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Mass exchange in a hydrogen–oxygen fuel cell with a capillary membrane

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The concentration and potential gradients across an electrolyte-containing membrane of the hydrogen-oxygen fuel cell have been calculated taking into account the following processes: diffusion of all solution components, ion migration in the electric field, permeation flux of the solution, external water vapour flows, water vapour transport in gas bubbles. A theory of the self-regulation of water removal has been developed, which takes account of the mass exchange conditions in the membrane and in the whole fuel cell, as well as the concepts of the buffer capacity of a fuel cell with a capillary membrane. The self-regulation of water removal during changes of the current or during changes of parameters influencing the rate of water removal, as well as the self-regulation in the case of a non-uniform process distribution over the electrode surface have been considered.

1. Introduction

By virtue of its convenience and compactness as well as reliability of operation under nonsteady state conditions, the hydrogen–oxygen fuel cell with a capillary membrane is a very promising current source for different applications.

Fig. 1 shows schematically a fuel cell of this kind. It consists basically of a porous electrolyte-containing membrane and two porous gas-diffusion hydrogen and oxygen electrodes pressed against it. In this paper cells with a membrane impregnated with alkaline solution (KOH) are considered. The following reactions occur on the electrodes

$$\text{anode } H_2+2\,OH^- \longrightarrow 2\,H_2O+2\,e^- \quad (1)$$

$$\text{cathode } \tfrac{1}{2}\,O_2+H_2O+2\,e^- \longrightarrow 2\,OH^- \quad (2)$$

The overall reaction product—water—is removed from the cell by evaporation from the surface of the anode (J_A) or/and the cathode (J_C).

Under steady state conditions, the rate of water removal should be equal to the rate of its formation in the electrochemical reaction

$$\frac{i}{2F} = J_A + J_C \quad (3)$$

The external water vapour streams from the electrodes J_A and J_C depend on the vapour concentrations (pressures) over the electrode surface $p = p\,(c, T)$ and over the surface of the condenser $\bar{p} = \bar{p}\,(\bar{T})$ (or of the evaporator if either J_A or J_C is negative, i.e. directed to the surface of the electrode). In most cases this dependence, to a sufficient degree of accuracy, is linear

$$J = k \cdot (p - \bar{p}); \quad (4)$$

the water transfer coefficient k depends on the particular mode of water removal.

When water is removed only from one of the electrodes (e.g. the anode) and when Equation (4) applies, the condition for water balance can be expressed as

$$\frac{i}{2F} = k \cdot (p - \bar{p}) \quad (5)$$

When balance is temporarily disturbed, the total volume of electrolyte solution in the fuel cell V changes and accordingly the solution concentration c. These changes are very important because the total amount of electrolyte is small and it is located in a limited volume—in

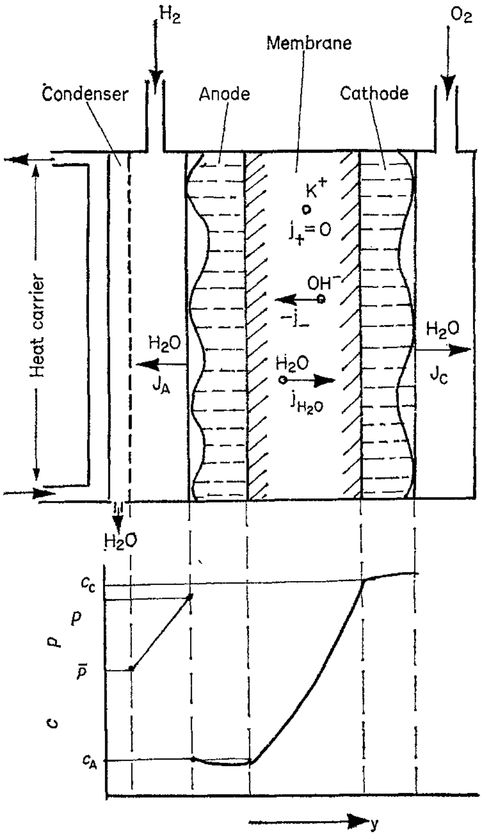

Fig. 1. Schematic diagram of a hydrogen–oxygen fuel cell with a capillary membrane; lower part: example of KOH concentration distribution across the electrolyte containing membrane and water vapour concentration gradient between electrode and condenser.

the porous volume of the membrane and in a part of the porous space of the electrodes. Therefore, under nonsteady state operating conditions of the fuel cell, the electrodes work with changing electrolyte content (the amount of electrolyte in the membrane remaining approximately constant).

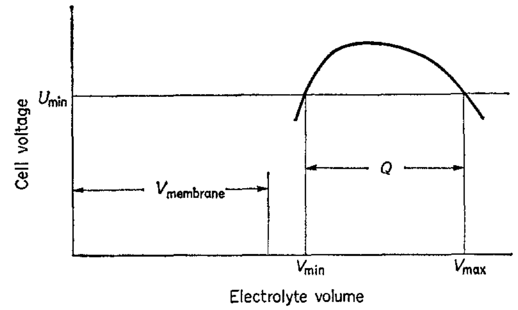

Fig. 2. Dependence of voltage on electrolyte volume in the fuel cell.

For a hydrogen–oxygen cell with a capillary membrane the dependence of voltage (at a given current) on the electrolyte volume is of an extreme type (Fig. 2). At small electrolyte volumes the energy losses are due to a large effective resistance of the electrolyte in the electrode pores, and at very large electrolyte contents the diffusion of hydrogen or oxygen through the electrolyte to the catalytic surface is impeded. For assessment of the cell efficiency it is convenient to use the notion 'buffer capacity' of the cell

$$Q = V_{max} - V_{min} \tag{6}$$

where V_{max} and V_{min} are the maximum and minimum permissible electrolyte volumes in the cell for a given minimum value of the cell voltage. The permissible values of the relative electrolyte content

$$x = \frac{V - V_{min}}{V_{max} - V_{min}} \tag{7}$$

accordingly will be in the range $0 \leqslant x \leqslant 1$.

There can be various reasons for the disturbance of water balance: change of current loading i, deviation of the values of p and $\bar{p}$ from their balance values due to instability of the temperatures T and $\bar{T}$ and deviation of the value of k from its balance value. In principle, the disturbance of water balance can be obviated by external controlling devices. But owing to their inertia and other shortcomings, the application of these devices in the case of cells with a capillary membrane does not ensure a reliable operation under real conditions of current and temperature variation.

The efficiency of these cells is determined mainly by the fact that they are able to control automatically the removal of water [1, 2]. The basic principle of self-regulation of water removal consists of the following. The unbalance with respect to water causes the mean concentration c_0 of the electrolyte in the cell and, hence, the concentrations c and p at the electrode surface, to vary. If after some time, as the result of this effect, the rate of water removal changes so as to equal the rate of its formation, the system is a self-regulating one. If the buffer capacity of the cell is not sufficient to establish a new balance state, the system is not a self-regulating one.

Depending on which parameters vary relative to their balance values, two possibilities of self-regulation should be considered; self-regulation with respect to water removal (when the values of p, $\bar{p}$ and/or k vary) and self-regulation with respect to water formation (when i varies).

2. Calculation and measurement of the concentration gradient in the membrane

In calculating the self-regulation range it is necessary to know the value of the electrolyte concentration c_A or c_C on the evaporation surface, which differs from c_0 owing to the presence of a concentration gradient across the membrane. To explain this phenomenon, let us consider the steady state mass exchange in a porous electrolyte-containing membrane [3].

The differential equations for the total fluxes of water and K^+ and OH^- ions under balance and steady state conditions are of the form

$$j_{H_2O} = \left(J_A + \frac{i}{F} = J_C + \frac{i}{2F} \right) = c_{H_2O} \cdot v = \alpha \frac{i}{F} \quad (8)$$

$$j_{K^+} = D_+ \cdot \frac{dc}{dy} + u_+ \cdot c \frac{d\psi}{dy} - c \cdot v = 0 \quad (9)$$

$$j_{OH^-} = D_- \cdot \frac{dc}{dy} - u_- \cdot c \frac{d\psi}{dy} - c \cdot v = \frac{i}{F} \quad (10)$$

The effective coefficients of diffusion and mobility of ions in the membrane D and u are related to the respective coefficients D^{00} and u^{00} for a free solution by

$$\frac{D^{00}}{D} = \frac{u^{00}}{u} = \varepsilon \quad (11)$$

where ε is the factor of transfer decrease. The quantity α is a stoichiometric coefficient of water transfer through the membrane from the hydrogen to the oxygen electrode. When water is removed by evaporation only from the surface of the hydrogen electrode ($J_C = 0$) $\alpha = \frac{1}{2}$ and when from the surface of the oxygen electrode ($J_A = 0$) $\alpha = 1$. In the case of a combined water removal from both electrodes, as can be seen from Equation (8) α is a complex function of i and the external vapour fluxes. The quantity in Equations (8)–(10) is not the absolute speed of permeation (convection) of the solution from anode to cathode but the excess velocity over the velocity of filtration v^* in an electrochemical cell in which $\alpha = 0$ and $J_A = J_C = 0$, e.g. for a reaction on both electrodes of the type

$$\mathrm{Me} + 2\,\mathrm{OH}^- \rightleftarrows \mathrm{Me(OH)_2} + 2\,\mathrm{e} \quad (12)$$

Therefore, the coefficients D and u in Equations (9) and (10) are also not true coefficients but effective coefficients in which the motion of the medium with the velocity v^* is already allowed for. The advantage of this approach to the solution of the problem is the fact that in experiments on the measurement of diffusion coefficients and mobility it is the effective values D^{00} and u^{00} that are measured.

Thus the set of Equations (8)–(10) takes account of the diffusion of all components, of the electrical forces acting on charged particles, water transport and also of the permeation motion of the entire solution from the hydrogen to the oxygen electrode. Using the well-known Einstein relation†

$$D^{00} = \frac{RT}{F} u^{00} \quad (13)$$

we can reduce the set of Equations (8)–(10) to one equation

$$\frac{dc}{dy} = \frac{\varepsilon \cdot i}{2FD_-^{00}} \left(1 + \frac{\alpha \cdot c}{t_+ \cdot c_{H_2O}} \right) \quad (14)$$

where t_+ is the cation transference number. As the boundary condition we can use the normalization equation

$$\int_0^\delta c \cdot dy = c_0 \cdot \delta \quad (15)$$

where δ is the membrane thickness.

The diffusion coefficient D_-^{00} depends strongly on concentration (Fig. 3). This dependence can be determined most accurately from the dependence of the specific conductance on concentration (assuming that Equation (13) is valid for all concentrations and that t_+ does not vary with concentration).

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† The validity of this equation for higher concentrations of the solution is not obvious; taking into account that, with rising concentration, different factors (viscosity, ion-hydration etc.) influence D^{00} and u^{00} in a similar way we shall use this relation in the whole concentration range.

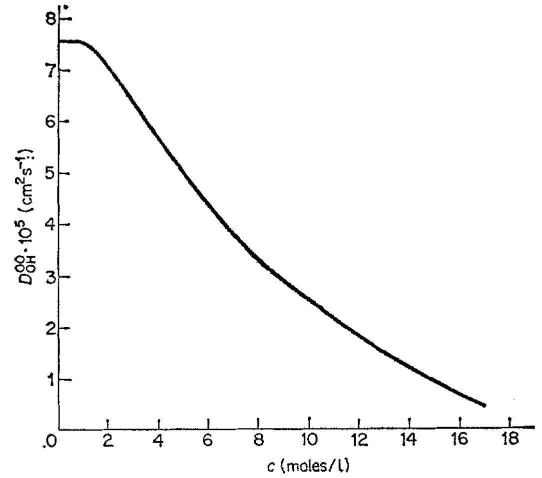

Fig. 3. Dependence of the diffusion coefficient of the OH$^-$ ion on KOH concentration in water.

Equation (14) is solved with the help of nomograms. Fig. 1 shows an example of the KOH concentration distribution across the membrane; c_A and c_C are the concentrations on the hydrogen and oxygen sides of the membrane. We see that the alkali concentration on the oxygen side is higher than on the hydrogen side. Fig. 4 shows the dependence of c_A and c_C on current density for cells with different constant values α. It is clear that the larger is α and, hence, the permeation flux of the solution from anode to cathode, the greater is the concentration gradient.

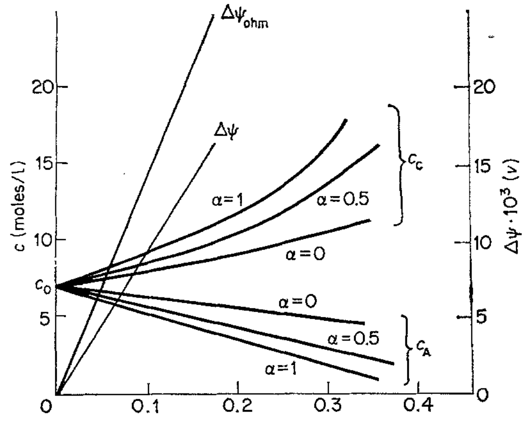

Fig. 4. Dependences on current density of KOH concentrations at the anode and the cathode for cells with $\alpha = 0, 0{\cdot}5, 1$ and of total and ohmic potential differences across the membrane for a cell with $\alpha = 0{\cdot}5$.

At a certain current density value i_l, the concentration c_A drops to zero. Thus i_l is the limiting current through the membrane, which is independent of the kinetics of the electrode reactions. However, at the alkali concentrations used in practice, the current density i_{cr} at which, on the oxygen side of the membrane, the concentration c_{cr} equal to the KOH solubility is reached, is much lower than i_l. In this case precipitation of alkali crystals starts in the pores of the oxygen electrode and the mean concentration of the solution in the membrane $(c_0)_m$ decreases with current.

In [4, 5] the mass exchange in the porous electrodes of the cell with a capillary membrane was analysed. It was shown that under real conditions the electrolyte concentration gradient in the electrodes is very small and hence the concentration at the interfaces of the membrane is practically equal to that at the surface of the electrodes.

From the basic equations for the membrane given above, it is possible to obtain an expression for the electric field as well. The potential gradient $d\psi/dy$ is made up of the ohmic and diffusion potential gradients

$$\frac{d\psi}{dy} = \frac{d\psi_{ohm}}{dy} + \frac{d\psi_{diff}}{dy} \tag{16}$$

The diffusion potential gradient is set up owing to the presence of the concentration gradient

$$\frac{d\psi_{diff}}{dy} = (t_+ - t_-)\frac{d\ln c}{dy} \tag{17}$$

It follows from the values of the transference numbers of ions that for KOH solutions the direction of the diffusion potential difference $\Delta\psi_{diff}$ is opposite to that of the ohmic potential difference $\Delta\psi_{ohm}$, which leads to a decrease of the total potential difference in the membrane (Fig. 4) and at higher concentrations even to a change in the electric field sign. It is necessary, however, to bear in mind that the decrease of $\Delta\psi$ does not mean that the energy losses during the cell operation will be less, since the same reasons which are responsible for the decrease of $\Delta\psi$ lead to a decrease of the e.m.f. of the cell caused by the shift of equilibrium potentials of the electrodes. This decrease of the e.m.f. is greater than that of $\Delta\psi$ in the membrane. For this reason in all cases the presence of a concentration gradient in the membrane with $c_C > c_A$ diminishes the cell voltage.

Since the concentration gradient value affects directly the rate of water removal and, hence, the efficiency of the fuel cell, it is expedient to carry out experimental measurements of this gradient. For this purpose a technique was developed [6] which consists in measuring the e.m.f. of a membrane cell with two hydrogen electrodes, on one of which hydrogen is oxidized and on the other evolved, i.e. for a cell with $J_A = J_C = 0$ and $\alpha = 1$. Knowing this e.m.f. it is possible from the thermodynamic relations to calculate the required concentration gradient by also taking into account Equation (15).

The measurements for cells with an asbestos membrane showed that the experimental values for the concentration gradient are much less than the calculated one. Similar results were obtained by measuring the vapour concentration near the surface of the hydrogen electrode. It proved that owing to the presence of hydrophobic inclusion and for other reasons the asbestos membranes used contained from 5–20% of blind gas pores. The diffusion coefficient of water vapour in the gas phase being, by 4 orders of magnitude, larger than the diffusion coefficient of the components of an aqueous solution, under certain conditions there can arise a considerable water transport through the gas phase in the direction of increasing electrolyte concentration in the membrane, which in its turn leads to a decrease of the concentration gradient. Water transport along this path through the membrane, if the bubbles are located close enough to one another, is ensured by the permeation water transport in solution resulting from the fact that the liquid water transfer path is by-passed by a vapour transfer path. To take into consideration the influence of gas porosity, Equation (8) for the water flux was substituted by Equation (8a), in which the water motion in the gas phase is also allowed for

$$j_{H_2O} = c_{H_2O} \cdot v - D^{g}_{H_2O} \cdot \frac{dp}{dy} = \alpha \cdot \frac{i}{F} \tag{8a}$$

This taking account of the effect of gas porosity has led to a satisfactory agreement between calculated (for gas porosity 10%) and experimental data on the concentration gradient (Fig. 5).

It can be seen from Fig. 4 and Fig. 5 that (for not excessively high current densities) the electrolyte concentration on both sides of the membrane changes practically linearly with current

$$c = c_0 \pm \beta \cdot i \tag{18}$$

The coefficient β rises with increasing membrane thickness δ and factor of transfer decrease ε. It also somewhat increases with increasing concentration, so that $\beta_C > \beta_A$ and $\beta^0 > \beta^1$ (for $x = 0$ and $x = 1$ respectively).

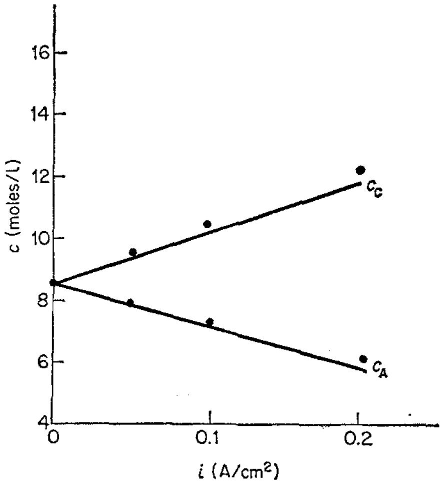

Fig. 5. Experimental (points) and calculated (lines) dependences of c_A and c_C on current density.

3. Self-regulation during variation of the water removal rate

The self-regulation process can be calculated either by analytical or graphical means.

Making use of Equation (18) and also of the fact that in the KOH concentration region of interest to us with change of this concentration the equilibrium vapour concentration changes practically linearly ($\Delta p = -\gamma \cdot \Delta c$), we can write the following approximate equations for the dependences of the vapour concentration on the hydrogen and oxygen sides on the relative electrolyte content x, on the current density i, on the mean concentration c_0^0 at $x = 0$ and on the electrolyte volume V_{min}

$$(p_{\text{i}}^x)_{\text{A}} = p_0^0 + \gamma \cdot c_0^0 \frac{V_{\text{min}}}{V_{\text{min}} + xQ} + \gamma \cdot \beta_{\text{A}}^x \cdot i \quad (19)$$

$$(p_{\text{i}}^x)_{\text{C}} = p_0^0 + \gamma \cdot c_0^0 \frac{V_{\text{min}}}{V_{\text{min}} + xQ} - \gamma \cdot \beta_{\text{C}}^x \cdot i \quad (20)$$

In these equations the superscripts and subscripts for p and c refer to the relative electrolyte content x and the current density i, respectively. The upper limit of $(p_i^x)_{\text{A}}$ is $p_{\text{H}_2\text{O}}$ and corresponds to a drop of c_{A} to zero.

For normal cell operation with current density i the maximum and minimum admissible water vapour concentrations at the evaporation surface are p_{i}^1 (at $x = 1$) and p_{i}^0 (at $x = 0$). Hence with changing p the maximum width of the self-regulation zone (i.e. the zone within which these quantities can change without affecting the normal operation of the cell) is

$$(\Delta p)_{\text{i}}^* = p_{\text{i}}^1 - p_{\text{i}}^0 \quad (21)$$

The maximum possible (from the view-point of electrode efficiency) temporary change of the water removal rate at its constant formation rate, according to Equation (4) is

$$(\Delta \text{J})_{\text{i}}^* = k \cdot (\Delta p)_{\text{i}}^* \quad (22)$$

For the case of water removal from the hydrogen electrode ($J_{\text{C}} = 0$) we have from equation (19)

$$(\Delta p)_{\text{iA}}^* = \gamma \cdot c_0^0 \frac{Q}{V_{\text{min}} + Q} - \gamma(\beta_{\text{A}}^0 - \beta_{\text{A}}^1) \cdot i \quad (23)$$

It follows from this expression that the value of $(\Delta p)_{\text{i}}^*$ rises with increasing buffer capacity Q and solution concentration c_0^0 and decreases with increasing thickness and porosity of the membrane (influencing the values of β and V_{min}) and with increasing current density. In Fig. 6 the dependences of p^1 and p^0 on δ for the current densities 0·1 and 0·4 A/cm^2 are given (assuming $\beta \sim \delta$).

The maximum width of the self-regulation zone can also be expressed in terms of the variations of the electrode $[(\Delta T)^* = T^0 - T^1]$ and condenser temperatures $[(\Delta \bar{T})^* = \bar{T}^1 - \bar{T}^0]$, which are the maximum admissible ones according to the flooding and drying conditions. The relations of $(\Delta T)^*$ and $(\Delta \bar{T})^*$ with $(\Delta p)^*$ depend on the absolute values of p^1 and p^0. A numerical analysis has shown that the value of $(\Delta T)^*$ increases with increasing buffer capacity Q, the mean concentration c_0^0 and decreases with increasing membrane thickness and value of the water transfer coefficient k.

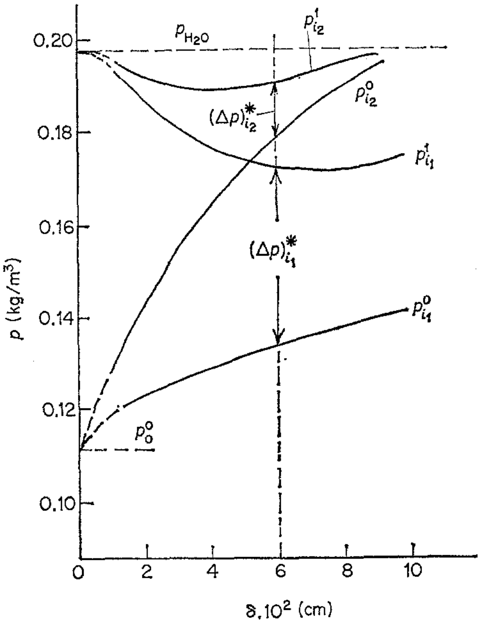

FIG. 6. Dependences of saturated vapour concentration over the surface of a hydrogen electrode at values $x = 0$ (p^0) and $x = 1$ (p^1) and current densities $i_1 = 0{\cdot}1$ A/cm^2 and $i_2 = 0{\cdot}4$ A/cm^2 on membrane thickness for $T = 70°$C, $Q = 0{\cdot}064$ cm^3/cm^2, $\varepsilon = 3{\cdot}3$, $c_0 = 7$ moles/l.

The analysis of the general case of self-regulation with respect to water removal with allowance for deviations from the balance values of T, $\bar{T}$ and k, can be most conveniently carried out with the use of nomograms of the type shown in Fig. 7. In the right part the dependences of p_{i}^0 and p_{i}^1 on T (for a given value of i) are plotted, in the left part—the dependences on the condenser temperature $\bar{T}$ of $\bar{p}$ ($= p_{\text{H}_2\text{O}}$) and of the balance pressure near the electrode p^*, calculated for the corresponding values of $\bar{p}$ from the balance equation (5) ($p^* = \bar{p} + i/[2Fk]$). The range of admissible condenser temperature values at the electrode temperature T_1 is $(\Delta \bar{T})_1^*$, and the range of admissible electrode temperatures at the condenser temperature $\bar{T}_2$ is $(\Delta T)_2^*$. Evidently, with

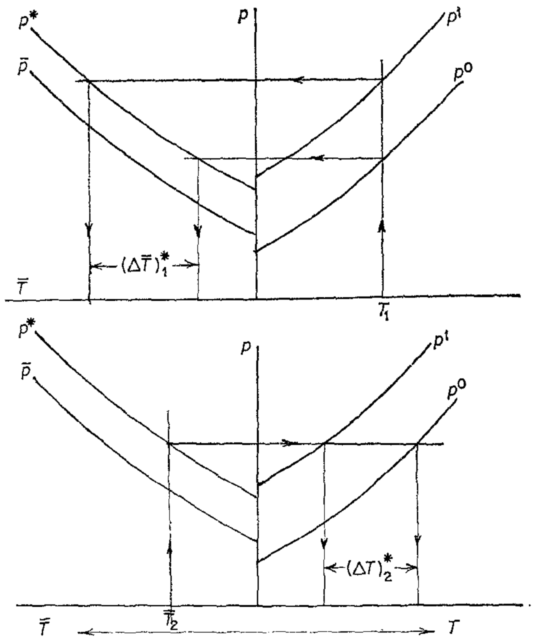

Fig. 7. Dependences on temperature of p^0, p^1, $\bar{p}$ and p^*

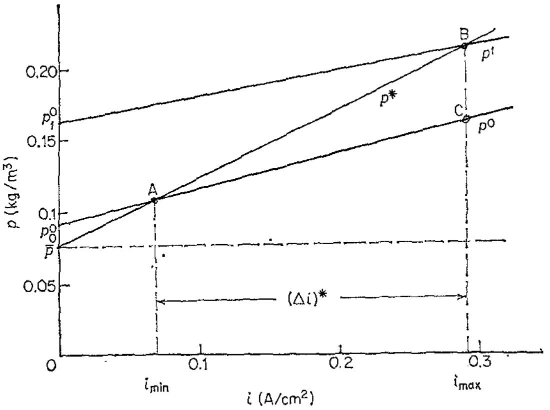

Fig. 8. Dependences on i of p^0, p^1 and p^* for the case. $\gamma \cdot \beta^0 < 1(2Fk)$

increasing $\bar{T}$ the electrode is flooded and with increasing T it dries up, and vice versa. With increasing k relative to its balance value the electrode dries up and vice versa.

The main difference in the mode of water removal from the oxygen electrode lies in the fact that owing to the concentration gradient through the membrane the vapour concentration on the oxygen side becomes lower than on the hydrogen side.

4. Self-regulation during variation of the water formation rate

In considering the self-regulation with respect to water formation, i.e. to current variation, we shall assume external regulation to be absent and the values T, $\bar{T}$ and k to be constant.

Water removal from the hydrogen electrode will be considered first. Figs. 8 and 9 show, for the surface of this electrode, the dependences on i of p^0 and p^1, and also of p^* (calculated as described for the given value of $\bar{p}$). The slopes for the lines for p^0, p^1 and p^* are, correspondingly, $\gamma \cdot \beta^0$, $\gamma \cdot \beta^1$ and $1/(2Fk)$. In Fig. 8 the case of water removal characterized by the inequality

$$\gamma \cdot \beta^0 < \frac{1}{2Fk} \tag{24}$$

is shown. The intercept of p^* between the lines for p^0 and p^1 (points A and B) determines the range of admissible current densities $(\Delta i)^* = i_{\max} - i_{\min}$, within which self-regulation takes place. With increasing current density the solution content of the electrodes x rises. For conventionally used membranes, the time of establishment of the balance water content in the cell τ_x is greater (10–60 min) than the time of establishment of the concentration gradient $\tau_{\Delta c}$ (1–2 min). Therefore with rising current, e.g. from $i_{\min}$ to $i_{\max}$ during the time $\tau_{\Delta c}$ the vapour concentration rises from $p^0_{i_{\min}}$ to $p^0_{i_{\max}}$ (point C) corresponding to the practically initial value $x = 0$. Then, owing to unbalance, the electrolyte content x and hence p will increase with time until a new balance state for water is established with $p^1_{i_{\max}}$ (point B). For any value in the range $\bar{p} < p^0_0$ it can be shown that

$$(\Delta i)^* = \frac{(\Delta p)^*_{i_{\max}}}{1/(2Fk) - \gamma \cdot \beta^0} \tag{25}$$

i.e. $(\Delta i)^*$ is proportional to the width of the self-regulation zone $(\Delta p^*_i)_{\max}$ whose dependence on various factors we considered earlier.

Fig. 9 gives similar plots for the case

$$\gamma \cdot \beta^1 > \frac{1}{2Fk} \tag{26}$$

From an analysis similar to that above we see that with gradual current increase the electrode

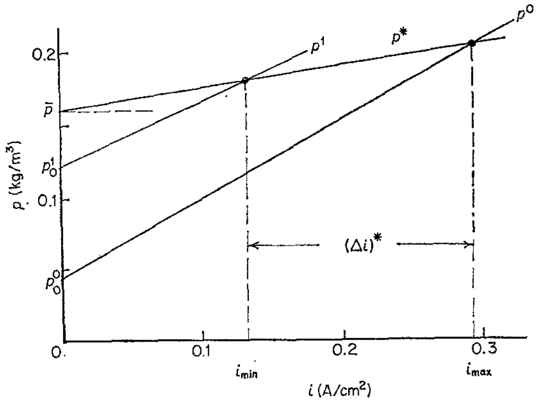

Fig. 9. Dependences on i of p^0, p^1 and p^* for the case. $\gamma \cdot \beta^1 > (2Fk)$

dries up and vice versa. This is due to the fact that with increasing current the vapour pressure at the evaporation surface increases (owing to a sharp increase of the concentration gradient across the membrane) more than it is necessary from Equation (5) for immediate establishment of a new balance state. It is also clear from the figure that with decreasing current the water vapour from the condenser can be transported back to the electrode. The expression for i at $\bar{p} > p_0^1$ is of the form

$$(\Delta i)^* = \frac{(\Delta p)^*_{i_{max}}}{\gamma \cdot \beta^0 - 1/(2Fk)} \tag{27}$$

Let us consider now the third possible case which is characterized by the relation

$$\gamma \cdot \beta^1 \leqslant \frac{1}{2Fk} \leqslant \gamma \cdot \beta^0 \tag{28}$$

at $p_0^0 \leqslant \bar{p} \leqslant p_0^1$. This case can be considered as being ideal self-regulation with respect to water formation, since here the minimum admissible current $i_{min} = 0$ and the maximum admissible current is very high (i.e. will be restricted by other factors bearing no relation to self-regulation). The physical sense of ideal self-regulation is that under these conditions the current change causes automatically such a change of p (owing to the dependence of the concentration gradient across the cell) which is equal to the change of p^* necessary for the maintenance of the balance state for any current change. It is most convenient to fulfil the conditions of ideal self-regulation (Equation 28) by choosing suitable parameters for the water removal system, *viz.* the water transfer coefficient k and the temperature on the condenser surface $\bar{T}$. Ideal self-regulation is illustrated by the dependence of i on k (Fig. 10) for water removal from the hydrogen electrode.

Among other factors, apart from k, which influence strongly the self-regulation with respect to water removal, we should mention first the quantity $\bar{p}$—the vapour concentration at the condenser surface. It can be seen from Figs 8 and 9 that for the first case (Equation 24) the optimum value is $\bar{p} = p_0^0$. In this case $(\Delta i)^*$ is maximum, $i_{min} = 0$ and no overdrying is possible. For the second case (Equation 26) the optimum is $\bar{p} = p_0^1$. In this case $(\Delta i)^*$ is maximum, $i_{min} = 0$ and no overflooding is possible.

In the case of water removal from the oxygen electrode, owing to the concentration gradient sign, the following inequality is always valid

$$\gamma \beta^0 < 0 < \frac{1}{2Fk} \tag{29}$$

i.e. we always have to deal with the first case. Thus, at constant temperature, with increasing current the electrodes are flooded and vice versa. In this case ideal self-regulation is impossible, which is clear from the dependence of $(\Delta i)^*_C$ on k (Fig. 10), Moreover, analysis has shown, that under the same conditions $(\Delta i)^*_C < (\Delta i)^*_A$. Therefore, the possibility of self-regulation with respect to water formation in the case of water removal from the oxygen electrode is much less than for water removal from the hydrogen electrode.

5. Self-regulation in the case of non-uniform water formation

Non-uniform current distribution over the surface of the electrode can be due to non-uniform distribution of the catalyst or to other reasons. For each part s of the surface we can write

$$i_s = i_0 \cdot \lambda_s \tag{30}$$

where i_s and i_0 are the differential and mean integral current densities and $\lambda_s \gtrless 1$—the

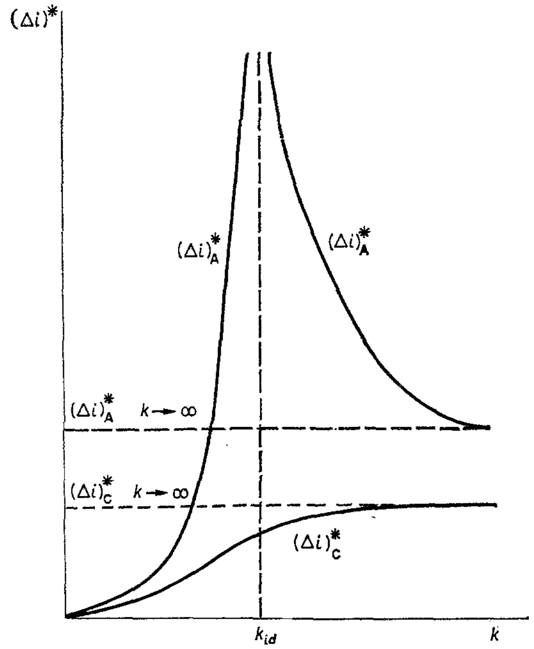

Fig. 10. Dependences of $(\Delta i)^*_A$ and $(\Delta i)^*_C$ on k at x = const. for water removal from hydrogen and oxygen electrodes, respectively.

coefficient of current distribution for the micro-area s. With increasing integral current from i_1 to i_2 the total change of the current densities is

$$\Delta i_s = \lambda_{\max} \cdot i_2 - \lambda_{\min} \cdot i_1 \qquad (31)$$

where $\lambda_{\max}$ and $\lambda_{\min}$ are the values for the most active and the least active part of the electrode surface. If the condition Equation (24) is fulfilled, the areas with greater λ_s values are more flooded than the areas with lesser ones; if the condition Equation (26) is fulfilled, the opposite is true. The condition of the inadmissibility of overdrying or overflooding of any area of the electrode surface for the case of Equation (24) is of the form

$$\Delta i_s \leqslant \frac{(\Delta p)^*_{i_{\max}}}{1/(2Fk)-\gamma\beta^0} \qquad (32)$$

From Equation (32) we obtain an expression for the maximum possible, from the view-point of cell operation, change of the mean integral current density

$$(\Delta i)^* = \frac{1}{\lambda_{\max}} \times \left[\frac{(\Delta p)^*_{i_{\max}}}{1/(2Fk)-\gamma\beta^0} - i_{\min}(\lambda_{\max}-\lambda_{\min})\right] \qquad (33)$$

One should bear in mind, however, that the levelling effect on the electrode surface produced by solution permeation and water vapour diffusion over the surface contributes to improvement of the conditions of electrode operation in the case of non-uniform current distribution.

6. Self-regulation as affected by several factors simultaneously

So far we have considered separately self-regulation with respect to water removal and formation. However, very often the rates of water formation and removal change simultaneously, for instance a change in the current generated by the fuel cell may involve a change in the electrode temperature and hence in the water removal rate. We have considered up to now isothermal conditions, i.e. a fuel cell with two heat circuits—condenser and heat-exchanger—which thermostatically controls the fuel cell.

Now let us consider the possibilities of self-regulation for a final cell with only one heat-exchanger–condenser. In this case the problem consists in simultaneous consideration and coordination of heat- and mass-exchange with account taken of self-regulation. First, on the basis of the design data and the current-voltage curve, one should calculate the dependence of electrode temperature on current density for a given condenser temperature. Then this rise of temperature with current must be taken into account in calculating the water vapour pressure. Fig. 11 shows the p/i dependences for a condenser temperature $\bar{T}$ = 70°C (water removal from the hydrogen electrode). The curves for p^0 and p^1 have been calculated taking into consideration the T/i dependence shown in this figure as well as the dependence of the electrolyte concentration gradient across the membrane on temperature and current. The values of p^* have been calculated for each current as described above. The combinations of p and T admissible from the view-point of heat and mass balance lie on the intercept of the p^* curve between the p^1 and p^0 curves. With i increasing from $i_{\min}$ to $i_{\max}$ the cell dries up although the rate of water formation is increased. This is due to a sharp increase of p as a result of increasing temperature.

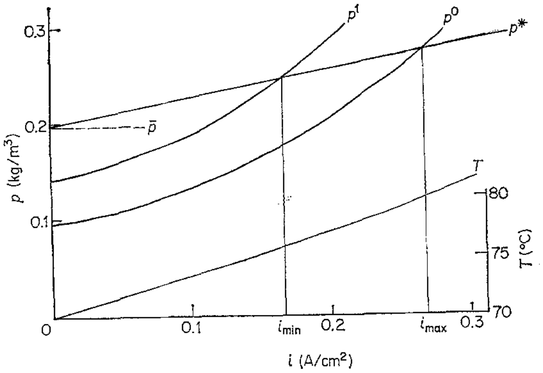

Fig. 11. Dependences of p^0, p^1, p^* and T on current density for fuel cell with one heat-exchanging circuit.

With increasing buffer capacity Q the values of $i_{\min}$ decrease and $(\Delta i)^*$ increase. But owing to the fact that for a one-circuit heat exchange scheme always $\bar{p} > p_0^1$ and consequently $i_{\min} > 0$, this scheme from the view-point of self-regulation is inferior to the two-circuit scheme with controlled electrode temperature.

In the case of a two-circuit scheme with insufficient thermostatic control, the rise of temperature on the evaporation surface with increasing current is less than for the one-circuit scheme. In this case, the condition $p_0^0 < \bar{p} < p_0^1$ can be realized for which the minimum admissible current is zero. Changing by means of a properly chosen T/i dependence (e.g. by choosing the heat transfer coefficient of the thermostatic circuit) the slopes of the p_i^0 and p_i^1 curves to values approximating the slope of the p* curve $(1/[2Fk])$, it is possible to attain high values of $i_{\max}$ and $(\Delta i)^*$, i.e. to achieve the conditions of ideal self-regulation for any given value of k. Such a scheme can be useful in cases where the value of k_{id} for isothermal conditions (Equation 28) are too high and would lead to high energy consumption (e.g. high gas circulation rates). Thus a preset dependence T/i in the case of a two-circuit thermostatic design of the fuel cell can serve as an additional factor, which can, provided it is used correctly, widen up the possibilities of the systems as regards self-regulation.

7. Conclusions

From the above consideration of mass and heat exchange in a hydrogen–oxygen fuel cell with a capillary membrane, we can conclude that this type of fuel cell, provided certain conditions are fulfilled, is quite efficient and shows significant possibilities with regard to improvements of its characteristics with respect to stability and reliability of operation.

List of Symbols

c	concentration of KOH in solution
c_0	mean KOH concentration in the membrane
c_{H_2O}	water concentration in the KOH solution
D	diffusion coefficient
F	Faraday constant
i	current density
i_l, i_{cr}	limiting current densities due to a drop of c at the anode to zero or to a beginning of KOH crystalization at the cathode
J	external water vapour flux from the electrode
j	flux of ions or water molecules in the cell from anode to cathode
k	water transfer coefficient (Equation 4)
p	water vapour concentration at the electrode surface
$\bar{p}$	water vapour concentration at the surface of the condenser (evaporator)
Q	buffer capacity of the cell (Equation 6)
R	gas constant
T	temperature at the electrode surface
$\bar{T}$	temperature at the surface of the condenser (evaporator)
t	ion transfer number
u	ion mobility
V	solution volume in the cell (for unit electrode area)
v	permeation speed of the solution
v^*	value of v for a cell with $\alpha = 0$
x	relative electrolyte content (Equation 7)
y	coordinate perpendicular to membrane surface
α	stoichiometric coefficient of water transfer (Equation 8)
β	proportionality factor defined by Equation (18)
γ	proportionality factor between Δp and $-\Delta c$
δ	membrane thickness

ε	factor of transfer decrease in the membrane
τ_x, τ_{AC}	characteristic time of establishment of the balance solution content in the cell and the concentration gradient in the membrane
ψ	electrostatic potential in the solution
$\Delta\psi_{\mathrm{ohm}}$	ohmic potential difference
$\Delta\psi_{\mathrm{diff}}$	diffusion potential difference

Subscripts

A	anode
C	cathode
+	cation
−	anion

Superscripts

^{0}	ref. to $x = 0$
^{1}	ref. to $x = 1$
^{g}	gas phase
^{00}	free solution
*	ref. to balance state

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