ANALYSIS AND DESIGN OF THE INTERNAL MASS TRANSFER IN OXYGEN – HYDROGEN FUEL CELL WITH A CAPILLARY MEMBRANE AND WITH CONVECTIVE DRAINAGE OF VAPOROUS REACTION PRODUCTS

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The mechanism of mass transfer is analyzed by which water vapor drains convectively from an electrode–condenser system in a fuel cell with a capillary membrane. The problem of optimizing the mass-transfer parameters in the water drainage system is also analyzed.

A special feature of a fuel cell with a capillary membrane was mentioned in [1], namely the interrelation between its performance characteristics and the conditions of external mass transfer during the drainage of reaction products (water) by evaporation from the active electrode. Under steady equilibrium, the electrolyte concentration c on the evaporator electrode is determined by the water mass balance in the cell

$$I_e = \int_f \beta_e [p_e(c, t_e) - p] \, df \tag{1}$$

and it is a function of the electrical load (current) I as well as of the conditions of external mass transfer (mass-transfer coefficient at the electrode β_e, water vapor pressure p above the electrode, etc.), which may vary during the operation of the fuel cell over wide ranges depending on the mode and the parameters of mass-transfer (water drainage) system.

Concentration (and, therefore, volume) fluctuations of the electrolyte in the fuel cell cause a variation of the moisture content in porous active electrodes, which affects directly the volt–ampere characteristic, and their quite definite allowable range is limited by the drop in terminal voltage. The design of a fuel cell with a capillary membrane and capable of operating over a sufficiently wide range of load current requires very specific measures concerning the external mass transfer; optimization of the mass-transfer parameters, in turn, requires a special analysis of the moisture transport mechanisms in the electrode–condenser system, these mechanisms being tied in with the conditions under which porous electrodes operate.

The subject of this study is the transport of water vapor by forced convection, when the external mass-transfer system includes a source of water vapor (a battery of fuel cells), a water drain (vapor condenser), and an impeller for driving the vapor–gas mixture. For a convenient analysis of the mass-transfer parameters, we consider ideally thermostatized electrodes and condenser at fixed surface temperatures; we also consider the following features of the system:

1. The weight of electrolyte in the cell increases only on account of added water, and the weight concentration is a function of the referred moisture content in the electrodes $\psi = (v - v^0)/v^0$:

$$c = c^0 \left(1 + \psi \frac{\rho_w}{\rho^0}\right)^{-1}, \tag{2}$$

where the minimum voltage-limited volume of electrolyte in the fuel cell v^0 is usually close enough to the initial volume poured into the membrane space ($v^0 = v_M$). The range of allowable

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electrode concentrations corresponding to the range of moisture content levels $0 \leq \psi \leq \psi^*$ is

$$\Delta c^* = c^0 - c^* = c^0 \left(1 + \frac{1}{\psi^*} \frac{\rho^0}{\rho_w}\right)^{-1} \tag{3}$$

and will be called the concentration capacity of a cell.

2. The plateau-like shape of the $V(\psi)$ characteristic [1] suggests that, within the range of allowable moisture levels in a cell with an equipotential surface, the current density distribution i is also almost uniform regardless of the different moisture levels in various electrode segments: $i = \text{inv}(\psi) = \text{inv}(c)$ at $0 < \psi < \psi^*$ or $c^0 < c < c^*$.
3. The pressure of saturated water vapor above the surface of an alkali electrolyte (KOH) used in fuel cells is accurately enough a linear function of the weight concentration, within the practical range of the latter $(0.2 < c < 0.5)$,

$$p_e = \xi(t_e)(a_c - c), \tag{4}$$

where

$$\xi(t_e) = \left(\frac{\partial p}{\partial c}\right)_{t_e} = a_1 + a_2 \exp(a_3 t_e); \tag{5}$$

and a_c represents the node point of the $p_e(c)$ lines on the x-axis; a_1, a_2, and a_3 are constants.

4. Consideration of increasing the mass-transfer rate at a minimum loss of energy on convection of the vapor–gas mixture has made laminar flow $(\text{Re} < 100)$ through channels of small cross section $(\text{Re} \cdot \text{Pr}_D \delta l^{-1} < 10)$ a typical mode in fuel cells; moreover, conditions of hydrodynamic and mass-transfer stability prevail over most of the channel lengths and the mass-transfer coefficients remain constant throughout the flow path.
5. During dehydration of the electrode (usually the hydrogen electrode where water is generated and the diffusivities are higher than in the oxygen electrode), the process is characterized by an exchange of equal molar quantities of H_2 and H_2O; the molar flow rate of the mixture remains constant, unlike the weight flow rate of the mixture and its components, and it is appropriate to specify the water flow rate in molar fractions: $G_w = J\mu_w(p/P) = \bar{J}p$.

In order to analyze the electrode performance, it is necessary to consider the equations of steady-state water mass balance:

for the battery of cells

$$I_e n = \bar{J}(p_s - p_d), \tag{6}$$

for the vapor condenser

$$\bar{J}(p_s - p_d) = \int_{F_c} \beta_c [p(p_s, F) - p_c]\, dF, \tag{7}$$

with the electrolyte concentration in an electrode determined by the conditions of electrode dehydration (1) as a function of the following variables:

$$c = c(i, \beta_e, p, t_e). \tag{8}$$

We will consider the dehydration of the hydrogen electrode, assuming first that the electrolyte concentration is uniform across its surface. For a disk electrode with a center inlet and radial passages for the vapor–gas mixture, the transport of water vapor through the vent above the electrode (with negligible lengthwise diffusion) is described by the equation

$$\bar{J}_e \frac{d}{dx}[p(x)] - \beta_e [p_e - p(x)]\, 2\pi x = 0 \tag{9}$$

with the initial condition $p = p_d$ at $x = 0$ and with the coefficient $\beta_e = [1/\beta_{sur} + (\delta_e/D_p\varepsilon)\chi]^{-1}$ of mass transfer from the electrolyte surface to the mixture stream depending on the mass-transfer coefficient in the channel $\beta_{sur} = \text{Nu}_D D_p/2\delta$ and on the resistance of the porous electrolyte to diffusion. This resistance is usually much lower than $1/\beta_{sur}$, since, according to our present knowledge of these phenomena, the distribution of electrolyte across the thickness of a porous electrode does not depend on the moisture content near equilibrium and since $\chi \ll 1$; furthermore, the relative electrode thickness is also very small: $\delta_e/\delta < 1$.

An analysis of the solution to Eq. (9) shows that the dehydration rate

$$\frac{g_w(x)}{g_{w(0)}} = \frac{p_e - p}{p_e - p_d} = \exp\left[-\frac{\beta_e}{\bar{j}}\left(\frac{x}{r_e}\right)^2\right] \tag{10}$$

decreases sharply along the flow path and, under conditions usually prevailing in the mass-transfer system ($\beta_e/\bar{j} = 20\text{-}100$), the vapor pressures tend to equalize within the entrance segment of the electrode $(x/r_e)^2 < 10\%$, i.e., most of the electrode surface does not participate in the mass transfer. This result has a physical significance in the case of a cell where the electrolyte concentration at the surface is artificially maintained constant (by electrolyte circulation, for example). In our case the drop in the dehydration rate below the rate of water generation $i\varepsilon$ has the effect of diluting the electrolyte and increasing the pressure $p_e(c)$ until mass-transfer equilibrium has been restored. Obviously, a lengthwise concentration gradient appears at that time and function $c(x)$ will be a decreasing one along the flow path.

In the general case, the appearance of a longitudinal moisture and concentration gradient will give rise to secondary mass transfer processes along the electrode and the membrane. If we treat the electrode as a slightly hydrophobic structure partly filled with liquid in pores which are, on the whole, larger than the pores in the hydrophilic membrane, then the secondary mass-transfer processes can be viewed as follows.

a) The rate of electrolyte transfer through the electrode by capillary moisture conduction, due to the gradient of relative volume concentration, is $G_\varkappa = -\varkappa\rho F_e(x)(\partial\varphi/\partial x)$. Taking into account (2), we have the relation $\varphi = \psi(v_M/v_e) = (\delta_M \pi_M \rho^0/\delta_e \pi_e \rho_W)[(c^0/c) - 1]$ and from there

$$G_\varkappa = a\varkappa\rho c^{-2} x \frac{\partial c}{\partial x}, \tag{11}$$

where $a = 4\pi\delta_M\pi_M\rho^0 c^0(\pi_e\rho_W)^{-1}$ is constant for a given system.

Inasmuch as the water component of the stream $G_{\varkappa(w)} = (1-c)G_\varkappa$ evaporates along the flow path in the electrode, the mass transfer by capillary moisture conduction should carry the electrolyte KOH from more moist to less moist regions of the electrode.

b) The diffusive mass transfer occurs essentially through the capillary membrane filled continuously with liquid. The diffusion flow of KOH through the membrane will oppose the capillary flow of $G_\varkappa$ through the electrode:

$$G_{D(\mathrm{KOH})} = -\bar{D}_e F_M(x)\,\mu_{\mathrm{KOH}}\frac{\partial N_{\mathrm{KOH}}}{\partial x} = -\bar{D}_e F_M(x)\frac{\partial}{\partial x}(c\rho), \tag{12}$$

while the diffusion flow of water will be in the same direction as $G_\varkappa$:

$$G_{D(w)} = -\bar{D}_e F_M(x)\,\mu_w\frac{\partial N_w}{\partial x} = -\bar{D}_e F_M(x)\frac{\partial}{\partial x}[(1-c)\rho], \tag{13}$$

where $F_M(x) = 2\pi\delta_M x$; $\bar{D}_e = D_e\varepsilon$.

c) Considering that the net steady-state flow of KOH is equal to zero, there must occur a convective flow of electrolyte which compensates for the difference between the opposing capillary and diffusive KOH flows:

$$G_U = 2\pi x\delta_M\rho U. \tag{14}$$

The equations of mass balance within an elementary segment dx (x is the radial coordinate) will be written as:

for water in the electrode and in the membrane

$$\left\{\frac{\partial}{\partial x}[(1-c)G_\varkappa] + \frac{\partial G_{D(w)}}{\partial x} + \frac{\partial}{\partial x}[(1-c)G_U]\right\}dx - 2\pi x i\,\mathrm{e}\,dx + \beta_e[p_e(x) - p(x)]\,2\pi x dx = 0, \tag{15}$$

for water in the vapor–gas stream above the electrode

$$\bar{J}_e \frac{\partial p}{\partial x} dx - \beta_e [p_e(x) - p(x)] \, 2\pi x dx = 0, \tag{16}$$

and for KOH in the membrane and in the electrode

$$cG_{\varkappa} + G_{D(\mathrm{KOH})} + cG_U = 0. \tag{17}$$

This system of equations includes also Eq. (4) $p_e = p(c)$ with the boundary conditions $p = p_d$ at $x = 0$ and $p = p_s$ at $x = r_e$.

Having determined the convective flow rate of electrolyte $G_U = -(G_{\varkappa} + G_{D(\mathrm{KOH})}/c)$ from (17) and inserted this quantity into (15), we obtain with the aid of (12), (13), and (4):

$$\delta_M \frac{\partial}{\partial x} \left[\frac{x\rho \bar{D}_e}{c} \frac{\partial c(x)}{\partial x} \right] - \beta_e \xi x c(x) - \beta_e x p(x) + (\beta_e \xi a_c - i_e) x = 0. \tag{18}$$

An evaluation of the relative significance of diffusion in the electrolyte, which is really a comparative order-of-magnitude estimate of the terms with c and $\partial^2 c/\partial x^2$ in Eq. (18), shows that in our case of a monotonic change in concentration (of the order of magnitude $\Delta c/\Delta x^2 \sim 10^0/0.1^2 = 100/\mathrm{m}^2$) the effect of diffusion on the shape of the concentration field is negligible because of the small relative membrane thickness $\delta_M/r_e \ll 1$ and the low coefficient of water diffusion in the electrolyte $\bar{D}_e \sim 10^{-6}$ m²/h (of the order of

$$\frac{\delta_M \rho \bar{D}_e}{c} \frac{\Delta c}{\Delta x^2} \sim \frac{10^{-3}\,\mathrm{m} \cdot 10^3 \frac{\mathrm{kg}}{\mathrm{m}^3} \cdot 10^{-6} \frac{\mathrm{m}^2}{\mathrm{h}}}{10^{-1}} \, 10^2 \frac{1}{\mathrm{m}^2} = 10^{-3} \frac{\mathrm{kg}}{\mathrm{m}^2 \cdot \mathrm{h}},$$

and the order of magnitude

$$\beta_e = \frac{\mathrm{Nu}_D D_p}{2\delta} = \frac{10 \cdot 10^{-6}\,\mathrm{h}}{10^{-3}\,\mathrm{m}} = 10^{-3} \frac{\mathrm{kg}}{\mathrm{h} \cdot \mathrm{N}};$$

$$\beta_e \xi c \sim 10^{-3} \frac{\mathrm{kg}}{\mathrm{h} \cdot \mathrm{N}} \cdot 10^5 \mathrm{N/m}^2 \cdot 10^{-1} = 10^1 \mathrm{kg/m}^2 \cdot \mathrm{h}).$$

With all this taken into account, the solution of Eqs. (16), (18) yields a parabolic distribution of vapor pressure above the electrode

$$p = p_d + \frac{i_e}{\bar{j}} \bar{x}^2 \left(\text{for } \bar{x} = 1, \; p = p_s = p_d + \frac{i_e}{\bar{j}} \right), \tag{19a}$$

distribution of vapor pressure above the electrolyte surface

$$p_e = p_d + \frac{i_e}{\beta_e} + \frac{i_e}{\bar{j}} \bar{x}^2, \tag{19b}$$

and distribution of electrolyte concentration along the flow path

$$c = a_c - \frac{1}{\xi(t_e)} \left(p_d + \frac{i_e}{\beta_e} + \frac{i_e}{\bar{j}} \bar{x}^2 \right). \tag{19c}$$

The difference between concentrations at the inlet and at the outlet ($x = 0$ and $x = 1$, respectively) is

$$\Delta c = c_d - c_s = \frac{i_e}{\bar{j} \xi(t_e)}. \tag{20}$$

From here one can draw the preliminary conclusion that during convective dehydration of an electrode in a stream of vapor–gas mixture there appears a gradient of electrolyte concentration and of moisture content at the cell surface whose magnitude is proportional to the ratio of load current to vapor–gas flow rate and which decreases with rising cell temperature.

The unknown quantity p_d in Eqs. (19) is determined by the efficiency of vapor–gas dehydration in the condenser η and by the vapor pressure above the condensation surface, according to the relation

$$p_s - p_d = \eta (p_s - p_c). \tag{21}$$

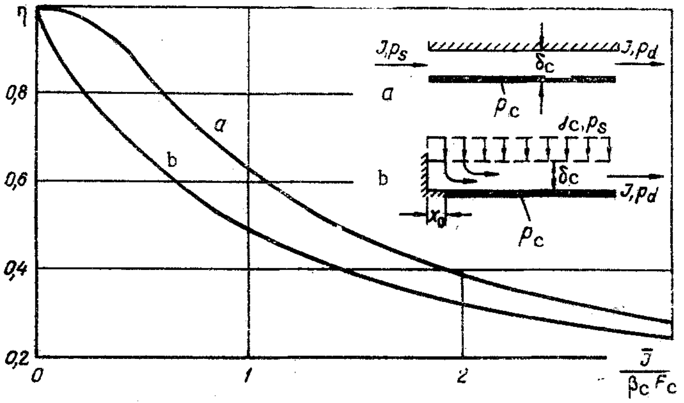

Fig. 1. Dehydration efficiency as a function of the ratio of vapor–gas flow rate to condenser power: longitudinal flow over the surface (a), flow with transverse injection (b).

The dehydration efficiency η depends on the condenser design and its parameters. For conventional condensers with a longitudinal flow through the channel above the cold surface (Fig. 1a), when the vapor pressure in the stream is nearly equipotential, the dehydration efficiency is defined as the ratio of condenser power $\beta_c F_c$ to vapor–gas flow rate $\bar{J} = \bar{j} F_e$:

$$\eta_{\mathrm{ref}} = \frac{p_s - p_d}{p_s - p_c} = 1 - \exp\left(-\frac{\beta_c F_c}{\bar{j} F_c}\right), \tag{22}$$

with β_c denoting the mean-over-the-surface F_c mass-transfer coefficient.

A condensation mode is feasible where the vapor–gas stream leaving the battery of cells flows directly and normally on a condenser surface and then longitudinally in a channel with transverse injection (Fig. 1b). The hydrodynamics of this scheme is unconventional and the dehydration efficiency here must be estimated as in a special case.

Considering the transverse injection to be uniform over the length l_c of the condenser channel ($j_c = J/l_c$) and disregarding the discreteness of injection, we can write the equations of mass balance for an element dx of the channel of width h:

with respect to water

$$\frac{1}{P}\frac{\partial}{\partial x}\left[J(x)\,p\right]dx + \frac{\beta_c}{\mu_w}\left[p(x) - p_c\right]h\,dx - j_c\frac{p_s}{P}dx = 0, \tag{23a}$$

with respect to the gas

$$\frac{1}{P}\frac{\partial}{\partial x}\left[J(x)(P - p)\right] - j_c\frac{P - p}{P} = 0 \tag{23b}$$

with the boundary conditions $p = p_s$ at $x = x_0$ and $p = p_d$ at $x = l_c$, where x_0 denotes some small initial adiabatic surface segment.

From (23b) we determine the flow rate at a given section $J(x) = j_c x[(P-p_s)/(P-p)]$, where the factor $(P-p_s)/(P-p)$, which represents the decrease in the vapor–gas volume flow rate due to condensation, is almost equal to unity when $p/P \ll 1$ and where the vapor–gas flow rate is a linear function of x. In order to solve Eq. (23a), one must know the function $\beta_c(x)$.

If one assumes that a boundary layer exists, then this case approaches a converging type flow [2] with a linearly increasing velocity of the outer stream $U = kx^m$ ($m = 1$), with a constant thickness of the hydrodynamic boundary layer $\delta_{bl} = 2.4(\nu/k)^{1/2}$, with the local Nusselt number Nu_x proportional to x ($Nu_x = \alpha x/\lambda = a(\Pr, m)(k/\nu)^{1/2}x$), and with both heat- and mass-transfer coefficients remaining constant along the stream: $\alpha = \lambda a(\Pr, 1)(k/\nu)^{1/2} = \mathrm{inv}(x)$ ($a(\Pr, 1)$, $k = j_c/\delta_c h$ constants). When the Reynolds number is low and the boundary layer of nominal thickness covers the entire channel height, then conditions of hydrodynamic and mass-transfer stability prevail in the stream, with the mass-transfer coefficients becoming constant: $\alpha = \mathrm{inv}(x)$ and $\beta_c = \mathrm{inv}(x)$.

An analysis of the solution to Eq. (23a) for this case

$$\frac{p_s - p(x)}{p_s - p_c} = \left(1 + \frac{\bar{J}}{\beta_c F_c}\right)^{-1} \left[1 - \left(\frac{x_0}{x}\right)^{1 + \frac{\beta_c F_c}{\bar{J}}}\right] \tag{24}$$

reveals a particular feature of this condensation mode, namely a rapid drop of vapor pressure p(x) along short initial segments, to an almost constant value along the rest of the channel. During contraction of this nominally adiabatic segment $(\bar{x} \rightarrow 0)$, the vapor pressure remains constant over the entire channel length. The dehydration efficiency is calculated from Eq. (24) at $x = l_c$ and from $p(x) = p_d$:

$$\eta_{\text{pop}} = \frac{p_s - p_d}{p_s - p_c} = \left(1 + \frac{\bar{J}}{\beta_c F_c}\right)^{-1}. \tag{25}$$

It is interesting to note that, with equal values of $J/\beta_c F_c$, the dehydration efficiency in the condenser with conventional lengthwise flow is somewhat higher (Fig. 1b). The essential conclusion from (22) and (25) is that the dehydration efficiency does not depend on the condenser load: $\eta = \text{inv}(i)$.

Closing the system of water balance equations for the battery of cells (6) and the condenser (7), we obtain the vapor pressure in the stream after condensation

$$p_d = p_c + \frac{i\,e}{\bar{j}_e}\left(\frac{1}{\eta} - 1\right) \tag{26}$$

and from (19b) the electrolyte concentration distribution over the cell surface

$$c = a_c - \frac{1}{\xi(t_e)}\left[p_c + \frac{i\,e}{\beta_e} + \frac{i\,e}{\bar{j}_e}\left(\frac{1}{\eta_c} + \bar{x}^2 - 1\right)\right], \tag{27}$$

shown graphically in Fig. 2a. At a zero electrical load (current) the electrolyte concentration is constant over the entire cell surface, determined by both the electrode and the condenser temperatures only:

$$c_0 = a_c - \frac{p_c}{\xi(t_e)}. \tag{28}$$

As the load current is increased, the electrolyte begins to dilute nonuniformly over the surface: the concentration is maximum c_d where the vapor-gas mixture enters the cell $(\bar{x} = 0)$ and minimum c_s, where the vapor-gas mixture leaves the cell $(\bar{x} = 1)$. In (c, i) coordinates the concentration-current curves $c_s(i)$ and $c_d(i)$ are straight lines originating at the point c_0 $(dc/di < 0)$; the differences Δc characterize the concentration field of the electrode surface (Fig. 2b).

If we mark on the c-axis the extreme allowable values of concentration c^0 and c^*, then obviously the factor which limits the maximum allowable current i^* will appear to be the overflooding of the electrode regions at the exit of the vapor-gas mixture from the cell, i.e.,

$$c_s = c_0 - \frac{i^* e}{\xi(t_e)}\left[\frac{1}{\beta_e} + \frac{1}{\bar{j}\eta}\right] = c^*. \tag{29}$$

It is also evident that the maximum allowable current i^* will be attained in a cell with a given concentration capacity Δc^*, if the minimum allowable concentration c^0 (usually close to the initial electrolyte charge installed in the membrane) is made equal to the zero-current concentration

$$c^0 = c_0(t_e, t_c). \tag{30}$$

With such a setup, the design temperatures t_e, t_c and the initial (installed) electrolyte concentration are interdependent according to relation (28). An incorrect choice of temperatures may result either in a lower maximum current $(c_0(t_e, t_c) < c^0)$ because of some loss of concentration capacity, or in an impermissible overdrying of the cell $(c_0(t_e, t_c) > c^0)$.

The maximum current limit is determined by the parameters of the mass-transfer system and by the concentration capacity $\Delta c^* = c^0 - c^*$, with (29), (30), (2), and (5) taken into consideration:

$$i^* = \frac{di}{dc_s}\Delta c^* = (a_1 + a_2 \exp a_3 t_e)\frac{\bar{j}\eta}{E} c^0 \left(1 + \frac{1}{\psi^*}\frac{\rho^0}{\rho_w}\right)^{-1}, \tag{31}$$

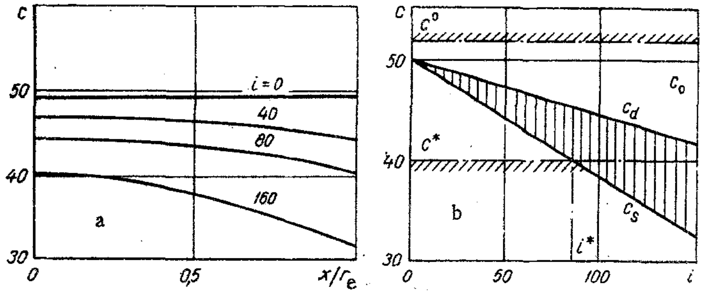

Fig. 2. Variation in the equilibrium concentration of electrolyte at the surface of the mass emitting electrode: a) surface distribution with increasing current; b) total concentration drop as a function of the current density (conditions: $t_e = 85°C$, $t_c = +55°C$, $\bar{j} = 0.005$ kg/h·N, $\eta = 0.5$) i (mA/cm²).

where $\eta = \eta(\bar{j}F_e/\beta_c F_c)$, $c^0 = c_0 = c(t_e, t_c)$, and $\rho^0 = \rho(c_0)$ (for simplicity, the quantity $1/\beta_e \ll 1/\bar{j}$ has been omitted here).

An analysis of expression (31) shows that the temperature level of the fuel cell t_e, the vapor–gas flow rate $\bar{j}$ through the system, and the dehydration efficiency η determine the slope of the characteristic $(c_s)'_i$ and directly affect the current limit i*.

The concentration capacity Δc^* of a cell is a function of the referred moisture content ψ^* in the electrodes and it increases appreciably with higher initial electrolyte concentration c^0, thus ensuring a proportional increase of the current limit (Fig. 3a).

The current limit is a progressive function of the cell temperature: $(i^*)''_{t_e} \sim \exp(a_3 t_e) > 0$; as temperature t_e rises, the slope of the $c_s(i)$ characteristic decreases and the curve shifts toward higher concentrations. The condensation temperature does not appear in the expression for $(c_s)'_i$ and a variation in this temperature (with condition (30) maintained) will cause the c(i) curve to shift parallel only, affecting the current limit indirectly only: through a change in the initial concentration $c^0(t_e, t_c)$ and in the concentration capacity $\Delta c^*(c^0)$.

In Fig. 3b is shown the current limit as a function of the temperature drop from electrode to condenser $\Delta t_{ec} = t_e - t_c$, for possible variations in temperature t_e or t_c while the initial concentration $c^0(t_e, t_c)$ passes through the range from 0.28 to 0.52 – practically acceptable in terms of optimum electrolyte conductivity. It is evident here that a relative increase in the temperature drop $\Delta t_{ec}/\Delta t_{ec(0)}$ by a factor of 3.5 ($\Delta t_{ec(0)} = 10°C$) due to the rise in the cell temperature raises the current limit by a factor of ~4.0, while a similar increase in Δt_{ec} due to a drop in the condensation temperature will raise the current limit only by a factor of ~1.5.

Considering that the upper temperature limit for a cell is defined by the boiling point of water under a given vapor–gas pressure $t_{e,\max} < t_{sat}(P)$ and that the initial concentration is determined by the condition of optimum electrical conductivity $0.3 < c^0 < 0.45$, the choice of parameter values becomes rather specific; the condensation temperature $t_c = t(t_e, c^0)$ follows from conditions (28) and (30).

The current limit i* is an asymptotic function of the vapor–gas flow rate (Fig. 3c), because the dehydration efficiency decreases with increasing $\bar{j}F_e/\beta_c F_c$; thus, $(i^*)''_j \sim -(c_1 + c_2/\bar{j}^3) < 0$. With a sufficiently small relative value of the first derivative $\varepsilon = (i^*)'_{j=j_{\max}}/(i^*)'_{j=j_0}$ (j_0 denoting the initial flow rate of the mixture at which $\eta \to 1$), we find that increasing the vapor–gas flow rate is worthwhile only up to a certain level limited by the condenser power:

$$\bar{J}_{\max} = \bar{j}_{\max} F_e \to \beta_c F_c \left(\frac{1}{\varepsilon^2} - 1 \right). \tag{32}$$

Let us consider the feasibility of improving the c(i) characteristics by regulating the mass-transfer parameters. One easy method is regulating the vapor–gas flow rate, which is proportional to the electrical load (current) of the cell $\bar{j} = Ki$ (where K = inv (i) is the multiplicity of circulation). It follows from

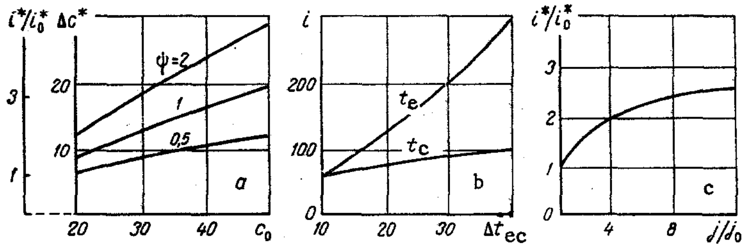

Fig. 3. Maximum allowable current i* as a function of the fuel cell parameters and of the mass-transfer parameters: a) as a function of the initial electrolyte concentration and of the moisture content in the electrodes (current i* corresponds to $c^0 = 20\%$); b) as a function of the temperature drop from cell to condenser, at a varying cell temperature t_e (t_e = var) and condensation temperature (t_c = var) (conditions: $\bar{j} = 0.005$ kg/h·N, $\eta = 1.0$, $\psi^* = 0.6$, $\Delta t_{ec(0)} = 10°C$); c) as a function of the flow rate (current i_0^* corresponds to the flow rate $\bar{j}_0$ for which $\bar{j}_0 F_e/\beta_c F_c = 0.5$). Concentration c (%), temperature t (°C).

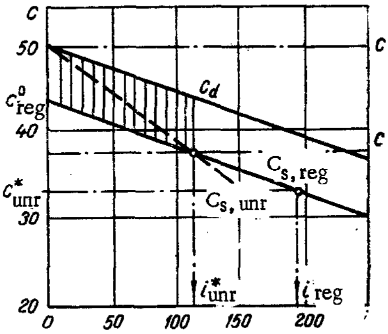

Fig. 4. Current–concentration characteristics, with the vapor–gas flow rate regulated ($c_d - c_{s(reg)}$) and unregulated ($c_d - c_{s(unr)}$): $i^*_{reg} - i^*_{unr}$ is the increase in the current limit at an equalized concentration in the electrode. Current (density) i, mA/cm^2.

an analysis of expressions (20) and (27) that in this case the concentration drop across the electrode surface remains constant $\Delta c = c_d - c_s = e/\xi(t_e)K$ at a value determined only by the electrode temperature and the multiplicity of circulation, while the upper and the lower branches of the $c_d(i)$ and the $c_s(i)$ characteristics become parallel straight lines with the slopes $(c_d)'_i = (c_s)'_i = e\xi(t_e)^{-1} \cdot \{\beta_e^{-1} + K^{-1}[\eta(i)^{-1}]'_i\}$. For a condenser with transverse injection (Eq. (25)), where $[\eta(i)^{-1}]'_i = KF_e(\beta_c F_c)^{-1} = \mathrm{inv}(i)$, the slope remains constant, the upper branch of the $c_d(i)$ characteristic is completely analogous to that corresponding to an unregulated flow rate $c_d = a_c - \xi(t_e)^{-1}\{p_c + ie[\beta_e^{-1} + F_e(\beta_c F_c)^{-1}]\}$, and the lower branch of the $c_s(i)$ characteristic is a straight line $c_s = c_d + \Delta c$ parallel to the $c_d(i)$ characteristic. By comparing the c(i) characteristics obtained with an unregulated flow rate J_{unr} (Fig. 4) and those obtained with proportional regulation for the same flow rate at some maximum load $Ki''_{unr} = J_{unr}$, one can ascertain that regulation of the flow rate alone does not ensure an improvement of the cell performance. In order to reduce the longitudinal concentration gradient and to raise the current limit, it is necessary to increase the absolute flow rate, just as in the case of $J_{unr} = \mathrm{inv}(i)$.

Let us consider the feasibility of improving the conditions for electrode dehydration by means of transverse injection into the channel above the electrode, with a distributed vapor–gas stream flowing at a rate which increases along the radius as follows: $J(x) = J_e(x/r_e)^n$. In this case the simultaneous solution to the water balance equations for the electrode and for an element dx of the channel above the electrode:

$$\frac{\partial}{\partial \bar{x}}\left[\bar{J}(\bar{x})\,\bar{x}^n\,p(\bar{x})\right]d\bar{x} - \bar{J}_e n\bar{x}^{(n-1)}\,p_d\,d\bar{x} - \beta_e\left[p_e(\bar{x}) - p(\bar{x})\right]2\pi\bar{x}r_e^2\,d\bar{x} = 0, \tag{33a}$$

$$ie - \beta_e\left[p_e(\bar{x}) - p(\bar{x})\right] = 0 \tag{33b}$$

with the initial condition $p = p_d$ at $x = 0$ yields for the vapor pressure in the stream $p = p_d + iej^{-1}\bar{x}^{(2-n)}$. When the exponent $n = 2$, then the vapor pressure is p and, consequently, the electrolyte concentration will remain constant along the flow path, equal to p_s and c_s, respectively, at the exit of the vapor–gas mixture from the cell with concentrated injection (Eqs. (19a) and (29)). (It is evident here that equalization will generally occur when the exponent in the power functions J(x) (flow rate) and f(x) (electrode surface) is the same, for a rectangular electrode n = 1.) The concentration field $\Delta c(i)$ shrinks to a $c_s(i)$ line, i.e., the concentration equalizes as a result of an appreciable electrolyte dilution within the initial electrode segments and, in the case of a constant vapor–gas flow rate, the current limit will not rise ($c_{s,\,unr}$ in Fig. 4).

When the vapor–gas flow rate is regulated at the same time, however, with the $\Delta c(i)$ field shrinking to a $c_{s,\,reg}(i)$ line not as steep as the $c_{s,\,unr}(i)$ line, then the current limit will become (Fig. 4)

$$i^*_{reg} = \xi(t_e)\,\frac{\beta_c F_c}{e F_e}\,\Delta c^*_{reg}, \tag{34}$$

where

$$\Delta c^*_{reg} = c^0_{reg} - c^*_{reg}; \quad c^0_{reg} = a_c - \xi(t_e)^{-1}(p_c - eK^{-1});$$
$$c^*_{reg} = c^0_{reg}\left(1 + \psi^*\,\frac{\rho_w}{\rho^0}\right)^{-1}.$$

By comparing the current limit for an unregulated vapor–gas flow rate $\bar{j}_{unr} = Ki^*_{unr}$ according to (31)

$$i^*_{unr} = \xi(t_e)\,\frac{\beta_c F_c}{e F_e}\,\Delta c^* - \frac{\beta_c F_c}{K F_e},$$

one can ascertain that regulating the flow rate during the concentration equalization will ensure a rise of the current limit approximately proportional ($\Delta c^*_{unr} \cong \Delta c^*_{reg}$) to the ratio of condenser power to multiplicity of circulation.

In an actual thermostatized fuel cell, where the electrode temperature may rise with increasing current, the equilibrium concentration of electrolyte will appreciably exceed the concentration levels at $t_e = \mathrm{inv}\,(i)$ considered in the foregoing analysis. Significant may also be the transverse (electrochemical) gradient of electrolyte concentration in the capillary membrane which is due to the transfer of 50% of the water generated at the hydrogen electrode from that electrode to the oxygen electrode and, at given allowable mean (over the cell thickness) electrolyte concentrations, resulting in a shift of the respective boundary conditions toward lower concentrations $c^0_H = c^0 - B(c^0,\, t_e)i$ and $c^*_H = c^* - B(c^*,\, t_e)i$ as the current increases. These effects, while raising the current limit i^* by a definite amount due to overflooding, can also limit the attainable current due to overdrying ($c > c^0$) and they have to be analyzed separately.

NOTATION

I, i	are the current and current density in the fuel cell;
V	is the voltage;
n	is the number of cells in a battery;
e	is the electrochemical equivalent of the reaction, in terms of water;
f	is the area of electrode surface;
$F_e = nf_e$;	
c, N	are the weight and molar concentration of electrolyte;
v	is the volume content of electrolyte per unit electrode surface;
$\psi = [(v/v^0) - 1]$	is the referred moisture content in the electrodes;
φ	is the relative moisture content in the electrodes;
p	is the partial pressure of water vapor;
P	is the total pressure of vapor–gas mixture;
t	is the temperature;
ρ	is the density;
μ	is the molecular weight;
D	is the diffusion coefficient;
ε	is the diffusion damping in a porous medium;
$D_p = D/RT$	is the referred coefficient of diffusion in the vapor–gas mixture;
α	is the heat-transfer coefficient;
β	is the mass-transfer coefficient;
$\varkappa$	is the capillary moisture conductivity;
Nu	is the Nusselt number of heat transfer;
Nu_D	is the diffusion analog of the Nusselt number;

Re	is the Reynolds number;
Pr	is the Prandtl number;
J, J_e	are the molar flow rate of vapor–gas mixture in the circuit and in one cell;
$\bar{J} = J\mu_w/P$	is the referred flow rate;
$\bar{j} = \bar{J}/F_e$;	
G, g	are the mass flow rate and mass flow intensity;
η	is the dehydration efficiency;
l, δ	are the longitudinal and transverse channel dimensions;
$\bar{x} = x/r_e$	is the dimensionless radial coordinate;
r_e	is the radius of disk electrode;
π	is the relative porosity of structure;
χ	is the mean-effective penetration of electrolyte into electrode pores.

Subscripts

e	denotes the electrode (electrolyte in the electrode);
M	denotes the membrane;
c	denotes the condenser;
w	denotes the water;
H	denotes the hydrogen;
s	denotes the entrance of vapor–gas mixture to condenser;
d	denotes the exit of vapor–gas mixture from condenser;
reg	denotes the regulated flow rate;
unr	denotes the unregulated flow rate.

Superscripts

0	denotes the overdrying-limited maximum values;
*	denotes the overflooding-limited maximum values.

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