The calculation of overall currents is carried out by taking into account that the polarization curve of oxygen reduction to water has two slopes [28]. The current generation in the cathode active layer is

described by the system of two equation of the second order

$$d^2 \eta / y^{*2} = (c_0/c) D^{*1/2} e^{\eta/2} \times \tanh \left[(i_0 S_{in} / nFD_{kn} c_0 L)^{1/2} e^{\eta/2} \right], \quad (25)$$

$$d^2 (c/c_0) / y^{**2} = (c_0/c) D^{*1/2} e^{\eta/2} \times \tanh \left[(i_0 S_{in} / nFD_{kn} c_0 L)^{1/2} e^{\eta/2} \right], \quad (26)$$

where $y^* = y/L_{ohm}$ and $y^{**} = y/L_d$ are the corresponding characteristic ohmic and diffusion lengths. In addition to expressions for characteristic currents (ohmic and diffusion) I_{ohm} and I_d , we have the following expressions (in the region of high potentials, where $b_1 = 2.6 \times 10^{-2}$ V):

$$L_{ohm} = [b_1 \kappa^{**} L^3 / g(nFD_{kn} c_0 L i_0 S_{in})^{1/2}]^{1/2}, \quad (27)$$

$$I_{ohm} = [b_1 \kappa^{**} g(nFD_{kn} c_0 L i_0 S_{in})^{1/2} / L^3]^{1/2}. \quad (28)$$

$$L_d = [nFc_0 D^{**} L^3 / g(nFD_{kn} c_0 L i_0 S_{in})^{1/2}]^{1/2}, \quad (29)$$

$$I_d = [nFc_0 D^{**} g(nFD_{kn} c_0 L i_0 S_{in})^{1/2} / L^3]^{1/2}. \quad (30)$$

7. When calculating the overall current of the active layer I , one has to fix the potential E distribution throughout the active layer thickness (for $x = 0$, at the active-layer frontal surface, the potential is 0.6 V and should increase as the coordinate increases) and also fix the distribution of the concentration ratio (c/c_0). The latter is 1.0 at the back surface of the active layer ($x = \Delta$). The other two boundary conditions for the potential E and the concentration ratio c/c_0 are the zero value of the electron flow for E on the active-layer back surface and the zero value of the oxygen diffusion flow on the active-layer frontal surface.

8. The next step is calculation of the initial distribution of the overall current (water inflow and outflow) $j = i - i_s$ along the active layer thickness. Knowing the behavior of the potential E and the ratio c/c_0 throughout the active layer thickness and assuming that in the instant the current is switched on, the diffusion coefficient $D = D_{kn} = 1.50 \times 10^{-5}$ cm²/s in any section of the cathode active layer, we can calculate the current j in any active layer section using Eqs. (9) and (22). Depending on the sign of j , the water amount in the support grain can either increase (for $j > 0$) or decrease (for $j < 0$); for $j = 0$, the water content in the support grain should remain unchanged. In principle, it can happen that immediately after the current was switched on, $j < 0$ in some locus of the active layer. This means that here the initial diffusion coefficient remains unchanged and maximum possible: $D = D_{kn}$. If the support grain is completely filled with water, then $D = 4.1 \times 10^{-9}$ cm²/s in it.

9. Now we set an arbitrary small increment of time from its zero value – Δt . In time Δt , the amount of evolved water is $j\Delta t \cdot 2 \times 18/4F = 9j\Delta t/F$ g or cm³, which is equivalent to filling of a fraction of the sup-

port-grain volume equal to $\Delta g_w = 9j\Delta t/FL^3$. Taking into account that parameters D and D_s in Eqs. (9) and (22) depend on g_w , we obtain the equation

$$dg_w/dt = 9j(D = f(g_w), D_s = \varphi(g_w))/FL^3. \quad (31)$$

The initial condition (the grain is completely free of water)

$$\text{for } t = 0, g_w = 0. \quad (32)$$

Using Eq. (31), we can assess the gain in the moisture amount (g_w) in support grains. According to data in Tables 1 and 3, this is associated with changes in the diffusion coefficients D and D_s . Note: if D has reached its extreme value in Table 1 (the grain is completely filled with water), then further on $D = 4.10 \times 10^{-9}$ cm²/s and does not change any more.

10. Now, we have to find the volume τ of water evolved in the active layer of thickness Δ according to the formula

$$\tau = (gL^3/L^2) \Sigma(n \text{ от } 1 \text{ до } \Delta/L) g_{wn}. \quad (33)$$

In the case under consideration, $\Delta/L = 100$. Then, the maximum filling of the support grain with water is

$$\tau_{max} = gL0.2347(\Delta/L) = 0.2347g\Delta. \quad (34)$$

In our case (for $g = 0.5$ and $\Delta = 10^{-3}$ cm), $\tau_{max} = 1.173 \times 10^{-4}$ cm.

11. The next step of calculations is again the calculation of the overall current with the new values of diffusion coefficients D and D_s . This is followed by repetition of all procedures listed above.

12. The chief ultimate goal is to build the dependence of the overall current I on the time and also to calculate the time variations in the active layer temperature T_s and the overall amount of water evolved in the cathode τ .

SOLUTION METHOD

Varying the temperature T_s at the fixed cathode potential E_0 until the overall current values calculated based on Eq. (24) and on the system of equations (25), (26) become equal. This will provide the sought values of T_s and I .

RESULTS OF CALCULATIONS OF CATHODE OVERALL CHARACTERISTICS

Table 4 shows the time dependences of cathode overall characteristics.

The data in these tables were calculated as follows. First, the initial average temperature of the active layer was determined (T_s is the result of heating). The overall current value I found in the calculations based on the system of equations (25), (26) was compared with the data found based on Eq. (24). In performing this operation, we assumed that water is absent in the sup-

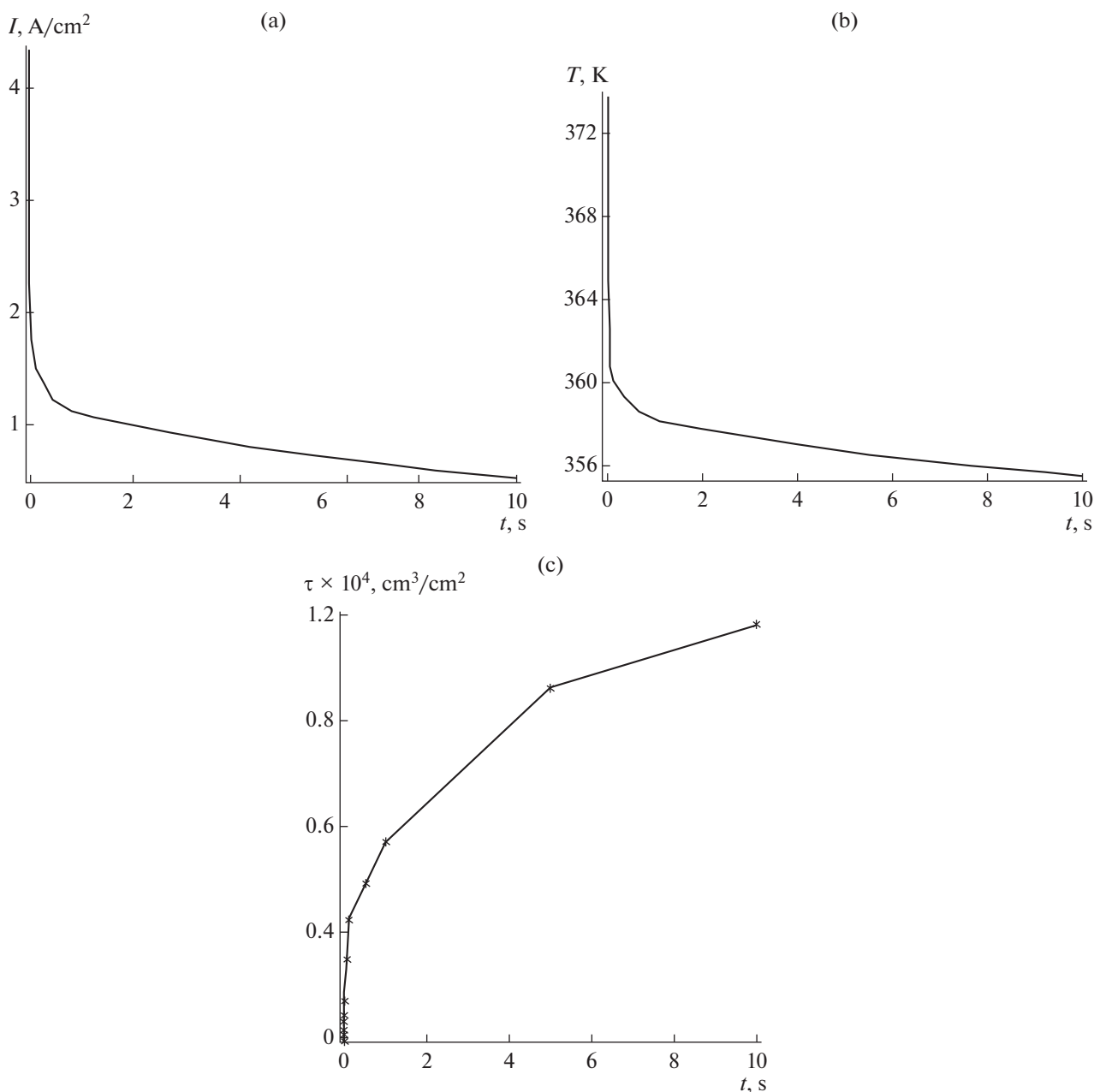


Fig. 1. Time dependences of (a) the overall current I ; (b) the active layer temperature; (c) the water content in support grains of the active layer τ .

port grains and that the current i takes its maximum possible value. Thus, by varying T_s , we could find the initial value of this quantity.

Figure 1a shows the time variations of the overall current I generated on the cathode. In the initial moment, when the cathode potential is fixed $E_0 = 0.6$ V and no moisture is present in the pores of all support grains, the overall current is the highest $I = 4.323$ A/cm².

This is associated with the fact that the active layer is heated (its temperature rises from its initial value

$T = 253$ K to $T_s = 373.765$); moreover, the effective diffusion coefficient of oxygen in the support grains is the largest $D = 1.5 \times 10^{-5}$ cm²/s, i.e., the Knudsen diffusion of oxygen molecules is observed. However, even after a very short time, the pores in the support grains, especially those near to the active layer front surface are progressively filled with water, parameter g_w in support grains increases; hence, according to data of Tables 1 and 3, the diffusion coefficients D and D_s in support grains change and, according to calculations, the overall current begins to decrease.

Table 4. Time dependence of active-layer characteristics: overall current I , temperature T , and specific content of water in support grains

t , s	I , A/cm ²	T , K	τ , cm ³ /cm ²
0	4.323	373.765	0
2×10^{-4}	4.086	372.623	7.493×10^{-7}
4×10^{-4}	3.953	371.979	1.29×10^{-6}
6×10^{-4}	3.86	371.532	1.727×10^{-6}
8×10^{-4}	3.808	371.28	2.107×10^{-6}
1×10^{-3}	3.759	371.043	2.447×10^{-6}
3×10^{-3}	3.393	369.291	4.902×10^{-6}
5×10^{-3}	3.153	368.136	6.943×10^{-6}
0.01	2.724	366.076	1.098×10^{-5}
0.05	1.739	361.349	2.242×10^{-5}
0.1	1.492	360.168	3.355×10^{-5}
0.5	1.226	358.862	4.39×10^{-5}
1.0	1.085	358.169	5.573×10^{-5}
5.0	0.758	356.643	9.965×10^{-5}
10.0	0.526	355.527	1.173×10^{-4}

Judging from the data in the 2nd column of Table 4, the overall current decreases by about 50% even in several hundredth fractions of s, which is followed by the second less steep region of the overall current decay. In ca. 10 s, the current I reaches its final small value $I = 0.526$ A/cm².

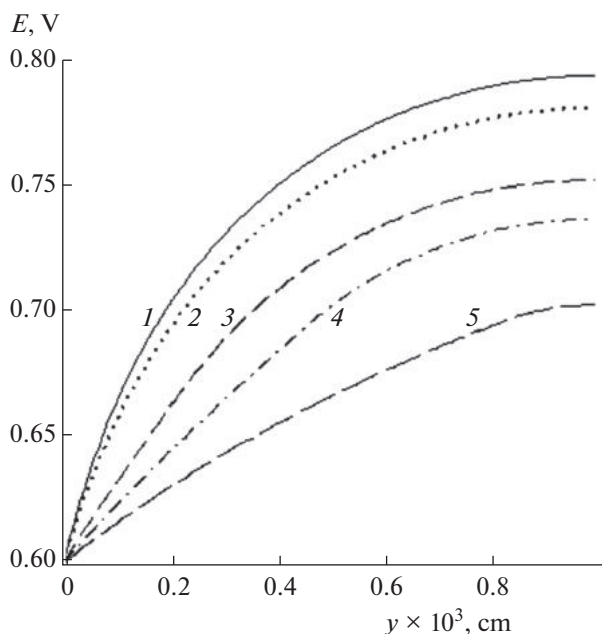


Fig. 2. The distribution of potential E over the active-layer thickness in different moments t , s: (1) 2×10^{-4} , (2) 5×10^{-3} , (3) 0.1, (4) 1.0, (5) 5.0.

The cathode temperature T_s behaves similarly (Fig. 1b and the data in the 3rd column of Table 4). First of all, it rapidly decreases from $T_s \sim 103$ C to approximately 90 C; then, the temperature decay decelerates and the final temperature difference turns out to be small: $T_s - T \sim 2.5$ C.

Figure 1b and the 4th column of Table 4 show the dependence of the total flooding of support-grain pores with water in the cathode active layer. Parameter τ reaches its maximum possible value, which means the complete filling of pores in support grains throughout the active layer.

To understand the character of variation of curves in Figs. 1a–1c, one should first of all take into account the fact that here we have the distribution of potential E throughout the active layer thickness (data of Fig. 2); hence, the filling of pores in support grain is also a nonuniform process. In initial moments, the current generation mainly occurs at the frontal surface of the active layer, because here the potentials are close to 0.6 V. At the same time, the potential at the back surface of the active layer where the current generation is considerably weaker increases to ca. 0.8 V (curve 1 in Fig. 2). On the other hand, when the support grains are completely filled with water (curve 5 in Fig. 2), the potential at the active-layer back surface increases merely to ~ 0.7 V.

The data in Fig. 3 convincingly illustrate the process of filling of pores in support grains with water. It is evident that the degree of filling of pores in support grains is the higher, the closer the support grains to the

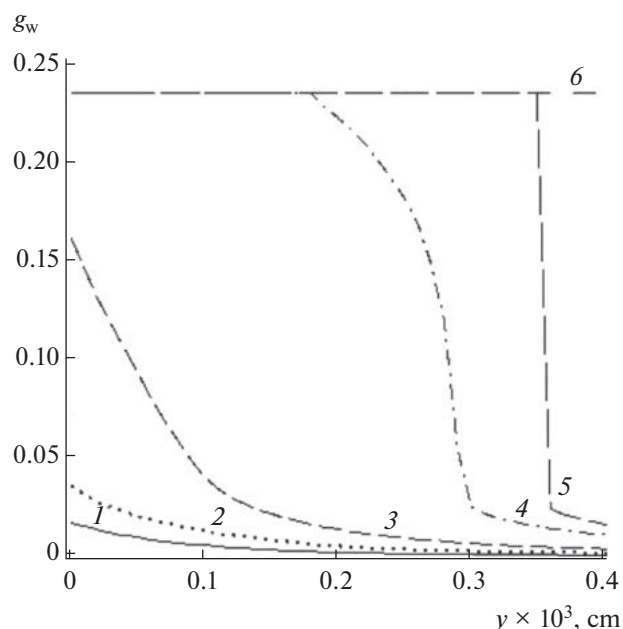


Fig. 3. The distribution of water content in support grains g_w over the active layer thickness as a function of time t , s: (1) 2×10^{-4} , (2) 6×10^{-4} , (3) 5×10^{-3} , (4) 0.1, (5) 0.5, (6) 1.0.

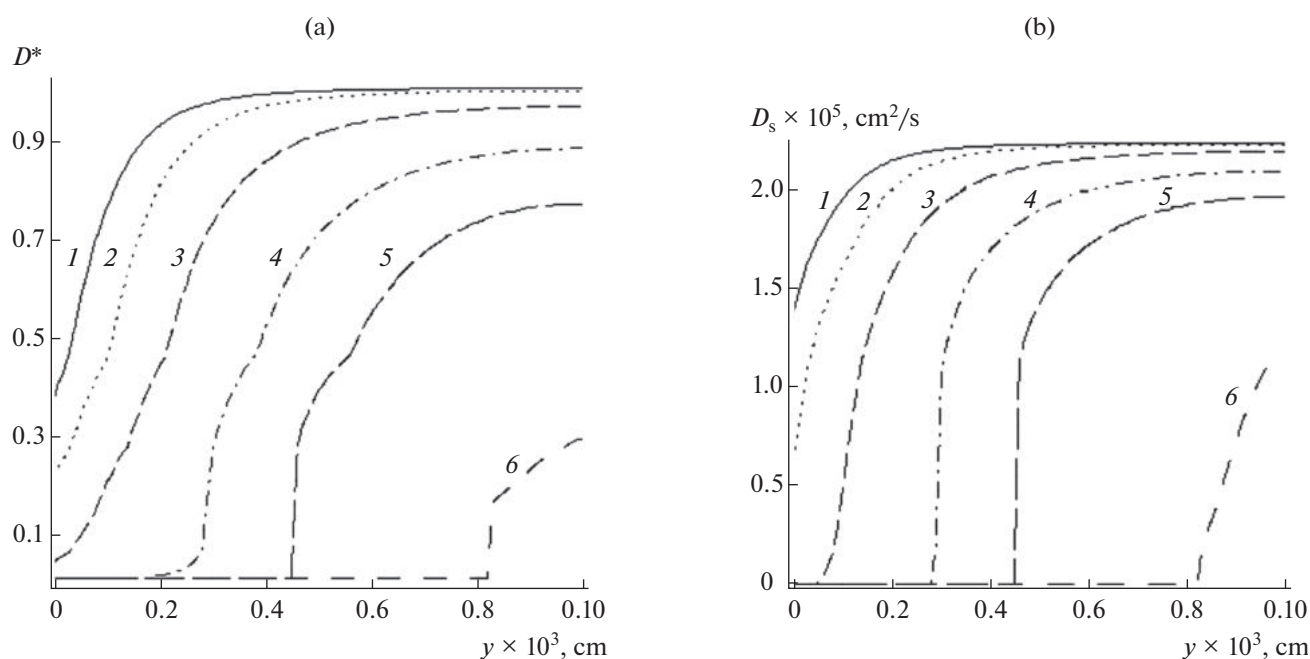


Fig. 4. (a) The distribution of the effective normalized diffusion current (filling process) in support grains D^* over the active-layer thickness in different moments t , s: (1) 2×10^{-4} , (2) 6×10^{-4} , (3) 5×10^{-3} , (4) 0.1, (5) 1.0, (6) 5.0; (b) the distribution of the effective diffusion current (evaporation process) in support grains D_s in different moments t , s: (1) 2×10^{-4} , (2) 6×10^{-4} , (3) 5×10^{-3} , (4) 0.1, (5) 1.0, (6) 5.0.

active layer frontal surface (curves 1–3, Fig. 3). Gradually, the degree of filling of support grains at this face reaches its maximum value ($g_w = 0.235$), the more so not only immediately at the surface but also at a certain depth (curves 4, 5 in Fig. 3). Ultimately, all grains in the active layer turn out to be completely filled with water (curve 6 in Fig. 3).

The data in Fig. 4a and Fig. 4b clearly illustrate the character of water distribution in the support grains in different moments. According to Tables 1 and 3, the effective diffusion coefficient of oxygen in support grains D and the effective diffusion coefficient of water vapors in support grains D_s are sensitive with respect to the degree of filling of support grains with water g_w . With time, the diffusion coefficient D in all support grains in the active layer gradually tends to its minimum value $D = 4.1 \times 10^{-9}$ cm²/s (Table 1) and, the more so, the diffusion coefficient of water vapors vanishes (Table 3).

The data of Figs. 5a–5c turn out to be very important for understanding how the moisture exchange in pores of support grains affects the overall characteristics of the cathode (Figs. 1a–1c). The former data indicate that the process of filling of pores in support grains with water dominates over the process of liberation of support grains from moisture due to evaporation. The process of filling is characterized by current i (Fig. 5a), the process of drying is characterized by current i_s (Fig. 5b), the difference between these currents $j = i - i_s$ is illustrated by Fig. 5c. It is seen that the

overall moisture flow j is always positive, i.e., the pores in support grains are always being gradually flooded.

The prevalence of the process of flooding over that of drying in support-grain pores also follows from the direct comparison of Figs. 5a and 5b. Whereas the range of current variation in Fig. 5a is $i \sim 7 \times 10^{-10}$ A, the same range in Fig. 5b for $i_s \sim 1.4 \times 10^{-10}$. According to data in Table 2, parameter β and also the current of drying i_s vanish sufficiently rapidly as the parameter g_w approaches both its zero value and the state of complete flooding of pores in support grains. The effect of this factor is clearly seen in curves of Fig. 5b.

If in our calculations we assume that at the inlet to the cathodic gas-diffusion layer, dry oxygen is supplied rather than humidified oxygen, then the oxygen concentration at the inlet to the support grain vanishes, $c_s = 0$. This means that now the evaporation process proceeds more intensively and, as a consequence, the time of the complete flooding of support grains in the active layer increases. Now, according to calculations, the flooding is completed in 15 s instead of 10 s.

It is reasonable to compare the above theoretical calculations with experimental data. Figure 6 shows the transient of overall current of the fuel-cell oxygen electrode supplied with humidified oxygen.

Experimental parameters: fuel cell with MEA of 25 cm², Nafion 212 membrane, 80 C; cathode: Pt/CNT, 0.42 mg_{Pt}/cm²; anode: Pt/C, 0.34 mg_{Pt}/cm². $V_{\text{const}} = 0.6$ V.

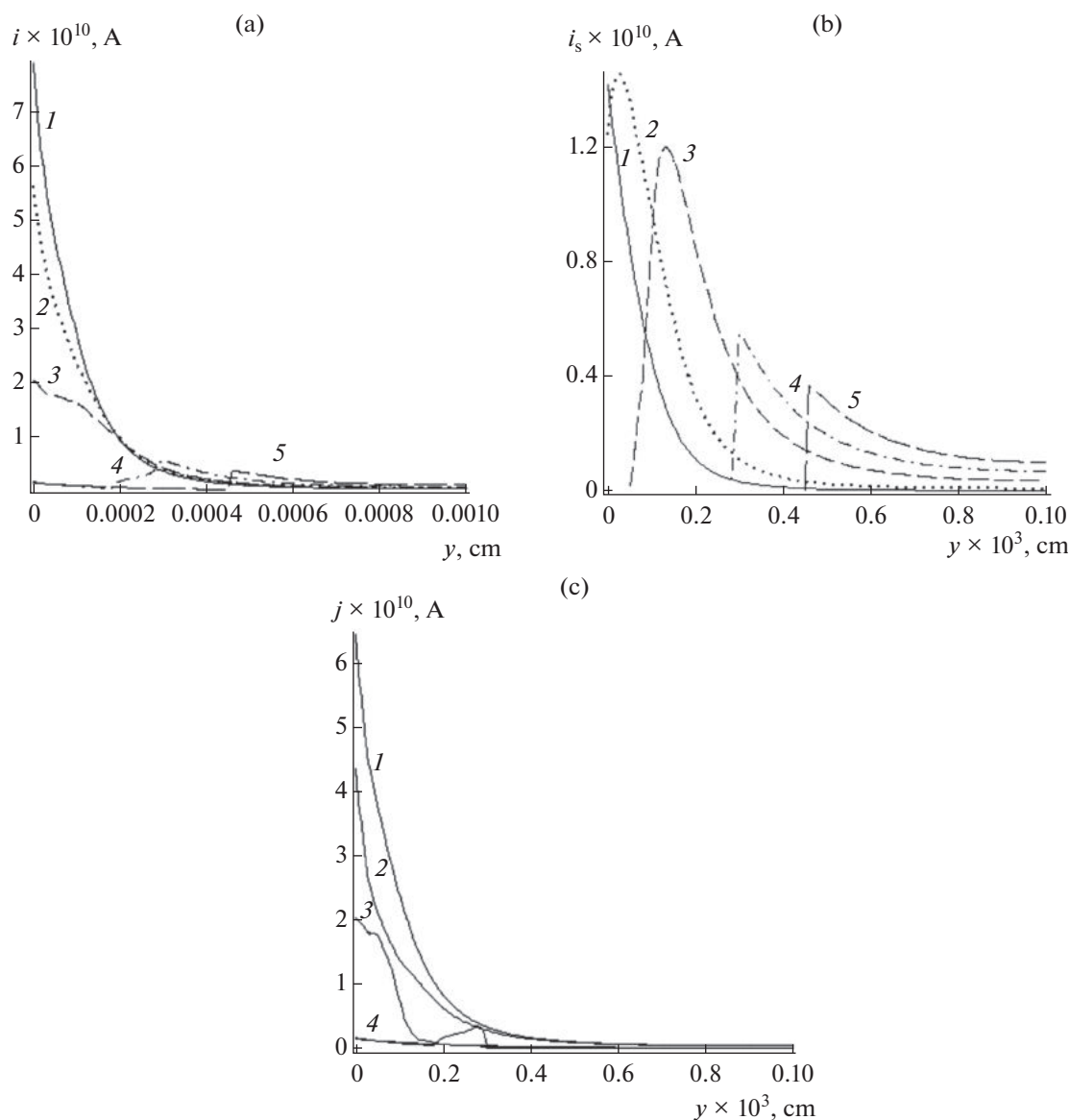


Fig. 5. (a) The current of filling of support grains with water i (A) at the active-layer frontal surface in different moments t , s: (1) 2×10^{-4} , (2) 6×10^{-4} , (3) 5×10^{-3} , (4) 0.1, (5) 1.0 (b) The current of evaporation from the pores of support grains i_s (A) at the frontal surface of the active layer in different moments t , s: (1) 2×10^{-4} , (2) 6×10^{-4} , (3) 5×10^{-3} , (4) 0.1, (5) 1.0. (c) The total current j (A) in pores of support grains at the frontal surface of the active layer in different moments t , s: (1) 2×10^{-4} , (2) 6×10^{-4} , (3) 5×10^{-3} , (4) 0.1.

Figure 5, like the theoretically calculated overall current transient (Fig. 1a), clearly demonstrates the presence of two segments in the curve: the initial fast increase in current is followed, in ca. 60 s, by the second region – the slower decay of the overall current.

The current density I , A/cm² remains within the limits from 1.18 (its upper limit) to 1.11 (the lower limit). The approximate length of the transient is 120 s. This is one order of magnitude higher than the theoretical value (10 s).

However, it is hardly reasonable to carry out direct quantitative comparison of theoretical and experi-

mental data. If all the parameters were strictly determined in calculations, it would be virtually impossible to reproduce the analogous parameters (for the structure of active layer and support grains and all the data defining the conditions of the active-layer, etc.) experimentally. Moreover, it should be remembered that in computer simulations, the structure and the characteristics of the model chosen should be maximally simple and selected sufficiently randomly.

According to theoretical calculations, the length of the transient is mainly determined by the degree of closeness between the flooding and evaporation cur-

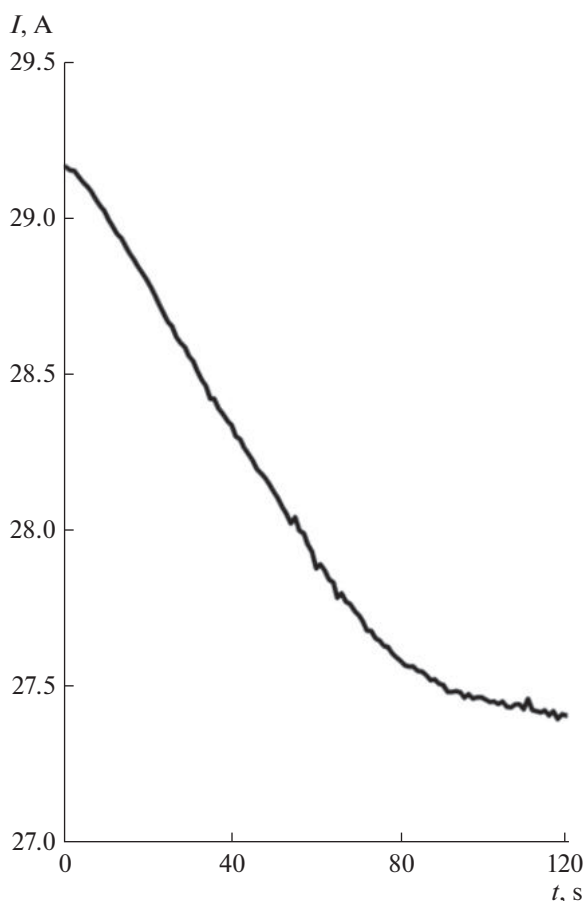


Fig. 6. Experimental reproduction of the transient of overall current. Experiment parameters: fuel cell with MEA of 25 cm², Nafion 212 membrane, 80 °C; cathode: Pt/CNT, 0.42 mg_{Pt}/cm²; anode: Pt/C, 0.34 mg_{Pt}/cm²; $E_{\text{const}} = 0.6$ V.

rents. In the above calculation, the flooding current far exceeded the evaporation current; this is why the time of complete flooding of pores in support grains turned out to be sufficiently small: 10–15 s. Obviously, if for a certain selected and fixed cathodic potential, we rise the evaporation rate to the flooding rate level, the length of the transient should increase.

CONCLUSIONS

In this study, we carried out computer-aided modeling of the structure and processes of the current generation in active layers of fuel cells with solid polymer electrolyte. In particular, we considered the process of functioning of such a system under potentiostatic conditions; in the calculations of the transient of current, the cathode potential was chosen to be $E_0 = 0.6$ V. For the first time, it was analyzed how the moisture exchange in the active layer can affect the overall characteristics of the cathode, first of all, its overall current I , A/cm². In calculations, we assumed that the fuel cell

operates at the temperature $t = 80$ °C and the pressure $p^* = 101$ kPa.

When the current was switched on (zero moment), all pores in support grains were assumed to be free of moisture; hence, the supply of oxygen to support-grain pores proceeded under the maximum beneficial conditions of Knudsen diffusion with the diffusion coefficient $D = 1.5 \times 10^{-5}$ cm²/s. Moreover, in the pores of support grains, the kinetic mode of current generation was established.

In the subsequent moments, the following two competitive processes of moisture exchange started to operate:

(1) flooding of support-grain pores with water, which is the product of the oxygen reduction that proceeds in the support grains, and

(2) drying of support-grain pores, i.e., their liberation from moisture as a result of water evaporation from the water/steam-gas interface, followed by the diffusion of water vapor to the frontal surface of the support grain. This process is possible due to the heating of the active layer, which gives rise to the temperature difference between water and the gas mixture of oxygen and water vapor in the pores of support grains.

We analyzed not only the changes (decrease) in the overall current I , A/cm² but also the variations (drop) in the average temperature of the cathode active layer T_s which is different from the fuel-cell working temperature T ($T_s > T$). The gradual increase in the degree of water-flooding of pores in support grains was also studied.

It was shown that under potentiostatic conditions with the cathode potential $E_0 = 0.6$ V, the process of flooding dominates over the process of drying of support-grain pores. As a result, in 10 s, all pores in support grains turn out to be completely filled with water.

Insofar as the diffusion coefficient of oxygen molecules in water is several orders of magnitude lower than in the gas phase (the Knudsen mode of diffusion in nanopores), then the effective diffusion coefficient of oxygen in support grains decreases from $D = 1.5 \times 10^{-5}$ cm²/s to $D = 4.1 \times 10^{-9}$ cm²/s. As a result, in support grains, the inner-diffusion mode of current generation is realized. As a consequence, the overall current generated in the active layer sharply decreases as compared with the initial value $I = 4.323$ A/cm², falling by approximately one order of magnitude to the value $I = 0.526$ A/cm².

The overall process of the rapid decrease of the overall current is naturally accompanied by the decrease in the active-layer temperature T_s from its initial value of 373.8 K (~101 °C) to the final value of 355.5 K (~82.5 °C).

Evidently, the question on the nature of the overall current transient should not be considered as ultimately solved. However, the results of experimental reproduction of the overall current transient, shown in

the present study confirmed qualitatively the conclusions of theoretical calculations and the validity of our assumptions on the origin of this transient – the gradual flooding of pores in active-layer support grains with water.

LIST OF DESIGNATIONS OF PARAMETERS CHARACTERIZING THE FUEL CELL WITH NAFION AND PLATINUM AND THEIR VALUES TAKEN IN CALCULATIONS

<i>Parameters of the Active Layer of a Cathode with Polymer Electrolyte</i>	
$T = 353 \text{ K} = 80 \text{ C}$	the temperature at which the fuel cell operates
T_s	the temperature of the active layer after its heating
$p^* = 101 \text{ kPa}$	the pressure in the oxygen-supplying chamber
$c_0 = 5 \times 10^{-6} \text{ g-mol/cm}^3$	the oxygen solubility in Nafion at $p^* = 101 \text{ kPa}$
$\Delta = 10 \text{ }\mu\text{m} = 10^{-3} \text{ cm}$	the active layer thickness
$k = 0.1 \text{ }\Omega^{-1} \text{ cm}^{-1}$	the specific optimal protonic conductivity of Nafion
$D_g = 0.2 \text{ cm}^2/\text{s}$	the coefficient of molecular diffusion of oxygen in grain-voids in the active layer at $t = 80 \text{ C}$ and the pressure in the gas-supplying chamber $p^* = 101 \text{ kPa}$
$L = 100 \text{ nm} = 10^{-5} \text{ cm}$	the length of edges of support grains, Nafion grains, and grain-voids
$I, \text{ A/cm}^2$	the overall current of the cathode active layer
$g = 0.5$	the fraction of support grains in the active layer
$g_i = 0$	the fraction of Nafion grains in the active layer
$g_{\text{gas}} = 0.5$	the fraction of grains-voids in the active layer
$k^{**} = 4.58 \times 10^{-3} \text{ }\Omega^{-1} \text{ cm}^{-1}$	the effective protonic conductivity of the cathode active layer
$D^{**} = 2.18 \times 10^{-2} \text{ cm}^2/\text{s}$	the effective diffusion coefficients of gas in the cathode active layer

Electrochemical Parameters

$E_{\text{st}} = 1.05 \text{ V}$	the steady-state potential of the cathode
$E^* = 0.825 \text{ V}$	the potential of the break point in polarization curve
E_0	the cathode potential

$b_1 = 2.6 \times 10^{-2} \text{ V}$	the Tafel plot slope in the region of high potentials
$b_2 = 5.2 \times 10^{-2} \text{ V}$	the Tafel plot slope in the region of low potentials
$n = 4$	the number of electrons involved in the electroreduction of oxygen
$i_0 = 1.01 \times 10^{-7} \text{ A/cm}^2$	the exchange current at $t = 80 \text{ C}$
$F = 9.65 \times 10^4 \text{ C/mol}$	the Faraday number

Parameters of Support Grains

$g_e = 0.279$	the volume concentration (fraction) of carbon microcubes in a support grain
$g_{ii} = 0.420$	the volume concentration (fraction) of Nafion involved in the protonic cluster in support grains
$g_{gg} = 0.301$	the porosity accounted for the voids in a support grain
$S_0 = 9.72 \times 10^{-10} \text{ cm}^2$	the total surface of the carbon cluster in a support grain
$S_{\text{in}} = 5.20 \times 10^{-10} \text{ cm}^2$	the active (as regards the electrochemical process) surface of the carbon cluster in a support grain
$D_{\text{kn}}, \text{ cm}^2/\text{s} = 1.50 \times 10^{-5} \text{ cm}^2/\text{s}$	the effective coefficient of Knudsen diffusion in the pores of a support grain (the grain is totally water-free)
$D_w = 4.1 \times 10^{-9} \text{ cm}^2/\text{s}$	the diffusion coefficient of oxygen in the pores of support grains completely filled with water
g_w	the degree of filling of pores in support grains with water
$k^{***} = 0.103$	the effective normalized conductivity of the protonic cluster in support grains

REFERENCES

1. Rubio, M.A., Urquia, A., and Dormido, S., *J. Power Sources*, 2007, vol. 171, p. 670.
2. Li, H., Tang, Y., Wang, Z., Shi, Z., Wu, S., Song, D., Zhang, J., Fatih, K., Zhang, J., Wang, X., Liu, Z., Abouatallah, R., and Mazza, A., *J. Power Sources*, 2008, vol. 178, p. 103.
3. Yousfi-Steiner, N., Mocoteguy, Ph., Candusso, D., Hissel, D., Hernandez, A., and Aslanides, A., *J. Power Sources*, 2008, vol. 183, p. 260.
4. Weber, A.Z. and Hickner, M.A., *Electrochim. Acta*, 2008, vol. 53, p. 7668.
5. Swamy, T., Kumbur, E.C., and Mench, M.M., *J. Electrochem. Soc.*, 2010, vol. 157, p. B77.
6. Wang, X. and Nguyen, T.V., *J. Electrochem. Soc.*, 2010, vol. 157, p. B496.

7. Rubio, M.A., Urquia, A., and Dormido, S., *Intern. J. Hydrogen Energy*, 2010, vol. 35, p. 2586.
8. Jiao, K. and Li, X., *Prog. Energy Combust. Sci.*, 2011, vol. 37, p. 221.
9. Li, Chen., Hui-Bao, Luan., Ya-Ling, He., and Wen-Quan, Tao., *Int. J. Therm. Sci.*, 2012, vol. 51, p. 132.
10. Chirkov, Yu.G. and Rostokin, V.I., *Al'ternativnaya Energetika i Ekologiya*, 2014, no. 6, p. 8.
11. Chirkov, Yu.G. and Rostokin, V.I., *Al'ternativnaya Energetika i Ekologiya*, 2014, no. 9, p. 8.
12. Chirkov, Yu.G., *Al'ternativnaya Energetika i Ekologiya*, 2014, no. 9, p. 59.
13. Chizmadzhev, Yu.A., Markin, V.S., Tarasevich, M.R., and Chirkov, Yu.G., *Makrokinetika protsessov v poristykh sredakh (Toplivnye elementy) (Macrikinetics of Processes in Porous Media (Fuel Cells))*, Moscow: Nauka, 1971.
14. Chizmadzhev, Yu.A. and Chirkov, Yu.G., in *Comprehensive Treatise of Electrochemistry*, Yeager, E., Bockris, J.O'M., Conway, B.E., and Sarangapani, S., New York: Plenum Press, 1983, vol. 6, p. 356.
15. Chirkov, Yu.G. and Rostokin, V.I., *Al'ternativnaya Energetika i Ekologiya*, 2014, no. 14, p. 58.
16. *PEM Fuel Cell Electrocatalysis and Catalyst Layers: Fundamentals and Applications*, Zhang, J.L., Ed., London: Springer, 2008.
17. Xie, J., Wood, I.D.L., Wayne, D.M., Zawodzinski, T.A., Atanassov, P., and Borup, R.L., *J. Electrochem. Soc.*, 2005, vol. 152, p. A104.
18. Mukherjee, P.P. and Wang, C.Y., *J. Electrochem. Soc.*, 2006, vol. 153, p. A840.
19. Rong, F., Huang, C., and Liu, Z.OS., Song, D., and Wang, Q., *J. Power Sources*, 2008, vol. 175, p. 699.
20. Rong, F., Huang, C., and Liu, Z.OS., Song, D., and Wang, Q., *J. Power Sources*, 2008, vol. 175, p. 712.
21. Chirkov, Yu.G. and Rostokin, V.I., *Russ. J. Electrochem.*, 2012, vol. 48, p. 1086.
22. Tarasevich, Yu.Yu., *Perkolyatsiya: teoriya, prilozheniya, algoritmy (Percolation: Theory, Applications, Algorithms)*, Moscow: Editorial URSS, 2001.
23. Chirkov, Yu.G. and Rostokin, V.I., *Al'ternativnaya Energetika i Ekologiya*, 2012, no. 2, p. 132.
24. Chirkov, Yu.G. and Rostokin, V.I., *Russ. J. Electrochem.*, 2013, vol. 49, p. 149.
25. Chirkov, Yu.G. and Rostokin, V.I., *Russ. J. Electrochem.*, 2014, vol. 50, p. 872.
26. Parthasarathy, A., Srinivasan, S., Appleby, A.J., and Martin, C.R., *J. Electrochem. Soc.*, 1992, vol. 139 P, p. 2530.
27. Chirkov, Yu.G. and Rostokin, V.I., *Al'ternativnaya Energetika i Ekologiya*, 2014, no. 17, p. 57.
28. Chirkov, Yu.G. and Rostokin, V.I., *Russ. J. Electrochem.*, 2006, vol. 42, p. 722.

Translated by T.Ya. Safonova

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