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Influence of electrodic properties on water management in a solid polymer electrolyte fuel cell

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The water transport in a solid polymer electrolyte fuel cell (SPEFC) can be regulated by varying the amount of hydrophobic agent (polyfluoroethylenepropylene) in the gas diffusion layer of the anode, which controls the ionic resistance as well as the gas diffusion in the cell. It has been found that at high water transport the ionic resistance of the electrolyte is lower, while gas diffusion is hindered by the presence of a high water content. A maximum in the cell performance is obtained at intermediate water transport, when the ionic resistance is reasonably low and the mass transport phenomena become negligible. Prototech electrodes, which are morphologically different from ours, also showed a low ionic resistance at low water transport.

1. Introduction

Currently, the major objective of R&D in fuel cell technology is to develop a fuel cell system for terrestrial transportation which combines high electrochemical performance and low cost components. To this end, the solid polymer electrolyte fuel cells (SPEFCs) showing higher power density than other cells, are especially attractive. However, to be cost effective these require reduction of the amount of noble-metal electrocatalyst, as well as improvement in their performance, including that of the ion exchange membranes, whose properties are largely influenced by the amount of the absorbed water during cell operation. Conditions that neither dehydrate the membrane nor cause excessive flooding should be selected to assure proper water balance and, therefore optimal performance. In the former case when ionic migration drags water through the membrane from the anode to the cathode, an extra quantity of water must be supplied to the anode feed stream to maintain unvaried membrane properties.

The phenomenon of water transfer across the cell is called "water transport", and is a function of the current and the characteristics of both the membrane and the electrodes. Although some authors have outlined processes regarding the water transport through membranes in contact with aqueous solutions [1–4], the influence of the characteristics of the electrodes on the water transport process in fuel cells has not been thoroughly investigated and is not well understood. Other authors [5–7] have reported values for water transport in SPEFC experiments run under different conditions, but no relation has been disclosed between water transport and the intrinsic properties of the electrodes. Furthermore, there is poor agreement among the experimental values reported, in fact, Koch [5] reports no water transport at current densities up to 500 mA cm^{-2} in a cell at 50 °C and at atmospheric pressure with Prototech electrodes and Dow membrane (thickness: 0.125 mm). On the other hand water transport of 0.67 mol H_2O per equivalent of H^+ was derived at 500 mA cm^{-2} from the results of Springer *et al.* [6] with a cell at 80 °C and a Nafion® membrane (0.18 mm thickness). Gottesfeld [7] reports a value of 0.2 mol H_2O/H^+ in a cell at 80 °C and 1 atm, but the kind of electrodes and membrane is not mentioned.

In this paper results are presented of a series of experiments using dual-layer electrodes with catalyst mixtures on carbon paper substrates. These electrodes are useful for studying water transport because they allow separation of the contributions coming from the catalytic and the diffusion layers. To further distinguish the contributions from the dual layers we have varied the content of hydrophobic component (FEP) in the diffusion layer and analysed the effect on water transport. The dependence of water transport on the hydrophobicity of the electrodes was investigated, and correlations among water transport and internal resistance, gas diffusion and electrochemical activity of the cell were obtained. Test using commercial electrodes (Prototech, Inc.), manufactured with carbon cloth, were compared with those performed with the present electrodes. The analysis of the results should help to ascertain the behaviour of electrodes having different morphology.

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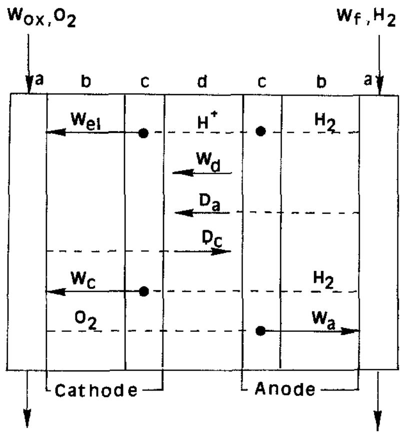

Fig. 1. Schematic diagram of fuel cell model. (a) Gas manifold, (b) diffusion layer, (c) catalyst layer, (d) membrane.

2. Water transport in SPEFC

Figure 1 shows a simplified scheme of the cell where the amounts of water considered in the analysis are represented.

The total water content (W_{TOT}) in the cell is the sum of the contributions from the water coming from the humidified fuel (W_f) and oxidant (W_{ox}) gases, the water coming from the electrochemical reaction (1) at the cathode side (W_{el}):

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O \qquad (1)$$

and finally the water produced at the cathode (W_c) and at the anode (W_a), due to a cross-over of gaseous reactants through the membrane with formation of water by chemical reaction (2) ($W_{chem} = W_c + W_a$):

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O \qquad (2)$$

Thus

$$W_{TOT} = W_f + W_{ox} + W_{el} + W_{chem} \qquad (3)$$

The amount of water produced by chemical reaction due to cross-over of gases is a function of the gas permeabilities through the Nafion®-117 membrane, whose values for H_2 and O_2 are $1.86 \times 10^{-3}\,cm^2\,h^{-1}\,atm^{-1}$ and $7.57 \times 10^{-4}\,cm^2\,h^{-1}\,atm^{-1}$, respectively [8], referred to a membrane having area $1\,cm^2$ and thickness 1 cm. From these values the calculated amount of water associated with the chemical reaction at o.c.v. are $4 \times 10^{-6}\,mol\,cm^{-2}\,h^{-1}$ and $3 \times 10^{-5}\,mol\,cm^{-2}\,h^{-1}$ at the anode and cathode side, respectively. These values are two to three orders of magnitude lower than the other amounts of water involved in the analysis and have been considered negligible in the water management calculations.

The water diffuses inside the cell due to the concentration gradient between anode and cathode and participates in the ion transport mechanism from the anode to the cathode as coordination water (dragged water, W_d). Diffusion from the anode (D_a) and back diffusion from the cathode (D_c), can be derived from the integrated form of Fick's law as:

$$D_{a,c} = (KS/\mu l)\Delta P \qquad (4)$$

where K is the permeability coefficient, μ the liquid viscosity, S the geometric area, and l the distance across which the pressure difference ΔP occurs. W_d depends on the current density and is a function of the number of water molecules associated with proton migration from the anode to the cathode. This number, in the absence of water concentration gradients, has been reported to vary from 2 to 3 [9].

Now we define as water transport, ϕ, the total amount of water transported from anode to cathode and vice versa which is a combination of the water coming from drag and diffusion phenomena. ϕ can be defined as:

$$\phi = (W_d + D_a)/[H^+] \qquad (5a)$$

if the diffusion is from the anode to the cathode side, or

$$\phi = (W_d - D_c)/[H^+] \qquad (5b)$$

if back diffusion from the cathode occurs. $[H^+]$ is the number of H^+ equivalents taking part in the process.

According to Equations 3 and 5a or 5b, and assuming $W_{chem} = 0$ the total water content at the cathode side is:

$$W_{tc} = W_{ox} + W_{el} + \phi \cdot [H^+] \qquad (6)$$

while at the anode side

$$W_{ta} = W_f - \phi \cdot [H^+] \qquad (7)$$

3. Experimental details

The electrodes were prepared by depositing an ink containing the catalyst on carbon paper (Toray TGP 90) which was wetproofed with a solution of polyfluoroethylenepropylene (FEP T 120, DuPont), dried at 70 °C and sintered at 340 °C for 15 min. The catalyst ink was prepared by mixing and stirring (50–60 °C, 15 min) the catalyst and an aqueous dispersion of PTFE (61% Teflon 30 N Dupont). To the cold solution, isopropyl alcohol was added and the flocculate was screen-printed onto the carbon paper. The electrodes were dried in air at 120 °C for 1 h, then at 280 °C for 30 min, and then sintered in air at 340 °C for 30 min. The catalyst layer contained $0.5\,mg\,Pt\,cm^{-2}$ and 40% w/w of PTFE; the diffusion layer contained a FEP loading varying in the range 0–60% w/w.

A Prototech electrode manufactured with carbon cloth [10] was also tested under the same experimental conditions for comparison with our electrodes; the nominal content of Pt was $0.5\,mg\,cm^{-2}$. All electrodes were impregnated with a 5% w/w Nafion® solution before assembling with the membrane. The final content of Nafion in the electrode was constant at about $1{,}1 \pm 0.1\,mg\,cm^{-2}$. The membrane, Nafion® 117 (DuPont) was treated in HNO_3 and purified, prior to testing, with H_2O_2 and H_2SO_4 according to the procedure utilized at Los Alamos National Laboratory [11].

The electrochemical activity and water transport measurements were carried out in a $5\,cm^2$ single cell at 50 °C and atmospheric pressure. Cell potential/current density measurements were made galvanostatically; during the tests, both the cathode and

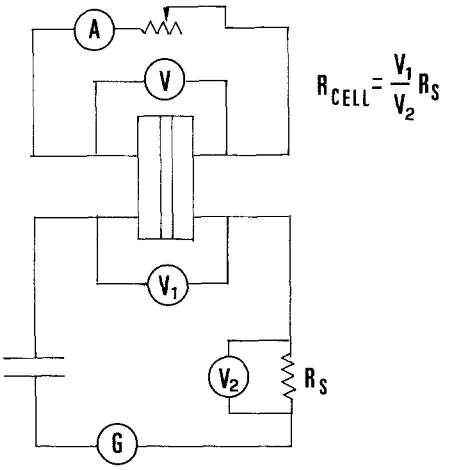

Fig. 2. System for ionic resistance measurements.

anode gases were humidified by bubbling these, before entering in the cell, through water in the stainless steel bottles at 55 °C and 65 °C, respectively. A dynamic hydrogen reference electrode (DHE) was used to measure the cathodic and anodic potentials. Values of the potential/current density were obtained from runs with H_2/O_2, H_2-N_2/O_2 and H_2/air, from which the H_2-gain and the O_2-gain values were derived. The water transport measurements were carried out at a fixed current density of 200 mA cm^{-2}, and by collecting water from the cathode side on dried silica gel. During these tests the anode gas was continuously humidified (r.h. in the anode chamber was 100%) while dried oxygen was fed to the cathode. Under these conditions, the water transport, ϕ, can be obtained from equation (6) where $W_{ox} = 0$:

$$\phi = (W_{tc} - W_{el})/[H^+] \tag{8}$$

W_{el} and $[H^+]$ can be calculated from the known quantity of electrical energy generated by the cell, i.e.:

$$W_{el} = Jt/2F \tag{9}$$

$$[H^+] = Jt/F \tag{10}$$

J, is the current in amperes, t the time in seconds and F the Faraday constant.

The internal resistance of the electrolyte was measured with a 1 kHz current generator which imposed a low alternate current through the cell (15 mA). The alternate current flowed in a circuit separated from the current/potential circuit of the cell, acccording to the scheme reported in Fig. 2. A non-polarized condenser was inserted into the alternating current circuit to prevent passage of duration current of the cell. In this circuit, voltage drops (V_2) on a known resistance (R_s) and on the cell (V_1) were measured and the cell resistance (R_{cell}) was calculated by the equation

$$R_{cell} = (V_1/V_2)R_s \tag{11}$$

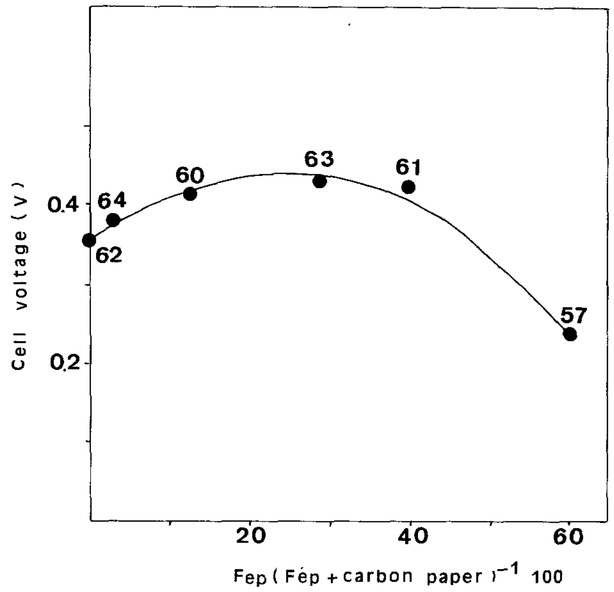

Fig. 3. Cell voltage at 200 mA cm^{-2} with electrodes having different FEP loading.

4. Results and discussion

Table 1 summarizes the FEP loadings and the electrochemical and water transport results obtained at 200 mA cm^{-2} with H_2/O_2 at 50 °C and atmospheric pressure using both our and Prototech electrodes. Figure 3 shows the effect of the FEP loading in carbon paper on cell voltage at 200 mA cm^{-2}. The FEP loading varied from 0 to 61% of the total weight of the diffusion layer. The curve in Fig. 3 shows a maximum at about 30% FEP loading, which indicates a strong influence of the hydrophobicity on the cell voltage. As discussed below, the observed maximum can be reasonably attributed to a combination of the effects of gas diffusion and ohmic resistances. Both are directly related to the water transport phenomenon, which was found to be strongly dependent on the FEP loading, as shown in Fig. 4. On the other hand, the results demonstrate that, to obtain lower ionic resistance of the membrane, a high water transport must occur in the cell (Fig. 5). This result implies that

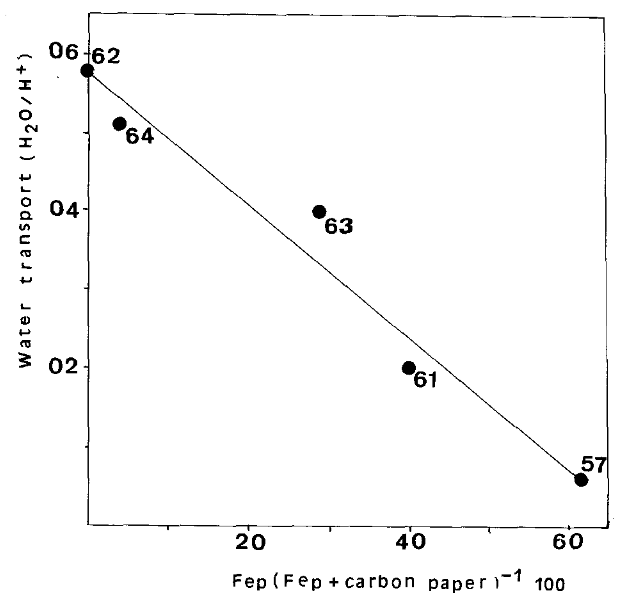

Fig. 4. Water transport measured at 200 mA cm^{-2} for cells running with electrodes with different FEP loading.

Table 1. Influence of FEP loading on water transport and cell voltage at 200 mA cm^{-2}

Run	*FEP(FEP + carbon paper)$^{-1}$/%*	*Water-transport [H_2O/H^+]*	Cell potential/mV
57	61	0.06	238
60	13	0.53	413
61	40	0.20	423
62	0	0.57	351
63	29	0.40	431
64	3	0.50	387
71*	Unknown	0.05	602
72*	Unknown	0.07	610

*Prototech electrodes

as water transport increases, an increased fraction of electrode pores must be occupied by water, which strongly limits gas diffusion. The increase in gas diffusion hindrance occurring from an increase in water transport is further demonstrated by the H_2-gain and O_2-gain, which reflect a resistance to gas transport in the electrodes (Fig. 6). The effects of water transport on cell activity can be observed in the results shown in Fig. 7. At first glance the left branch of this curve should be more controlled by the ionic resistance and the right branch by diffusion polarization. In particular, three distinct regions can be distinguished corresponding to electrodes having low, middle and high FEP loading in the carbon paper. At low FEP loading (right side of curve Fig. 7), water transport is relatively high and this produces low ionic resistance and limits the gas diffusion; the cell activity is relatively low. In the case of middle FEP loadings, water transport has an intermediate value, the ionic resistance is still low (Fig. 5) and gas diffusion is not an issue. Under these conditions the cell activity, at least for the carbon-paper based electrodes, reaches a maximum. At the extreme i.e. for the high FEP loadings, water transport is lower and, consequently, ionic resistance of the electrolyte at the fuel side become relatively high, which dominates any effect from gas diffusion. In essence, gas diffusion becomes more difficult as water transport increases, as demonstrated by the H_2 and O_2-gains (Fig. 6). At low water transport, drying caused by water drag prevails and the ionic resistance is high. To assess the role of the ionic resistance, as derived from the method shown in Fig. 2 and presented in Fig. 5, one needs to justify the lower values with respect to those expected from the cell voltage of Fig. 7. At lower water transport, a high fraction of the total ionic resistance comes from the electrolyte in the active layer, which starts to dry in the proximity of the H_2 gas and continues towards the membrane. As the electrolyte is located here in parallel with the electronic conductor (Pt/C catalyst) the ionic resistance of this region is not measurable with the present technique. The results reported in Fig. 5 are related only to the resistance from the interface between the geometric surface of the electrode and the membrane, and are only a part of the total resistance, which controls the cell activity.

The bulk of the electrolyte within the membrane is less influenced by the drying effect because the water can reach this by back diffusion from the cathode. An index of this behaviour is given from the values of the measured resistances, which, high at lower water transport, decrease as this increases after which they level-off (Fig. 5).

It is interesting to note that the ionic resistances for the whole cell, at open circuit, were almost constant at 0.42 Ω cm^2. The Prototech electrodes, are characterized by very low water transport and low ionic resistance (Fig. 5). It is suggested that the high performance of these electrodes is related to their lower resistances. An explanation for this can be found in the particular structure of carbon cloth on which the catalytic and diffusion layer are made to interpenetrate [10]. Because of this, the hydration of the Nafion® in the electrode should occur more readily, probably through the open channels among the fibres

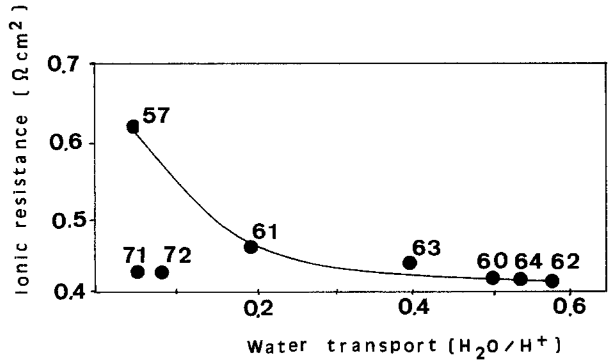

Fig. 5. Influence of water transport on ionic resistance.

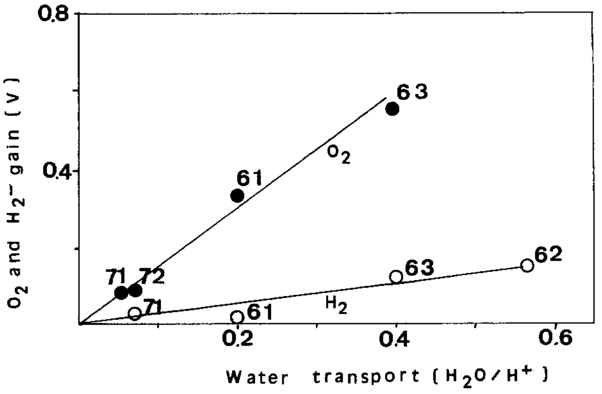

Fig. 6. O_2 and H_2-gain at 200 mA cm^{-2} in cell having different water transport.

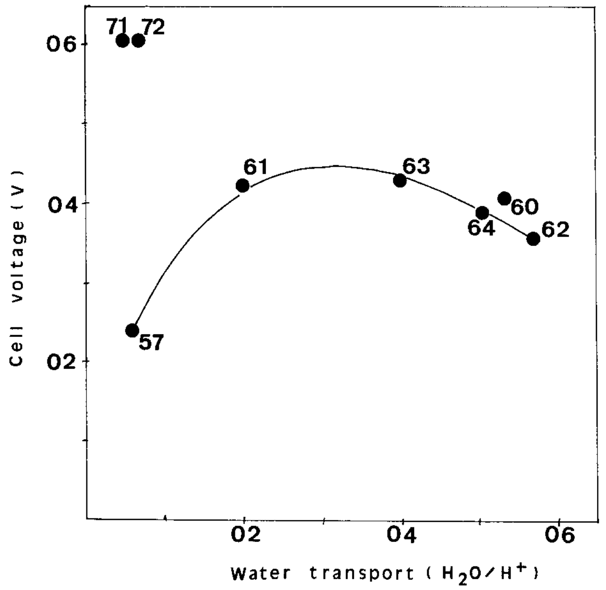

Fig. 7. Influence of water transport on cell voltage at 200 mA cm^{-2}.

in the yarns. Moreover, water is also in continuous contact with the membrane when the electrochemical reaction occurs in the catalytic zones located in the pores of the carbon cloth. The possibility of two different paths for gas and water diffusion may explain the low ionic resistance and gas diffusion polarization in the Prototech electrodes.

5. Conclusions

(i) The FEP loading in the carbon paper plays an important role in controlling water transport by influencing both the ionic resistance as well as the diffusion phenomena.

(ii) Electrodes with different catalyst substrate (carbon paper or carbon cloth) behave differently with changing water transport: in the case of electrodes made from carbon paper, a low water transport corresponds to a higher ionic resistance. The better performance of electrodes with carbon cloth is probably due to the greater penetration of water in this electrode, which does not hinder the gas flow pattern.

(iii) When water transport varies, larger variation of the ionic resistance occurs in the electrolyte in the catalyst layer because in the membrane relatively little variation of the ionic resistance is observed.

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