

MATHEMATICAL MODEL FOR THE SOLID ELECTROLYTE FUEL CELL CATHODE

V. E. Nakoryakov and V. G. Gasenko

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An analytically solvable mathematical model for the cathode of a solid polymer electrolyte fuel cell is proposed. The problem of diffusion in a multicomponent air–vapor mixture in a porous cathode and water transport due to hydrodynamic and electroosmotic forces is solved. The volt–ampere characteristic of the fuel cell is determined taking into account the polarization characteristics and finite conductivity of the electrolyte. An expression is obtained for the thickness of the electrochemical-reaction zone, which gives an estimate of the catalyst efficiency. It is shown that the finiteness of the rate of oxygen diffusion into the reaction zone limits the current density and the fuel cell efficiency. A comparison of the results with available theoretical and experimental data shows that the solutions obtained for the model coincide with the solutions for the more complex Bernardi and Verbrugge model.

Key words: fuel cell, solid electrolyte, gas diffusion.

Introduction. A solid polymer electrolyte fuel cell (FC) is one of the most advances and promising electric power supplies [1]. The most complete and widely used mathematical model for a solid electrolyte FC is described in [2], It is solved only numerically and does not give physically clear estimates and criteria required to optimize the FC design and operation.

The goal of the present paper is to construct a mathematical model for a solid electrolyte FC that is consistent with the model of [2] but uses simpler analytically solvable equations. Initially, a mathematical model for a solid electrolyte FC is described and conditions providing an analytical solution of the model equation are discussed. Then, the equations are solved for all FC regions. Finally, results of numerical calculations for the model are given and compared with experimental data from [2, 3].

Mathematical Model. A solid electrolyte FC consists [1] of two identical porous (graphite) electrodes — an anode and a cathode with electronic conductivity. Part of the electrode pore surface is coated with fluoroplastic; therefore, wettable and nonwettable gas pores are distinguished. On the outside, the electrodes adjoin gas chambers. In this case, we consider a hydrogen–air pair with hydrogen present in the anode gas chamber and air with saturated water vapor in the cathode gas chamber. Between the electrodes there is a solid electrolyte, i.e., a membrane from PSA polymer (polyfluorosulfonic acid or Naphion), which in the hydrated state becomes permeable to water and H^+ hydrogen ions (protons). The sites of contact of the membrane with the electrodes or the catalytic layers are water impermeable thin porous regions filled with the membrane material containing platinum catalyst inclusions. At the anode, hydrogen is catalytically oxidized with the formation of H^+ ions and electrons e^- with the energy U_{th}^0 determined by the change in the Gibbs free energy. The hydrogen ions diffuse further through the membrane to the cathode. At the cathode, air passes through nonwettable pores to the catalytic layer of the cathode. The air oxygen dissolves in water and diffuses into the depth of the cathode catalytic layer, where it participates in the electrochemical oxygen-reduction reaction



Institute of Advanced Studies, Novosibirsk 630090; nakve@itp.nsc.ru; gasenko@itp.nsc.ru. Translated from *Prikladnaya Mekhanika i Tekhnicheskaya Fizika*, Vol. 46, No. 5, pp. 27–37, September–October, 2005. Original article submitted November 29, 2004.

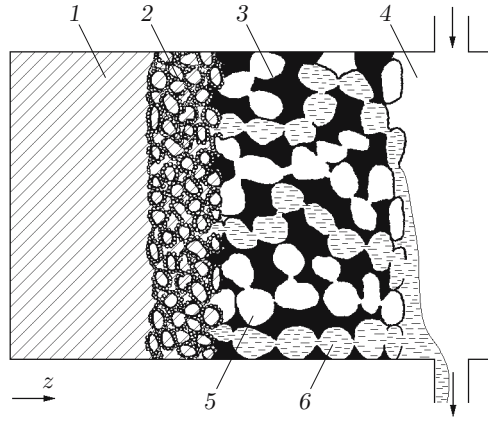


Fig. 1. Diagram of the solid electrolyte fuel cell cathode: 1) membrane material; 2) catalytic layer; 3) porous carbon skeleton of the cathode; 4) gas chamber with a gaseous mixture of O_2 , N_2 , and H_2O ; 5) hydrophobic pores of the cathode filled with a gaseous mixture of O_2 , N_2 , and H_2O ; 6) hydrophilic pores of the cathode filled with water.

The electrons necessary for the reduction reaction (1) pass over the solid electrode skeletons from the anode through the external circuit and load.

In reaction (1), the limiting factor is always the amount of oxygen because of its lower (by almost two orders of magnitude) concentration [1, 2]. The finiteness of the oxygen-reduction rate leads to the polarization of the reaction zone, which decreases the FC output voltage: $U_{\text{out}} < U_{\text{th}}^0$. The polarization and the voltage drop due to the finiteness of the ionic conductivity of the membrane determine the volt-ampere characteristic of the FC.

Thus, to construct a model for the solid electrolyte FC, it suffices to consider the cathode. Figure 1 shows a diagram of the FC cathode, which includes a membrane of thickness l_m , a catalytic layer of thickness l_c , a porous cathode of thickness l_g , and an air chamber. The state of the FC is characterized by three groups of variables: hydrodynamic variables [the pressure $p(z)$ and the water velocity $u(z)$], electric variables [the potential $\varphi(z)$ and the ionic-current density $j(z)$]; and the concentrations of the reactants of reaction (1) [protons $c_H(z)$ and oxygen c_{O_2}]. We consider the processes occurring in all indicated regions, confining ourselves to one-dimensional approximations and using the estimates of [1, 2].

The membrane is characterized by only pressure and potential variations. The current density $j(z) = j_0$ and the water velocity $u(z) = u_0$ are unchanged by virtue of the conservation laws. In addition to the constancy of the proton concentration $c_H(z) = c_H^{\text{ref}}$ [2], we assume that the oxygen concentration is zero and the membrane is impermeable to oxygen. The pressure and potential are found, respectively, from the Schlogl equation [4] and Ohm's law [5] for a charged liquid

$$u = -\frac{k_\varphi}{\mu} c_H F \frac{d\varphi}{dz} - \frac{k_p}{\mu} \frac{dp}{dz}; \quad (2)$$

$$k \frac{d\varphi}{dz} = -j_0 + F c_H u. \quad (3)$$

Equation (3) follows from the Nernst-Planck equation [6] for the proton flux N_H related to the FC current density $j_0 = N_H F$:

$$N_H = -\frac{F}{RT} D_H c_H \frac{d\varphi}{dz} - D_H \frac{dc_H}{dz} + c_H u$$

(the current diffusion component is omitted). Here k_φ and k_p are the electrokinetic and hydrodynamic permeabilities of the membrane, respectively, $k = F^2 D_H c_H / (RT)$ is the ionic conductivity of the membrane, F is the Faraday constant, φ is the electric potential, and μ is the viscosity of the liquid. The FC design is such that the electroosmotic and the hydrodynamic forces in the membrane are always opposite [2]; therefore, the direction of water motion is arbitrary.

Equations (2) and (3) are integrated subject to the boundary conditions at the membrane inlet $p(0) = p_0$ and $\varphi(0) = \varphi_0$, resulting in linear pressure and potential profiles:

$$p(z) = p_0 + \left[\frac{k_\varphi c_{\text{HF}} F}{k_p k} j_0 - \left(\frac{k_\varphi c_{\text{H}}^2 F^2}{k_p k} + \frac{\mu}{k_p} \right) u_0 \right] z; \quad \varphi(z) = \varphi_0 + \frac{F c_{\text{H}} u_0 - j_0}{k} z.$$

The catalytic layer begins at the point $z = l_m$ and ends at the point $z = l_m + l_c$. The oxygen-reduction reaction in the catalytic layer leads to variation in all variables [2]:

$$\frac{k_p^{\text{eff}}}{\mu} \frac{dp}{dz} = -\frac{k_\varphi^{\text{eff}}}{\mu} c_{\text{HF}} F \frac{d\varphi}{dz} - u; \quad (4)$$

$$k^{\text{eff}} \frac{d\varphi}{dz} = -j + F c_{\text{H}} u; \quad (5)$$

$$\rho \frac{du}{dz} = -\frac{2}{4F} \frac{dj}{dz}; \quad (6)$$

$$\frac{dN_{\text{O}_2}}{dz} = \frac{d}{dz} \left(-D_{\text{O}_2}^{\text{eff}} \frac{dc_{\text{O}_2}}{dz} + u c_{\text{O}_2} \right) = \frac{1}{4F} \frac{dj}{dz}; \quad (7)$$

$$\frac{dj}{dz} = -i_0^{\text{ref}} \frac{c_{\text{O}_2}}{c_{\text{O}_2}^{\text{ref}}} \left[\exp \left(\frac{\alpha_a F}{RT} \varphi \right) - \exp \left(-\frac{\alpha_c F}{RT} \varphi \right) \right]. \quad (8)$$

But because the initial proton concentration is 65 times higher than is required by the stoichiometry of reaction (1), the proton concentration in the catalytic layer is ignored. Here i_0^{ref} is the specific volume density of the exchange current, which determines the catalyst efficiency; $c_{\text{O}_2}^{\text{ref}}$ is the oxygen concentration constant, and α_a and α_c are the mass-transfer coefficients (Sherwood's criterion) of the anode and cathode, respectively. In the transfer equations (4)–(6), the effective properties of the membrane, denoted by the superscript “eff,” become distributed and are calculated taking into account the porosity of the catalytic layer $\varepsilon_{m,c}$. The Butler–Volmer kinetic equation (8) [6] describes transition from the ionic current j to an electronic current with a change in the former from the specified value j_0 at the entrance to the layer ($z = l_m$) to zero at the exit from the layer ($z = l_m + l_c$).

The oxygen diffusion equation (7) is written for convenience in divergent form and is integrated using the natural boundary conditions of membrane impermeability to oxygen $N_{\text{O}_2}(l_m) = 0$:

$$D_{\text{O}_2}^{\text{eff}} \frac{dc_{\text{O}_2}}{dz} - u c_{\text{O}_2} = \frac{j_0 - j}{4F}.$$

The continuity equation (6) is also integrated subject to the boundary conditions at the entrance to the catalytic layer $u(l_m) = u_0$, $j(l_m) = j_0$:

$$u = u_0 + (j_0 - j)/(2F\rho).$$

The permeabilities and conductivities of the catalytic layer and the membranes are of the same order of magnitude, and the thickness of the former is three orders of magnitude smaller [1, 2]; consequently, the relative changes in the pressure and potential are three orders of magnitude lower in the catalytic layer than in membrane. Therefore, Eqs. (4) and (5), which define pressure and potential variations, are ignored below, assuming that these quantities in the catalytic layer are constant.

Thus, the initial system (4)–(8) for the catalytic layer reduces to solving the boundary-value problem for the ionic current j and the oxygen concentration c_{O_2} with specified boundary values at the points $z_m = l_m$ and $z_c = l_m + l_c$:

$$\frac{dj}{dz} = -\frac{2i_0^{\text{ref}}}{c_{\text{O}_2}^{\text{ref}}} \sinh \left(\frac{\varphi_p}{\varphi_R} \right) c_{\text{O}_2}, \quad j(z_m) = j_0, \quad j(z_c) = 0; \quad (9)$$

$$D_{\text{O}_2}^{\text{eff}} \frac{dc_{\text{O}_2}}{dz} - \left(u_0 + \frac{j_0 - j}{2F\rho} \right) c_{\text{O}_2} = \frac{j_0 - j}{4F}, \quad c_{\text{O}_2}(z_c) = c_{\text{O}_2}^{\text{sat}}(j_0). \quad (10)$$

Here $\varphi_R = RT/F\alpha_a = 0.0152$ V is the threshold potential of the reaction, φ_p is the polarization potential of the electrochemical reaction, whose value is found by solving (9) and (10). The other two parameters ($c_{\text{O}_2}^{\text{sat}}$ and u_0) are found after the solution of the gas-diffusion problem at the porous cathode.

The gas-diffusion region of thickness l_g begins at the point $z = l_m + l_c$ and ends at the point $z = l_m + l_c + l_g$. The pressure and temperature in the nonwetttable pores of the cathode are considered constant. The pore gas is

humid air with the dimensionless relative molar concentrations of saturated water vapor x_w^{sat} , oxygen x_{O_2} , and nitrogen x_{N_2} linked by the relation

$$x_w^{\text{sat}} + x_{\text{O}_2} + x_{\text{N}_2} = 1.$$

In this case, the true molar concentration c_i (in mole/m³) is defined as $c_i = x_i p / (RT)$. The water vapor concentration remains constant in the entire region. The oxygen flux N_{O_2} is linked to the FC current by the relation

$$N_{\text{O}_2} = -j_0 / (4F).$$

Nitrogen does not participate in the reaction, and, hence, its flux is zero: $N_{\text{N}_2} = 0$. Water vapor diffusion is absent but there is a general nonzero gas-mixture flux at $u_g < 0$, which includes, in particular, water vapor. In this case, the water vapor flux ($N_w < 0$) should be taken into account in the balance with the liquid water flux in the wettable channels:

$$\rho \frac{du_L}{dz} = -\frac{dN_w}{dz}. \quad (11)$$

In this case, the effective velocity of liquid water u_L is defined by Darcy's law

$$u_L = -\frac{k_p^d}{\mu} \frac{dp}{dz}, \quad (12)$$

where k_p^d is the water permeability of the cathode. In the gas-diffusion region, it is necessary to find the main parameter — the oxygen concentration on the boundary with the catalytic layer. For this, it is necessary to solve the problem of diffusion in a three-component gas mixture. An exact but cumbersome solution of this problem using the model of [7] is given in [2]. In the present paper, a simpler method for solving the gas-diffusion problem is considered.

Let us write the Stefan flux for nitrogen:

$$-D_{\text{N}_2}^{\text{eff}} \frac{dx_{\text{N}_2}}{dz} + u_g x_{\text{N}_2} = 0. \quad (13)$$

Here $D_{\text{N}_2}^{\text{eff}}$ is the effective diffusivity of nitrogen in the mixture and u_g is the equivalent velocity of the gas mixture. Since the mixture contains more than 90% nitrogen and oxygen, we ignore the contribution to the diffusivity due to the presence of water vapor and assume that $D_{\text{N}_2}^{\text{eff}} = D_{\text{N}_2-\text{O}_2}^{\text{eff}}$. To estimate the velocity of the mixture, we write the Stefan flux for oxygen:

$$-D_{\text{O}_2}^{\text{eff}} \frac{dx_{\text{O}_2}}{dz} + u_g x_{\text{O}_2} = \frac{RT}{p} N_{\text{O}_2}. \quad (14)$$

Here $D_{\text{O}_2}^{\text{eff}}$ is the effective diffusivity of oxygen in the mixture, which for the same reasons as above, is defined as $D_{\text{O}_2}^{\text{eff}} = D_{\text{N}_2-\text{O}_2}^{\text{eff}}$. Since $x_{\text{O}_2} = 1 - x_{\text{N}_2} - x_w^{\text{sat}}$ and $\nabla x_{\text{O}_2} = -\nabla x_{\text{N}_2}$, Eq. (14) becomes

$$-D_{\text{N}_2}^{\text{eff}} \frac{dx_{\text{N}_2}}{dz} + u_g x_{\text{N}_2} = u_g (1 - x_w^{\text{sat}}) - \frac{RT}{p} N_{\text{O}_2}. \quad (15)$$

The velocity of the mixture is found from the identity condition of Eqs. (13) and (15):

$$u_g = \frac{RT}{p} \frac{N_{\text{O}_2}}{1 - x_w^{\text{sat}}}. \quad (16)$$

By virtue of (16), Eq. (14) is written in dimensionless form

$$\frac{dx_{\text{O}_2}}{d\xi} = Kv(1 - x_w^{\text{sat}} - x_{\text{O}_2}),$$

where $\xi = (z - l_m - l_c) / l_g$, and is easily integrated subject to the initial condition $x_{\text{O}_2}(1) = x_{\text{O}_2}^L$:

$$x_{\text{O}_2}(\xi) = 1 - x_w^{\text{sat}} - (1 - x_w^{\text{sat}} - x_{\text{O}_2}^L) \exp[Kv(1 - \xi)]. \quad (17)$$

Here the nondimensional oxygen flux v and the parameter K are defined similarly [2]:

$$v = -\frac{RT}{4Fp} \frac{j_0}{D_{w-\text{O}_2}^{\text{eff}}} l_g, \quad K = \frac{D_{w-\text{O}_2}^{\text{eff}}}{D_{\text{N}_2-\text{O}_2}^{\text{eff}}} \frac{1}{1 - x_w^{\text{sat}}}.$$

TABLE 1

Initial Parameters of Fuel Element

| Parameter | Notation | Values at 80°C |
|--|------------------------|---|
| Membrane thickness | l_m | $2.3 \cdot 10^{-4}$ m |
| Thickness of catalytic layer | l_c | 10^{-7} m |
| Thickness of gas-diffusion region | l_g | $2.6 \cdot 10^{-4}$ m |
| Molar composition of inlet gas | x_{N_2}/x_{O_2} | 0.79/0.21 |
| Membrane inlet pressure | p_0 | $3 \cdot 10^5$ N/m ² |
| Gas chamber pressure | p_L | $5 \cdot 10^5$ N/m ² |
| Proton diffusivity | D_H | $4.5 \cdot 10^{-9}$ m ² /sec |
| Ionic conductivity of membrane | k | 17 S |
| Corrected ionic conductivity of membrane | k | 7 S |
| Proton concentration | c_H^{ref} | $1.2 \cdot 10^3$ mole/m ³ |
| Oxygen diffusivity in membrane | D_{O_2} | $1.2 \cdot 10^{-10}$ m ² /sec |
| Electrokinetic permeability of membrane | k_φ | $1.13 \cdot 10^{-19}$ m ² |
| Hydraulic permeability of membrane | k_p | $1.58 \cdot 10^{-19}$ m ² |
| Pore water viscosity | μ | $3.365 \cdot 10^{-4}$ kg/(m · sec) |
| Pore water density | ρ | $5.4 \cdot 10^4$ mole/m ³ |
| Saturation water vapor pressure | p_w^{sat} | $0.467 \cdot 10^5$ N/m ² |
| Henry constant for oxygen | K_{O_2} | $2 \cdot 10^4$ J/mole |
| Porosity of catalytic layer | $\varepsilon_{m,c}$ | 0.5 |
| Coupled gas diffusivity | $D_{O_2-N_2}$ | $0.279 \cdot 10^{-4}$ m ² /sec |
| Coupled gas diffusivity | D_{w-N_2} | $0.387 \cdot 10^{-4}$ m ² /sec |
| Coupled gas diffusivity | D_{w-O_2} | $0.370 \cdot 10^{-4}$ m ² /sec |
| Water permeability of cathode | k_p^d | $3.03 \cdot 10^{-16}$ m ² |
| Current concentration | i_0 | 500 A/m ³ |
| Mass-transfer coefficient of cathode | α_c | 2 |
| Mass-transfer coefficient of anode | α_a | 2 |
| Oxygen concentration in membrane | $c_{O_2}^{\text{ref}}$ | 4.62 mole/m ³ |
| Faraday constant | F | 96 487 C/mole |
| Gas constant | R | 8.31 J/(mole · K) |
| Temperature | T | 353 K |
| Thermodynamic potential at no load | U_{th} | 1.197 V |

The dissolved oxygen concentration at the boundary of the catalytic layer $c_{O_2}^{\text{sat}}$ calculated from the expression for $x_{O_2}(0)$ using Henry's law with the constant K_{O_2} is found in explicit form:

$$c_{O_2}^{\text{sat}} = [1 - x_w^{\text{sat}} - (1 - x_w^{\text{sat}} - x_{O_2}^L) \exp(-Kv)]p_L/K_{O_2}. \quad (18)$$

To limiting oxygen flux v_{max} and the limiting current density j_{max} correspond to zero oxygen concentration in (18), whence, for the values of the FC parameters taken from [2] and given in Table 1, we obtain

$$v_{\text{max}} = \frac{1}{K} \ln \left(\frac{1 - x_w^{\text{sat}} - x_{O_2}^L}{1 - x_w^{\text{sat}}} \right) = -0.1116, \quad j_{\text{max}} = 75.1 \frac{\text{kA}}{\text{m}^2}. \quad (19)$$

The values (19) differ insignificantly from those calculated in [2] $v_{\text{max}} = -0.11$ and $j_{\text{max}} = 74$ kA/m², which proves the validity of the approach employed to solve the diffusion problem.

Using (16), the water vapor flux can be written as

$$N_w = \frac{p}{RT} u_g x_w^{\text{sat}} = \frac{x_w^{\text{sat}}}{1 - x_w^{\text{sat}}} N_{O_2},$$

whence, integrating Eq. (11), we obtain the constant water velocity

$$u_L = u(l_m + l_c) - \frac{N_w}{\rho} = u_0 + \frac{2 - x_w^{\text{sat}}}{1 - x_w^{\text{sat}}} \frac{j_0}{4\rho F}, \quad (20)$$

and then, from (12), the linear pressure profiles in the wettable pores:

$$p(z) = p_c - (\mu/k_p^d)u_L(z - l_m - l_c).$$

We now formulate the final system of equations for the FC using the obtained analytical solutions for the membrane and the gas-diffusion region. Using the continuity condition for the pressure, potential and water fluxes at the boundaries of the regions with the specified pressure difference $p_0 - p_L$ and current density j_0 , we find the water velocity in the membrane and the volt-ampere characteristic of the membrane, i.e., the quantity $\Delta U_m(j_0) = \varphi_0 - \varphi_m$:

$$u_0(j_0) = \frac{p_0 - p_L + \left(\frac{k_\varphi c_H F l_m}{k_p k} - \frac{2 - x_w^{\text{sat}}}{1 - x_w^{\text{sat}}} \frac{\mu l_g}{4 \rho F k_p^d} \right) j_0}{\left(\frac{k_\varphi c_H^2 F^2}{k_p k} + \frac{\mu}{k_p} \right) l_m + \frac{\mu}{k_p^d} l_g}, \quad (21)$$

$$\Delta U_m(j_0) = \frac{F c_H (p_L - p_0) + \mu \left[\frac{l_m}{k_p} + \frac{l_g}{k_{p,s}^d} \left(1 + \frac{2 - x_w^{\text{sat}}}{1 - x_w^{\text{sat}}} \frac{c_H}{4 \rho} \right) \right] j_0}{\frac{k_\varphi c_H^2 F^2}{k_p} + \mu \left(\frac{k}{k_p} + \frac{k}{k_p^d} \frac{l_g}{l_m} \right)} j_0. \quad (22)$$

To find the total volt-ampere characteristic of the FC $U_{\text{out}}(j_0) = U_{\text{th}} - \varphi_0$, it is necessary to solve system (9), (10) and to find the polarization potential of the catalytic layer φ_p . For this, we formulate the boundary-value problem (9), (10) in the dimensionless variables $J(\xi) = 1 - j(z)/j_0$, $C(\xi) = c_{\text{O}_2}(z)/c_{\text{O}_2}^{\text{sat}}$, and $\xi = (z - z_m)/l_c$:

$$\frac{dJ}{d\xi} = axC, \quad J(0) = 0, \quad J(1) = 1; \quad (23)$$

$$\frac{dC}{d\xi} = (b + sJ)C + dJ, \quad C(1) = 1. \quad (24)$$

Here the dimensionless coefficients are defined as

$$a = \frac{2l_c i_0^{\text{ref}} c_{\text{O}_2}^{\text{sat}}}{j_0 c_{\text{O}_2}^{\text{ref}}}, \quad x = \sinh \frac{\varphi_p}{\varphi_R}, \quad b = \frac{u_0 l_c}{D_{\text{O}_2}^{\text{eff}}}, \quad s = \frac{j_0 l_c}{2 \rho F D_{\text{O}_2}^{\text{eff}}}, \quad d = \frac{j_0 l_c}{4 F c_{\text{O}_2}^{\text{sat}} D_{\text{O}_2}^{\text{eff}}} \quad (25)$$

and all quantities except for x are known functions of the current density j_0 . System (23), (24) can be formulated as a Cauchy problem because both functions are defined at the point $\xi = 1$. In this case, the satisfaction of the second boundary condition at the point $\xi = 0$ should be provided by a choice of the coefficient x directly related to the polarization potential in accordance with (25). In the subsequent calculations of the liquid velocity (21), it will be shown that the relation of the coefficients in the convective term (24) $|s/b| \ll 1$ is satisfied for all values of the current density j_0 except for a narrow region $j_0 \approx 1.5 \text{ kA/m}^2$; therefore, for all practical calculations, the nonlinear boundary-value problem (23), (24) can be reduced to the linear problem

$$\frac{d^2 J}{d\xi^2} - b \frac{dJ}{d\xi} - adxJ = 0, \quad J(0) = 0, \quad J(1) = 1, \quad \frac{dJ(1)}{d\xi} = ax,$$

whose solution has the form

$$J(\xi) = \frac{\exp(\lambda_1 \xi) - \exp(\lambda_2 \xi)}{\exp \lambda_1 - \exp \lambda_2},$$

where $\lambda_{1,2} = b/2 \pm \sqrt{b^2/4 + adx}$ are always real roots of the characteristic equation $\lambda^2 - b\lambda - adx = 0$, which depend on the parameter x , whose value is found from the transcendental equation

$$\frac{\lambda_1 \exp \lambda_1 - \lambda_2 \exp \lambda_2}{\exp \lambda_1 - \exp \lambda_2} = ax.$$

In two limiting cases (high and low current densities), the solution of (23), (24) is found in explicit form. For the case of low current densities, where $b \gg d$, we obtain $x = 1/a$ and

$$j(\xi) = \xi, \quad C(\xi) = 1. \quad (26)$$

The polarization potential following from (26) is known as Tafel's law [6]

$$\varphi_p = \frac{RT}{\alpha_a F} \ln \frac{j_0}{i_0^{\text{ref}} l_c}.$$

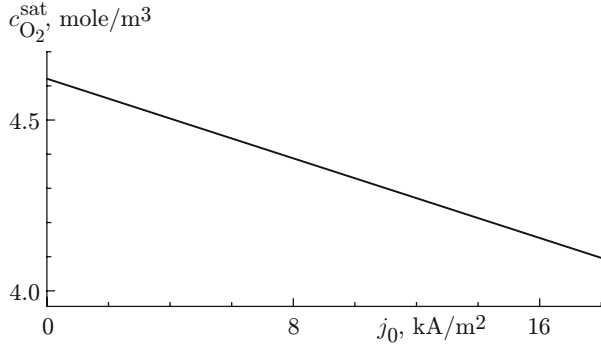


Fig. 2

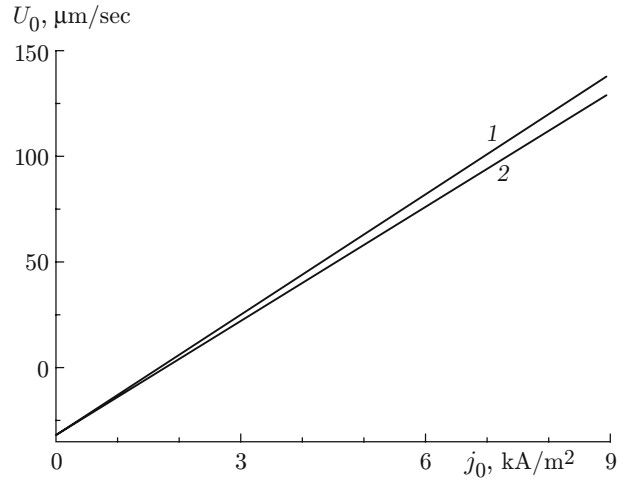


Fig. 3

Fig. 2. Concentration of oxygen dissolved in water at the boundary between the catalytic layer and the gas-diffusion region versus FC current density as a solution of the gas-diffusion problem.

Fig. 3. Water velocity in the membrane (curve 1) and in the gas-diffusion region (curve 2) versus current density.

For the case of high current densities ($d \gg b$), we obtain $x = d/a$ and

$$J(\xi) = C(\xi) = \cosh [d(1 - \xi)] - \sinh [d(1 - \xi)]. \quad (27)$$

The polarization potential

$$\varphi_p = \frac{RT}{\alpha_a F} \ln \left[\frac{c_{O_2}^{\text{ref}}}{4F i_0^{\text{ref}} D_{O_2}^{\text{eff}}} \left(\frac{j_0}{c_{O_2}^{\text{sat}}(j_0)} \right)^2 \right], \quad (28)$$

which follows from (27), can be treated as nonlinear Tafel's law in which the effective thickness of the reaction zone $l_c^{\text{eff}} \approx l_D = D_{O_2}^{\text{eff}} c_{O_2}^{\text{sat}} / (j_0 / 4F)$ is determined by the oxygen-diffusion length, which decreases with a rise in the current density j_0 . The solution (27) is suitable for practical calculations for $j_0 > 1.5 \text{ kA/m}^2$.

Calculation Results. The calculations were performed for the FC parameters taken from [2] and given in Table 1. Figure 2 gives a curve of the dissolved oxygen concentration at the catalytic-layer boundary versus current density obtained by analytical solution of the gas-diffusion problem (18). In the range of operating currents $j_0 \leq 20 \text{ kA/m}^2$, the change in the dissolved-oxygen concentration is not more than 20%, which is significant for the calculations of the volt-ampere characteristic of the FC.

Figure 3 gives curves of the water velocity in the membrane and in the gas-diffusion region calculated by formulas (21) and (20), respectively, versus the current density j_0 . One can see that these curves are linear. For low currents, the water velocity is negative. Zero velocity is reached in our case for the same current value $j_0 \approx 1.5 \text{ kA/m}^2$ as in [2].

The results of calculation of the volt-ampere characteristic of the membrane using formula (22) are given in Fig. 4. As in [2], the calculations were performed for a corrected value of the ionic conductivity of the membrane. A comparison of the voltage drop across the membrane at a current density $j_0 = 8.8 \text{ kA/m}^2$ (in our case, $\Delta U_m = 0.186 \text{ V}$) with the voltage drop $\Delta U_m = 0.19 \text{ V}$ given in [2] at the same current density shows the validity of model (22). We note that the final voltage drop across the membrane at zero current density [$\Delta U_m(0) \approx 10 \text{ mV}$] is due to neglect of proton diffusion in the membrane.

Figure 5 shows the relative current density profiles in the catalytic layer given by the relation $j(\xi)/j_0 = 1 - J(\xi)$ and calculated for current densities $j_0 = 0.1, 1.0, \text{ and } 8.0 \text{ kA/m}^2$ based on the solution of boundary-value problem (23), (24) (curves 1–3, respectively). Figure 6 gives their corresponding profiles of the relative oxygen concentration $c_{O_2}(\xi)/c_{O_2}^{\text{ref}}$ as solutions of the boundary-value problem (9), (10) calculated for the same current densities (curves 1–3). In the same figure, the oxygen concentration profiles $x_{O_2}(\xi)/x_{O_2}^L$ as normalized

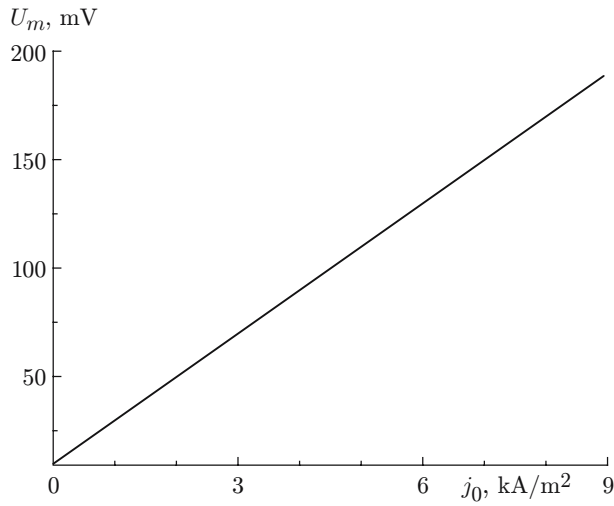


Fig. 4

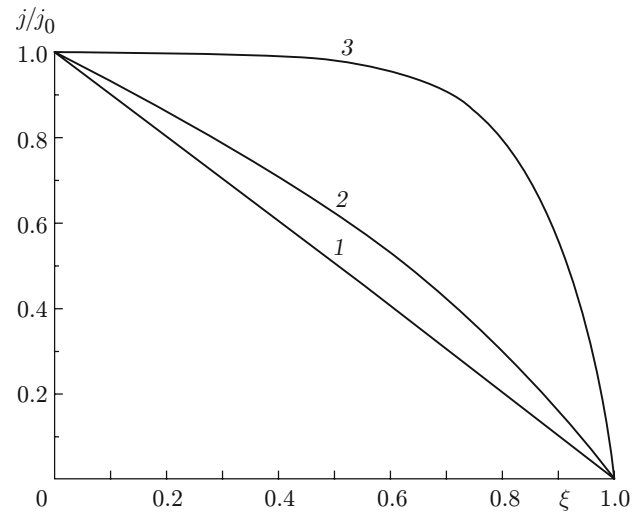


Fig. 5

Fig. 4. FC voltage drop versus current density.

Fig. 5. Dimensionless ionic-current density profiles $j/j_0 = 1 - J(\xi)$ in the catalytic layer for $j_0 = 0.1$ (1), 1.0 (2), and 8.0 kA/m² (3).

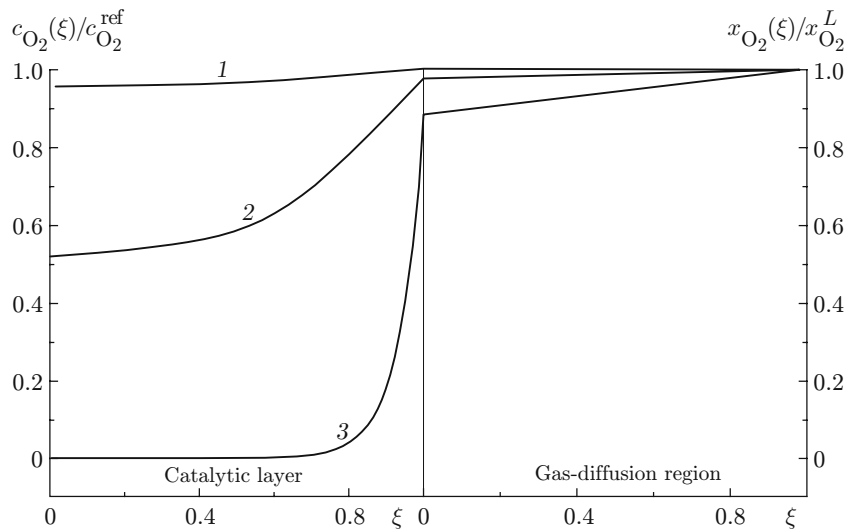


Fig. 6. Dimensionless oxygen concentration profiles in the catalytic layer and the gas-diffusion region for ionic current density $j_0 = 0.1$ (1), 1.0 (2), and 8.0 kA/m² (3).

solutions of (17) are continued to the gas-diffusion region. The chosen normalizations preserve the continuity of the oxygen concentration at the boundary between the regions and provide an insight into the extent to which the solution of the gas-diffusion problem (17) affects the solution in the catalytic region. It is easy to see that in the main FC operation modes at high current densities $j_0 \geq 5$ kA/m², all profiles are nonlinear and vary in a narrow layer adjacent to the boundary between the catalytic layer and the gas-diffusion region. For such current densities, the nonlinear Tafel's law approximation (28) is valid. In this case, the oxygen concentration and flux decrease to zero within the catalytic layer, and the employed approximation of membrane impermeability to oxygen is satisfied *a priori*). In the case of low current densities, the solutions $J(\xi)$ and $C(\xi)$ do not coincide. As follows from the plots in Figs. 5 and 6, the region of the linear Tafel's law approximation for the current density is considerably narrower $j_0 < 0.1$ kA/m².

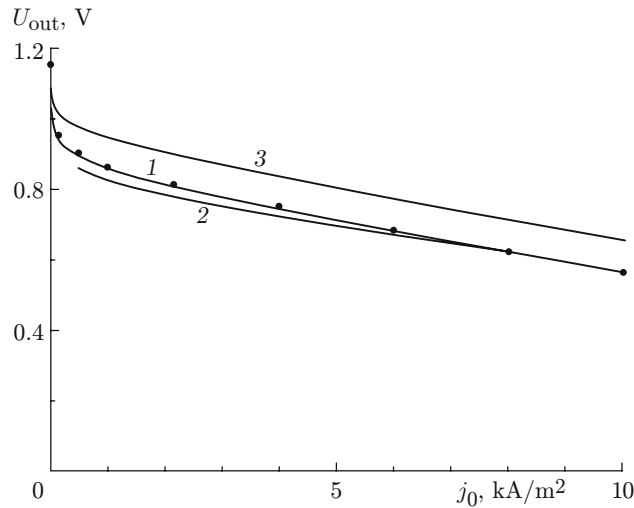


Fig. 7. Output volt–ampere characteristic of the FC at 80°C: curve 1 refers to numerical calculations of the nonlinear problem (9), (10) and curve 2 refers to calculations by formulas (22) and (28); the points are the experimental data of [4]; curve 3 is the volt–ampere characteristic of the FC at 20°C.

Figure 7 gives the total volt–ampere characteristic of the FC $U_{\text{out}}(j_0)$ calculated from the tabulation of solution (22) for the membrane and numerical solution of the complete system (23), (24) (curve 1). For comparison, the figure gives the volt–ampere characteristic of the analytical solution (22), (28) (curve 2) and the experimental data of [4] (points). In the calculations, as in [2], the value of the parameter i_0^{ref} was chosen to coincide with one experimental point for a current density $j_0 = 8.8 \text{ kA/m}^2$, and then it was not varied.

It is easy to see that the given numerical calculations, as well as the calculations of [2], are in good agreement with the experimental points. The agreement between the limiting analytical solution (28) and the experiment is worse but it can be improved by correcting the parameters k and i_0^{ref} .

Discussion of Results. The fuel cell efficiency depends primarily on the limiting current density at which the output voltage and, hence, the FC efficiency still remain adequate and are determined by the voltage loss in the membrane and in the catalytic layer due to polarization. The voltage loss in the membrane, as follows from formula (22) is determined by both the electric and hydrodynamic parameters of the membrane. Without considering the problem of improving the solid electrolyte performance, we analyze all factors related to the polarization value and its dependence on the FC performance.

According to the formulation of the problem (9), (10), the polarization value in the catalytic layer is determined by the electrochemical-reaction rate and, generally, by convective oxygen diffusion. If the exchange current density is treated as a parameter that depends exclusively on the type of catalyst and the method whereby it is added to the catalytic layer, the oxygen limit becomes the single factor that restricts the FC current density. The convective oxygen transfer is very low because $b = \text{ReSc} < 1$, where $\text{Re} = u_0 l_c / \nu$ is the Reynolds number and $\text{Sc} = \nu / D_{\text{O}_2}^{\text{eff}}$ is the Schmidt number; therefore, the degree of dependence of the polarization value on the parameters determining the oxygen diffusion is given by solution (28). The polarization value depends on temperature both directly and indirectly, via the dependences $D_{\text{O}_2}^{\text{eff}} \sim \exp(-2768/T)$ and $K_{\text{O}_2} \sim \exp(-666/T)$ [2]. As the temperature decreases to 20°C the oxygen diffusivity decreases by a factor of 5, and the boundary concentration of dissolved oxygen $c_{\text{O}_2}^{\text{sat}}$ increases by a factor of 1.47 because of a decrease in the Henry constant. These two factors have opposite effects on the polarization value but the cooperative effect is positive, i.e., the polarization value decreases with decrease in the temperature, and, hence, the FC output voltage increases. The calculated volt–ampere characteristic of the FC at 20°C is shown by curve 3 in Fig. 7. Here the increase in U_{th}^0 to 1.234 V with decrease in temperature is additionally taken into account [2] but the membrane characteristics are considered unchanged.

The second method of increasing the diffusive oxygen flux is to raise the dissolved-oxygen concentration $c_{\text{O}_2}^{\text{sat}}$ by increasing the air gas chamber pressure. This method is technically more complicated but it is more effective than the one of decreasing the temperature because the value of the diffusion coefficient is not decreased in this case.

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