

Cathode of a Fuel Cell with a Solid Polymer Electrolyte: Calculating Overall Currents in the Presence of a Gas-Diffusion Layer

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Abstract—Mathematical apparatus, which makes it possible to perform calculations of the current–voltage characteristics of cathodes of fuel cells with a solid polymer electrolyte in conditions where there are present extraneous diffusion restrictions is proposed. In so doing, the partial pressure of oxygen and the absolute pressure of gas in the gas chamber may assume any values. First of all presented are the results of calculations of the current–voltage characteristics intrinsic to active layers of the air and oxygen cathodes, which are performed under the assumption that the extraneous diffusion restrictions are absent altogether. Thereafter, in the same conditions (at the same parameters that characterize the active layer of a cathode), obtained are results of a calculation of the current–voltage characteristics inherent in the air and oxygen cathodes in the presence of extraneous diffusion restrictions. Afterward there is performed an analysis of the way a gas-diffusion layer restricts the process of generation of current in a cathode and of what measures should be taken in order for the extraneous diffusion restrictions to become less significant.

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INTRODUCTION

In between a gas chamber and the active layer of a cathode there is present a gas-diffusion layer (backing layer). Its functions are multifarious. These include the tasks of distributing the gas reactant throughout the active layer, serving as a bridge for relaying electrons, providing structural support for a polymer membrane, regulating flows of water and water vapor, and so forth [1]. Before this time, only one gas-diffusion layer was used on the cathodic side. The gas-diffusion layer in question was fabricated out of special carbon paper (for example, Toray Paper), which had been hydrophobized with the aid of Teflon particles, or manufactured out of graphitized cloth (for example, Carbon Cloth). Highly porous were these layers (for example, paper Kherea had a porosity equal to 65–75%) and with sufficiently large pores, too, whose dimensions fell in the interval that was extending from 3 to 100 μm (average radius of pores was equal to 30 μm) [2]. However, at the present time, combined gas-diffusion layers have been started to be employed ever more frequently. This is connected with that the discharge currents in a fuel cell sharply increased. The layers are assembled of two layers. One

layer is a thin, of a thickness equal to 20–30 μm , heavily hydrophobized small-pore carbon black layer with pores whose dimensions fall in the interval extending from 0.05 to 2 μm [3, 4]. This first layer is positioned closer to the active layer. The other layer in the combined gas-diffusion layers is a traditional gas-diffusion layer, whose thickness reaches hundreds of micrometers, with pores in the interval 0.5–20 μm [1].

Many groups of researchers investigated how dependent are overall characteristics of fuel cells with Nafion and with a combined gas-diffusion layer on the type (composition of components) of a small-pore sub-layer [5–7], the concentration of the hydrophobizing agent (Teflon) in it, its thickness, and the composition of gas mixtures in the cathodic chamber [8–11]. Also investigated was the effect of the character of the distribution of pores by size [3, 4]. It was demonstrated that the combined gas-diffusion layers optimize the distribution of flows of moisture in fuel cells.

The number of publications in this region is on the rise, for fuel cells with a solid polymer electrolyte and high current characteristics ($I > 1 \text{ A cm}^{-2}$) have long since been tried to be used in automobile transport. That is why it is absolutely necessary to understand well enough the mechanism that is responsible for the

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current restrictions, which unavoidably arise when using gas-diffusion layers. Sadly enough, the progress in the understanding in this region is not great. As was stated for example in [12], the effect produced by the application of combined gas-diffusion layers is very dependent on the conditions in which fuel cells operate and the reasons for the improvement reached when using a small-pore sublayer are still unknown and have not been characterized quantitatively.

We believe that the elucidation of the role played by combined gas-diffusion layers should be conducted stage by stage. In the first place one should have learned how to conduct calculation of overall currents in the active layer of a cathode under the conditions where the gas-diffusion layer introduced no restrictions whatsoever to the process of generation of current. We have solved this problem in [13, 14]. Thereafter one should pass to exploring gas-diffusion restrictions under the condition that the process of generation of current is affected not by a two-component gas-diffusion layer but by a one-component gas-diffusion layer. And it is only afterward that one may pass to an investigation of the role played by combined gas-diffusion layers.

The program of investigations that are presented in this communication included the following salient points.

(1) Calculation of current–voltage characteristics intrinsic to active layers of the air and oxygen cathodes under the conditions where extraneous diffusion restrictions are absent.

(2) Creation of mathematical apparatus that would allow us to conduct calculation of current–voltage characteristics intrinsic to the air and oxygen cathodes under the conditions where extraneous diffusion restrictions are present.

(3) Calculation of current–voltage characteristics intrinsic to the air and oxygen cathodes under the same conditions as in point 1 (invariance of all parameters that characterize the active layer of a cathode) under the conditions where extraneous diffusion restrictions are present (one-component diffusion layer). Values of the gas pressure in a gas chamber were the same as in point 1 of the program.

(4) An ultimate analysis of the way a gas-diffusion layer restricts the process of generation of current in a cathode.

CALCULATION OF OVERALL CURRENTS IN THE ACTIVE LAYER OF A CATHODE IN THE ABSENCE OF EXTRANEIOUS DIFFUSION RESTRICTIONS

Let us perform calculation of values of currents that are generated in the active layer of a cathode with the thickness $\Delta_1 = 10 \mu\text{m}$ under the condition that the gas-diffusion layer introduces no restrictions whatsoever into the process of generation of current in the cathode. For the catalyst we will select 20% Pt on carbon black

XC-72 (E-TEK). Further on, let the temperature be equal to 80°C ; the number of electrons participating in an elementary act, $n = 4$; and Faraday's constant, $F = 9.65 \times 10^4 \text{ C g-mol}^{-1}$. The pressure-dependent solubility of oxygen in Nafion will be represented in the form of $c_0 = 5 \times 10^{-6} \varepsilon \text{ g-mol cm}^{-3}$ (Nafion). Here, parameter $\varepsilon = p^*/p_0^*$, where $p_0^* = 101 \text{ kPa}$ and p^* is the pressure in the gas chamber. At the pressure $p^* = 505 \text{ kPa}$, we have $\varepsilon = 5$ and solubility $c_0 = 2.5 \times 10^{-5} \text{ g-mol cm}^{-3}$.

Let us consider a model of equidimensional grains [13]. We will presume that the structure of the active layer is optimal. What this means is that the bulk concentrations of grains of Nafion g_e and the carbonaceous support g_p are equal to one another: $g_e = g_p = 0.5$. Further on, we will adopt the size of grains $L = 3 \times 10^{-5} \text{ cm}$ and the size of pores in between the support particles $d = 3 \times 10^{-6} \text{ cm}$. Then, according to calculations, the effective coefficient of the oxygen diffusion D^* is equal to $4.5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$, the reduced effective conductivity κ^* is equal to $1.09 \times 10^{-2} \text{ S cm}^{-1}$ (in the case where the Nafion conductivity κ is equal to $1 \times 10^{-1} \text{ S cm}^{-1}$), and the characteristic bulk current i^* is equal to 7.44 mA cm^{-3} (in the case where the weight concentration of platinum in the support grains g_w is equal to 20 wt %). Additional factors that had been taken into account when performing the calculations included the following. First, the Tafel plots for the process of reduction of oxygen on platinum have two different slopes, specifically, $b_1 = 2.6 \times 10^{-2} \text{ V}$ and $b_2 = 5.2 \times 10^{-2} \text{ V}$. Second, the steady-state potential $E^{\text{st}} = 1.05 \text{ V}$. And third, the potential at which a Tafel plot alters its slope is $E^* = 0.825 \text{ V}$.

Calculation of the dependence of the overall current I of a cathode on the electrode potential E_0 (potential of the cathode is presented relative to a hydrogen anode) will be conducted in two versions: for an oxygen electrode (under these conditions the oversaturation of water with oxygen in Nafion at the interface between the active layer and the gas-diffusion layer is $c_s = 1$) and for an air electrode (in this case, $c_s = 0.2$). The results of calculations for three values of pressure in the gas chamber ($p^* = 101, 303, \text{ and } 505 \text{ kPa}$) are presented in Fig. 1.

In the case where some internal diffusion restrictions take place inside the active layer, the overall current increases with increasing p^* proportionally to $(p^*)^{1/2}$. As is demonstrated by the data we obtained after performing the calculations, in the region of high potentials ($1.05 \text{ V} \geq E_0 \geq 0.6 \text{ V}$), diffusion restrictions in the active layer are practically absent. Raising the pressure in the gas chamber discernibly improves the current characteristics of the cathode solely in the region of low potentials. Moreover, the lower the cathode potential, the more discernible the improvement. Had the extraneous diffusion restrictions been absent altogether, with the gas pressure in the gas chamber increasing, the overall currents in both the air cathode and the oxygen cathode could have reached impressive values.

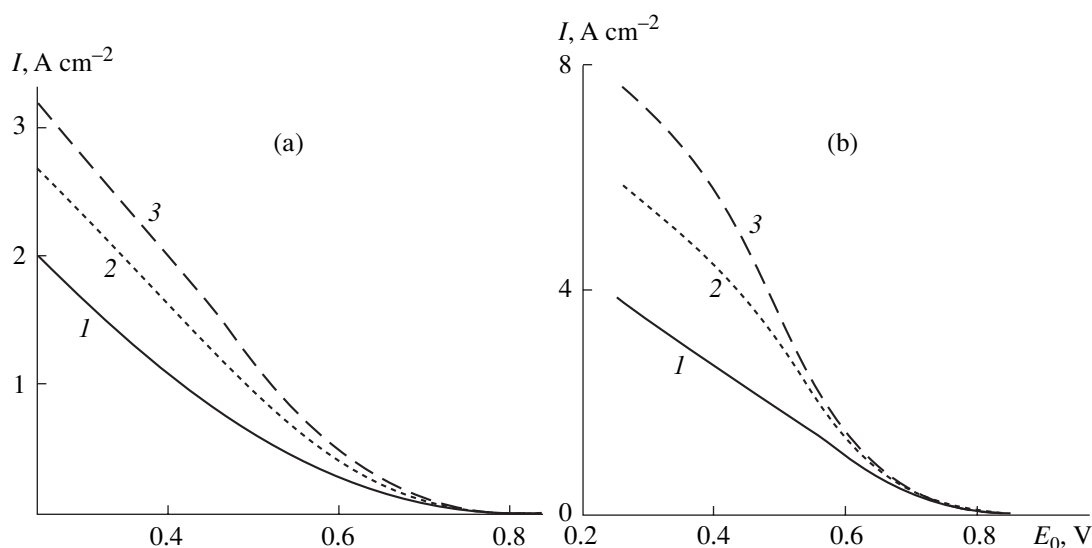


Fig. 1. Current–voltage curves for (a) air cathode ($c_s = 0.2$) and (b) oxygen cathode ($c_s = 1$) in the absence of extraneous diffusion restrictions, calculated for pressures p^* equal to (1) 101, (2) 303, and (3) 505 kPa.

A GAS-DIFFUSION LAYER: THEORETICAL FORMULAS

And now we are about to embark on exploration of the effect a gas-diffusion layer (its thickness will be denoted with symbol Δ) exerts on the current characteristics of a cathode. Various approaches to solving this problem have been described in the relevant literature. There were suggested a multitude of 0- D models in which the current–voltage curve for a fuel cell was characterized by merely one equation. The authors of [15], for example, analyzed the equality

$$E = E^* - b \log I - RI - m \exp(nI), \quad (1)$$

where E is a potential, E^* is a thermodynamic potential, and R is an overall ohmic resistance. The last addend in the right-hand part of equation (1) describes processes that proceed in a gas-diffusion layer. Parameters m and n in (1) are fitting parameters that have no physical meaning.

The authors of other works of a similar sort made attempts to introduce into the 0- D models in an explicit form such parameters as the limiting current I_{lim} , the partial pressure of oxygen, and so forth. Equality (1) and other expressions analogous to it are sometimes capable of describing experimental data for one system or another sufficiently successfully, indeed. Nevertheless, expressions of this kind give no chance to understand the mechanism of their action and optimize the gas supply toward an active layer.

It would be better to use 1- D models for analyzing processes that go on in a gas-diffusion layer. In so doing, written are systems of equations of a balance type, in which all quantities that feature in calculations depend solely on one coordinate. The coordinate in

question is directed normally to the membrane as well as to other elements-layers that enter the composition of the cathode of a fuel cell.

Consider processes that proceed in a gas-diffusion layer. The interpretation usually resorted to in this case is as follows. It is known [16] that, if an electrochemical (heterogeneous) reaction is accompanied by a decrease in the volume of the reacting mixtures (in our case, gaseous oxygen is consumed in the active layer of an air cathode and liquid water is produced), then there arises a general flowing of the reacting mixture (of nitrogen with oxygen) in the direction that is perpendicular with respect to the surface on which the reaction takes place. This is the way in which Stephanian flows arise in the cathode [17, 18].

The common assumption usually made is that, in porous membranes, filtration flows that are caused by a pressure difference considerably exceed Stephanian flows [19]. As a result, the overall pressure of a gas mixture may be viewed constant (there occur rapid leveling of the overall pressure of the gas):

$$p + p_1 = 1. \quad (2)$$

Here, p and p_1 are the reduced (divided by p^*) partial pressures of oxygen and nitrogen. The Stephanian fluxes of oxygen and nitrogen have the following form:

$$-dp/d\bar{y} + \bar{u}p = \bar{I}, \quad (3)$$

$$-dp_1/d\bar{y} + \bar{u}p_1 = 0. \quad (4)$$

Here, $\bar{y} = y/\Delta$ is a reduced coordinate in the direction that is perpendicular to the active layer; $\bar{u} = u/u^*$ is the reduced bulk (molal) velocity of the flow of the gaseous mixture; $u^* = D^{**}/\Delta$ is a characteristic velocity, where D^{**} is the effective diffusion coefficient of the gas in

the gas-diffusion layer; $\bar{I} = I/I_d$ is a reduced current, where I_d is a characteristic diffusion current, which is given by the equation

$$I_d = nFD^{**}p^*/RT\Delta = [nFD^{**}p_0^*/RT\Delta]\varepsilon = I_d^* \varepsilon. \quad (5)$$

With allowance made for (2), the boundary conditions for equations (3) and (4) are as follows:

$$\dot{y} = 0 \quad p = p_0, \quad p_1 = 1 - p_0, \quad (6)$$

$$\dot{y} = 1 \quad p = p_s, \quad p_1 = 1 - p_s. \quad (7)$$

Here, p_0 is the reduced partial pressure of oxygen in the gas chamber and p_s is the reduced partial pressure of oxygen at the interface between the active and gas-diffusion layers. After integrating equations (3) and (4) with allowance made for boundary conditions (6) and (7), we obtain

$$\bar{I} = \ln[(1 - p_s)/(1 - p_0)]. \quad (8)$$

The limiting current ($p_s = 0$), then

$$\bar{I}_{\text{lim}} = -\ln(1 - p_0). \quad (9)$$

For pure oxygen ($p_0 = 1$) $\bar{I}_{\text{lim}} = \infty$, which means that the limiting current happened to be equal to infinity. One of the reasons for the result being meaningless from a physical viewpoint is that we did not take into account the presence of vapors of moisture in the gas chamber and in the active layer. If this is done, then under the logarithm sign in equation (9) at $p_0 = 1$ there must stand a quantity of the partial pressure of vapor that is other than zero. We will not consider allowance for this factor in the present exploration. Another reason is that in the foregoing we presumed the magnitude of the gas-diffusion layer penetrability $\tau = \infty$, which is precisely what leads to the fulfillment of condition (2). However, more likely than not this presumption is problematic, the more so upon going to membranes with small pores, which are partially filled with a liquid, to boot. In view of this, in some works there were put forth suggestions to complement the system of Stephanian fluxes with respect to oxygen and nitrogen (3) and (4) with the Darcy equation

$$U = -(\tau p^*/\mu)d(p + p_1)/dy, \quad (10)$$

where U is the velocity of the gas flow and μ is the viscosity of air in the gas-diffusion layer. And now the overall pressure of gases is constant no longer:

$$p + p_1 \neq 1. \quad (11)$$

The velocity that appears in the Darcy law is not a bulk (molal) velocity but a mass velocity. However, in view of the fact that the molecular weight of oxygen (32 arbitrary units) is approximately equal to the molecular weight of nitrogen (28 arbitrary units), the difference between the velocities is not that significant, which

allows us to adopt the following simplification. Let us consider that

$$u = U. \quad (12)$$

Then the Darcy equation (10) may be rewritten in the following form:

$$\dot{u} = -\alpha d(p + p_1)/d\dot{y}. \quad (13)$$

The last equation contains the basic parameter of the problem, which is the ratio of the gas filtration rate to the gas diffusion rate

$$\alpha = \tau p^*/D^{**}\mu = [\tau p_0^*/D^{**}\mu]\varepsilon = \alpha^* \varepsilon. \quad (14)$$

Parameter α may be presented in the form of two co-factors. One co-factor, a α^* , is structural. It is defined by properties of the gas-diffusion layer. The other factor, ε , is "barometric." It depends on the magnitude of the overall pressure in the gas chamber.

Once equation (13) was introduced, boundary condition (7) must be replaced with

$$\dot{y} = 1 \quad p = p_s, \quad p_1 = p_n, \quad (p_s + p_n) < 1. \quad (15)$$

Here, p_n is the partial pressure of nitrogen at the interface between the active layer and the gas-diffusion layer.

As we have four quantities to be determined, specifically, $-p$, p_1 , \dot{u} , and p_n , the system of equations (3), (4), and (13) should be complemented with one more condition. Let us demand the fulfillment of the continuity equation [20]

$$d[\dot{u}(p + p_1)]/d\dot{y} = 0. \quad (16)$$

And now let us find a general solution for the system of equations (3), (4), (13), and (16) with boundary conditions (6) and (15). Upon introducing designation $\Sigma = p + p_1$ and taking the sum of equations (3) and (4) we have

$$-d\Sigma/d\dot{y} + \dot{u}\Sigma = \bar{I}, \quad (17)$$

and, instead of equations (13) and (16) we obtain

$$\dot{u} = -\alpha d\Sigma/d\dot{y}, \quad (18)$$

$$d(\dot{u}\Sigma)/d\dot{y} = 0. \quad (19)$$

Equations (17) through (19) are complemented with boundary conditions

$$\dot{y} = 0 \quad \Sigma = 1, \quad (20)$$

$$\dot{y} = 1 \quad \Sigma = p_s + p_n. \quad (21)$$

Having eliminated velocity \dot{u} from equations (17)–(19) we obtain two differential equations

$$-d\Sigma/d\dot{y} - \alpha\Sigma d\Sigma/d\dot{y} = \bar{I}, \quad (22)$$

$$d(\Sigma d\Sigma/d\dot{y})/d\dot{y} = 0. \quad (23)$$

After integrating equation (22) with allowance made for boundary conditions (20) and (21), we obtain

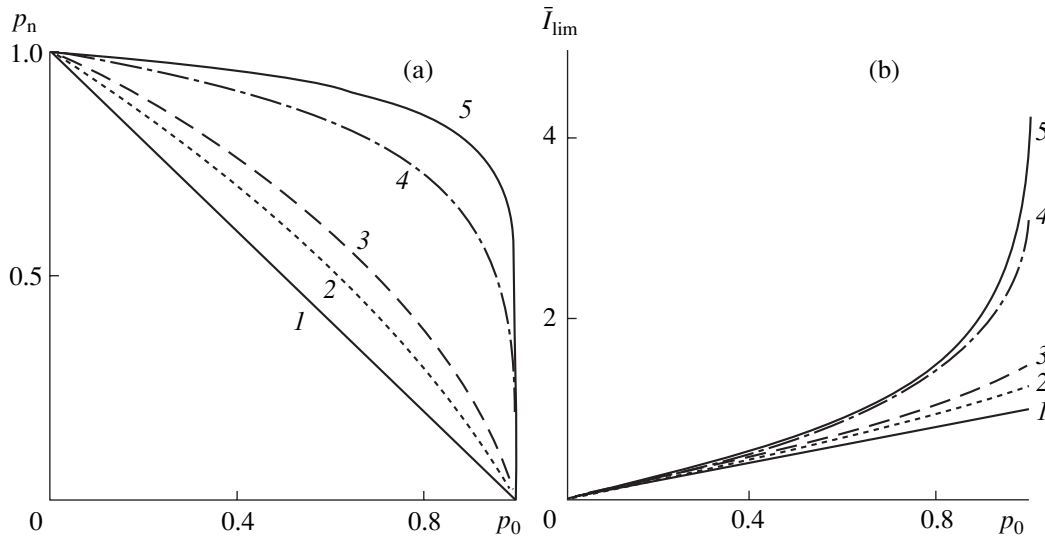


Fig. 2. (a) Partial pressure of nitrogen at the interface between the active layer and the gas-diffusion layer and (b) reduced limiting current as functions of the partial pressure of oxygen in the gas chamber. The curves are calculated for α equal to (1) 0, (2) 0.5, (3) 1, (4) 5, and (5) 10.

$$\bar{I} = 1 - p_s - p_n + \alpha[1 - (p_s + p_n)^2]/2. \quad (24)$$

After integrating equation (23) with allowance made for boundary conditions (20) and (21), we obtain the distribution, over the thickness of the gas-diffusion layer, of the sum of partial pressures Σ :

$$\Sigma = p + p_1 = \{1 - [1 - (p_s + p_n)^2]y\}^{1/2}. \quad (25)$$

And now, with the aid of expression (18), we can determine velocity \dot{u} :

$$\dot{u} = \alpha[1 - (p_s + p_n)^2]/2 \{1 - [1 - (p_s + p_n)^2]y\}^{1/2}. \quad (26)$$

In turn, the last expression gives us a chance to integrate equation (4) relative to the partial pressure of nitrogen p_n with allowance made for boundary conditions (6) and (15). As a result,

$$p_n = (1 - p_0)\exp[\alpha(1 - p_s - p_n)]. \quad (27)$$

Expressions (24) and (27) fully determine the magnitude of current in the system under investigation. If $\alpha = 0$ (the filtration flux after Darcy is infinitesimally small as compared with the diffusion flux, the velocity of the movement of the gas mixture in the gas-diffusion layer is equal to zero), then, according to (27), $p_n = 1 - p_0$ (the partial pressure of nitrogen in the gas-diffusion layer is constant). And, according to (24), as it should be, the regime of generation of current is purely a diffusion regime:

$$\bar{I} = p_0 - p_s. \quad (28)$$

If, on the other hand, which is another extreme case, $\alpha = \infty$ (a powerful Darcy flow equalizes the overall pressure in the gas-diffusion membrane), then, according to (27), it is necessary to demand the fulfillment of the condition $p_s + p_n \equiv 1$ and, with allowance made for

(24), we will obtain formula (8). Note also that, for the limiting current \bar{I}_{lim} (at $p_s = 0$), instead of relationships (24) and (27), we have the following system of two equations:

$$\bar{I}_{lim} = 1 - p_n + \alpha[1 - p_n^2]/2, \quad (29)$$

$$p_n = (1 - p_0)\exp[\alpha(1 - p_n)]. \quad (30)$$

In conclusion it is necessary to make an important statement. In the general case, the gas pressure at the interface between the active layer and the gas-diffusion layer (we will denote it by symbol p^{**}) is lower than the pressure in the gas chamber p^* . It is obvious that

$$p^{**} = p^*(p_s + p_n). \quad (31)$$

That is why the overall current in the active layer, if there take place diffusion limitations in it, increases now proportionally not to $(p^*)^{1/2}$ (the case where the gas-diffusion layer introduces no restrictions whatsoever into the process of generation of current (Fig. 1)) but proportionally to $(p^{**})^{1/2} = (p^*)^{1/2}(p_s + p_n)^{1/2}$, which is a smaller quantity.

RESULTS OF CALCULATIONS

We will now pass to final calculations and numerical evaluations of overall characteristics of the cathode of a fuel cell with Nafion and platinum in the active layer in the presence of a gas-diffusion layer.

At the beginning we will determine the dependence of the reduced limiting current \bar{I}_{lim} on the partial pressure of oxygen in the gas chamber p_0 with the aid of formulas (29) and (30). We will vary the magnitude of parameter α from zero to infinity. In Fig. 2a we present the p_n, p_0 dependences for five values of parameter α ,

specifically, 0, 0.5, 1, 5, and 10. If $\alpha = \infty$, then $p_n \equiv 1$. In Fig. 2b we present the corresponding $\bar{I}_{\text{lim}}, p_0$ dependences.

As seen, in the first place, the limiting current that is generated on the cathode, according to the definition given by (5), is proportional to a characteristic diffusion current. In so doing, the value of the limiting current increases with increasing diffusion coefficient D^{**} in the gas-diffusion layer, with increasing pressure of the gas mixture in the gas chamber p^* , and with decreasing thickness of the gas-diffusion layer Δ . Secondly it is seen that the limiting current may perceptibly increase with increasing parameter α . Simultaneously, Fig. 2b also demonstrates that this increase is small in the case of an air cathode (at $p_0 = 0.2$), so that the major role in it is now played by the oxygen diffusion in nitrogen. However, for an oxygen cathode, the increase in the current that occurs with increasing parameter α may become substantial, for the Stephanian effects vanish at $p_0 = 1$ (pure oxygen) and there is observed filtration of a single-component gas through the porous membrane. The rate of this filtration is proportional to the penetrability τ of the gas-diffusion membrane, i.e. to the magnitude of parameter α .

We will now busy ourselves with the task of estimating parameters that appear in theoretical formulas. In the general case, the magnitude of the overall current of a cathode is defined by three quantities that characterize the gas-diffusion layer, namely, I_d^* , α^* , and ε . In order to evaluate the characteristic diffusion current I_d^* with the aid of formula (5), it is necessary for us to know the value of the effective diffusion coefficient D^{**} . The formula that is usually used in such a case is

$$D^{**} = Dg/\beta. \quad (32)$$

Here, D is the diffusion coefficient for oxygen in air (in nitrogen), g is the porosity of the gas-diffusion layer, and β is the tortuosity factor. The last quantity has no physical meaning whatsoever and is merely a fitting parameter. It shows how many times the effective diffusion coefficient D^{**} is as small as the matrix possible effective diffusion coefficient ($D_{\text{max}}^{**} = Dg$). Let us set $D = 0.2 \text{ cm}^2 \text{ s}^{-1}$, $g = 0.75$ (as we have already stated in the foregoing, heretofore there were used gas-supplying layers that had a high porosity [2]), and $\beta = 1$ (we presume that the pores inside a gas-diffusion layer are straight cylindrical channels that do not cross one another). Under these conditions we have $D^{**} = 0.15 \text{ cm}^2 \text{ s}^{-1}$. We could also set $p^* = 101 \text{ kPa}$ and $\Delta = 1 \times 10^{-2} \text{ cm}$. Then, for air, the characteristic limiting diffusion current $I_d^{\text{lim}} = nFD^{**}(p^*/RT)p_0/\Delta = 51.6 \text{ A cm}^{-2}$. This quantity is very large and, under these conditions, there can be no arguing about any extraneous diffusion restrictions.

Estimates of a similar kind, which were conducted in [21], gave for the limiting diffusion current the value

6 A cm^{-2} . And, at such values of parameter I_d^* , diffusion restrictions in an air cathode seemingly should not have manifested themselves in any manner. And, nevertheless, they are fixed experimentally. This contradiction between the estimates and experiments is explained by that we obviously selected for D^{**} a very exaggerated value. In reality, the tortuosity factor β is, of course, not equal to unity. In fact, $\beta \gg 1$.

Let us now turn our attention to literature data. The surprising thing is that there are practically absent works where authors would have determined the value of the effective diffusion coefficient D^{**} . It is only in [22] that a hydrophobized carbon air electrode with a gas-diffusion layer was examined experimentally. The authors of [22] came to the conclusion that the effective diffusion coefficient in the gas-diffusion layer is very small, specifically, $D^{**} = 6 \times 10^{-4} \text{ cm}^2/\text{s}$ (i.e. $\beta = 250$). It is precisely the value we will adhere to in our subsequent calculations. Then, estimates show that $I_d^* = 1.035 \text{ A cm}^{-2}$.

It is now the turn of parameter α^* to be evaluated. The data concerning the penetrability of gas-diffusion membranes can be found in many studies. We will assume that the penetrability of a gas-diffusion layer $\tau = 1.8 \times 10^{-14} \text{ cm}^2$ [12]. Moreover, to our minds, the pores in a gas-diffusion layer have radii largely in excess of $0.5 \mu\text{m}$. This implies the absence of the necessity to take into account the Knudsen diffusion and allows us to take the air viscosity $\mu = 1.89 \times 10^{-4} \text{ P}$ [23] in the role of the viscosity in the Darcy equation. Then, as follows from the definition (14), we have $\alpha^* = 0.156$. These two parameters, $I_d^* = 1.035 \text{ A cm}^{-2}$ and $\alpha^* = 0.156$, are the parameters with which we will subsequently conduct all calculations.

Of most interest in the presence of restrictions on the oxygen supply out of the gas chamber toward the active layer of a cathode is a calculation of current-voltage curves. The results of such a calculation for the air and oxygen cathodes are presented in Tables 1 through 4 and in Fig. 3. In the air cathode, following a decrease in potential, all the overall currents achieve limiting values (Fig. 3a). In the oxygen cathode, the limiting current is observed at the pressure $p^* = 101 \text{ kPa}$ and practically disappears at the pressure $p^* = 505 \text{ kPa}$ (Fig. 3b). However, a comparison of Fig. 1b to Fig. 3b shows the presence of substantial extraneous diffusion restrictions in the region of low potentials even in this case.

The common practice used for improving characteristics of a cathode is to elevate the temperature to 95°C and raise the pressure p^* to 505 kPa . That the application of higher pressures in the gas chamber exerts a beneficial effect on current-voltage characteristics was mentioned in many studies [24–26].

The reasons that are responsible for the considerable increase in the overall current are pretty obvious. Fol-

lowing an increase in the pressure p^* , parameter ε increases. As a result, the diffusion current I_d increases as well (relationship (5)), specifically, $I_d = 5.175 \text{ A cm}^{-2}$ at $p^* = 505 \text{ kPa}$. Following an increase in the pressure inside the gas chamber, parameter α increases as well (relationship (14)), for example, $\alpha = 0.78$ at $p^* = 505 \text{ kPa}$. All this combines together to entail a considerable increase in the overall current of a cathode.

It would now be useful to compare current–voltage characteristics for cathodes that are presented in Tables 1 through 4 (see also Figs. 1, 3). From the start we will consider an oxygen electrode. If considerable extraneous diffusion restrictions are absent, then the partial pressure of oxygen at the interface between the active layer and the gas-diffusion layer is constant and equals $p_s \equiv 1$. If, on the other hand, extraneous diffusion restrictions are present, the partial pressure of oxygen p_s steadily decreases with decreasing cathode potential E_0 and increasing the overall current I (third columns in Tables 3 and 4), which is precisely what serves as the reason for the decrease in the overall current. Naturally, in accord with formula (31), the absolute pressure p^{**} at the interface between the active layer and the gas-diffusion layer also drops proportionally. Under these conditions, the drop in p_s and p^{**} slows down following an increase in the gas pressure p^* in the gas chamber, as follows from a comparison of data presented in Table 3 with data presented in Table 4. Thus, the data obtained heretofore show the effectiveness of employing higher pressures in the gas chamber.

Let us pass to an air cathode. Here, the partial pressure of oxygen (dilution of oxygen with nitrogen, $p_0 = 0.2$) is not high from the very beginning. That is why the drop of the partial pressure of oxygen at the interface between the active layer and the gas-diffusion

Table 1. Dependence of the overall current I in the active layer of a cathode with thickness $\Delta = 10 \text{ }\mu\text{m}$, the relative pressure of oxygen p_s , and the relative pressure of nitrogen p_n at the interface between the active layer and the gas-diffusion layer on the cathode potential E_0 . Air electrode in the presence of extraneous diffusion restrictions, pressure in the gas chamber $p^* = 101 \text{ kPa}$

$E_0, \text{ V}$	$I, \text{ A cm}^{-2}$	$p_s = c_s$	p_n
0.8	0.012	0.188	0.801
0.75	0.029	0.173	0.803
0.7	0.057	0.146	0.806
0.65	0.093	0.112	0.810
0.6	0.124	0.082	0.813
0.55	0.148	0.059	0.816
0.5	0.166	0.042	0.818
0.45	0.180	0.029	0.819
0.4	0.190	0.019	0.820
0.35	0.197	0.012	0.821
0.3	0.202	0.008	0.822
0.25	0.205	0.005	0.822

layer p_s , which occurs following a decrease in the cathode potential E_0 , is far more considerable than the drop that takes place in an oxygen cathode. To be convinced that this is exactly the case, suffice it to compare the

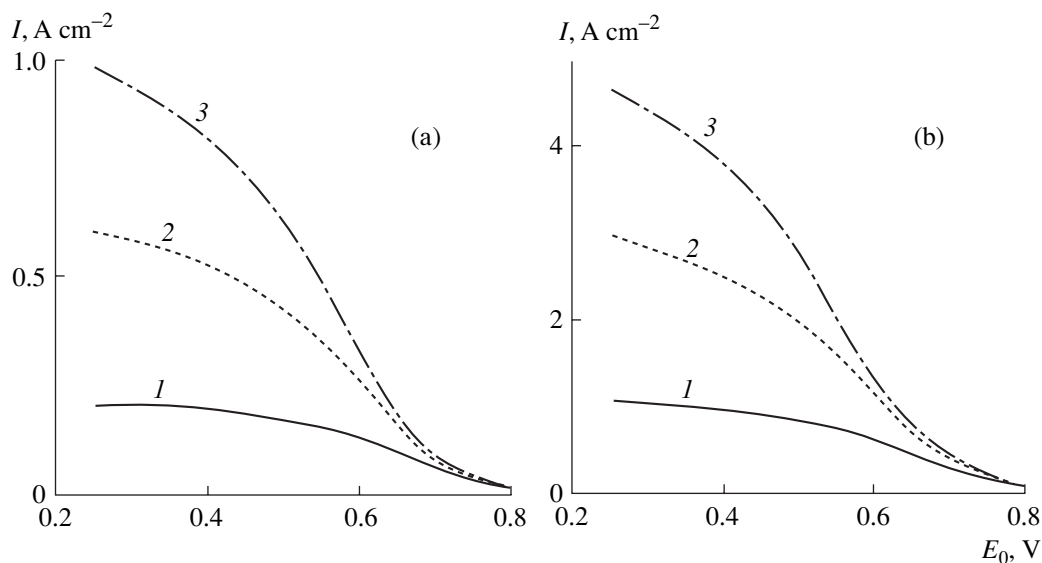


Fig. 3. Current–voltage curves for (a) air cathode ($p_0 = 0.2$) and (b) oxygen cathode ($p_0 = 1$) in the presence of extraneous diffusion restrictions, calculated for pressures p^* equal to (1) 1, (2) 3, and (3) 5 kPa; $I_d^* = 1.035 \text{ A cm}^{-2}$, $\alpha^* = 0.156$.

Table 2. Dependence of the overall current I in the active layer of a cathode with thickness $\Delta = 10 \mu\text{m}$, the relative pressure of oxygen p_s , and the relative pressure of nitrogen p_n at the interface between the active layer and the gas-diffusion layer on the cathode potential E_0 . Air electrode in the presence of extraneous diffusion restrictions, pressure in the gas chamber $p^* = 505 \text{ kPa}$

E_0, V	$I, \text{A cm}^{-2}$	$p_s = c_s$	p_n
0.8	0.0135	0.198	0.801
0.75	0.034	0.194	0.802
0.7	0.081	0.186	0.806
0.65	0.174	0.169	0.812
0.6	0.319	0.143	0.822
0.55	0.483	0.113	0.834
0.5	0.625	0.087	0.844
0.45	0.731	0.067	0.852
0.4	0.813	0.052	0.858
0.35	0.881	0.039	0.863
0.3	0.9375	0.028	0.868
0.25	0.982	0.020	0.871

Table 3. Dependence of the overall current I in the active layer of a cathode with thickness $\Delta = 10 \mu\text{m}$ and the relative pressure of oxygen p_s at the interface between the active layer and the gas-diffusion layer on the cathode potential E_0 . Oxygen electrode in the presence of extraneous diffusion restrictions, pressure in the gas chamber $p^* = 101 \text{ kPa}$

E_0, V	$I, \text{A cm}^{-2}$	$p_s = c_s$
0.8	0.062	0.948
0.75	0.139	0.883
0.7	0.27	0.771
0.65	0.437	0.626
0.6	0.594	0.485
0.55	0.715	0.376
0.5	0.807	0.292
0.45	0.882	0.222
0.4	0.944	0.164
0.35	0.994	0.116
0.3	1.033	0.08
0.25	1.061	0.053

Table 4. Dependence of the overall current I in the active layer of a cathode with thickness $\Delta = 10 \mu\text{m}$ and the relative pressure of oxygen p_s at the interface between the active layer and the gas-diffusion layer on the cathode potential E_0 . Oxygen electrode in the presence of extraneous diffusion restrictions, pressure in the gas chamber $p^* = 505 \text{ kPa}$

E_0, V	$I, \text{A cm}^{-2}$	$p_s = c_s$
0.8	0.066	0.993
0.75	0.160	0.983
0.7	0.361	0.960
0.65	0.726	0.920
0.6	1.279	0.857
0.55	1.9851	0.773
0.5	2.725	0.682
0.45	3.355	0.601
0.4	3.812	0.540
0.35	4.141	0.4945
0.3	4.407	0.457
0.25	4.645	0.423

data presented in Tables 1 and 2 with the data presented in Tables 3 and 4. On the air cathode, the partial pressure of oxygen p_s drops practically to zero. This is precisely the explanation for the rapid achievement of a limiting value by the overall currents on the air cathode (Fig. 3a).

CONCLUSIONS

Thus, the general conclusions of our investigation are as follows.

(1) A theory was suggested, which makes it possible to conduct calculation of overall characteristics inherent in cathodes of fuel cells with allowance made for extraneous diffusion restrictions.

(2) It was demonstrated that the presence of a gas-diffusion layer in cathodes with Nafion substantially diminishes the magnitude of the overall currents.

(3) In order to obtain high overall current–voltage characteristics, especially on an air cathode, it is necessary to increase values of parameter α^* and characteristic diffusion current I_d^* . To this end it is necessary to raise the effective diffusion coefficient D^{**} and the penetrability τ of the gas-diffusion layer and reduce its thickness Δ .

(4) An improvement of overall characteristics of a cathode may also be attained by raising the pressure of the gas mixture p^* in the gas chamber.

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