Water transport in polymer membranes for PEMFC

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Abstract

To determine the net electro-osmotic drag coefficient of Nafion 115 and Hanwha membrane, we measured the fluxes of water discharged from anode and cathode at different current densities. Also, we investigated the contribution of water supply for membrane from anode and cathode. When the cathode was humidified, water supply for membrane at low current densities was achieved via the cathode, but the contribution of the anode became more important as current density gradually increased. The net electro-osmotic drag coefficient decreased sharply with current density, but it had a nearly constant value over 200 mA cm^{-2}. When the cathode was not humidified, at low current densities, most of water generated at cathode was supplied for membrane, but water supply from cathode at high current densities decreased proportionately, and the net electro-osmotic drag coefficient showed larger value. © 2000 Elsevier Science S.A. All rights reserved.

1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC) has many advantages compared with other types of fuel cell as power generators for transport [1]. Using a solid polymer electrolyte such as Nafion® solves a corrosion problem of cells and makes it possible to operate at low temperature. In the early years, the PEMFC was developed for space and military, but it has been developed for electric vehicles as a hybrid power system with battery since the late 1980's [2].

In PEMFC, polymer membrane requires supplying with water in order to retain its proton conductivity, which depends strongly on the hydration of the polymer, and water management, which is essential for the enhancement of cell performance [3–7]. Up to now, water has been supplied for the membrane indirectly by humidifying reactants, and then water content of membrane changes dynamically with the operating conditions.

Two main reasons cause water molecules to move within the membrane. One is an electro-osmotic drag by potential gradient and the other is a back diffusion by concentration gradient of water [3,8]. When protons move into the cathode by potential difference, they carry several water molecules in the form of the hydrated proton. At the same time, water generation by electrochemical reaction provides additional water at cathode. So a concentration profile of water is formed between anode and cathode [9].

Electro-osmotic drag coefficient is defined as the number of water molecules transported from anode to cathode per proton. Earlier methods to determine it measured the flux of water across the membrane at constant current [3]. However, the changes in the pretreatment of the membrane permitted a variation in the water content of membranes that were equilibrated with liquid water, and thus it was not easy to measure an electro-osmotic drag coefficient experimentally. This method still does not allow an exact examination of electro-osmotic drag coefficient at low water content.

We have measured the fluxes of water discharged from anode and cathode at different current densities and determined the net electro-osmotic drag coefficient with current density. Also, we investigated the contribution of water supply for membrane from anode and cathode.

2. Experimental

2.1. Membrane and electrode assembly (MEA) fabrication

Nafion® 115 (127 μm) and Hanwha membrane (70 μm) were used as an electrolyte, and E-Tek electrode (0.4 mg Pt cm^{-2}) was used for fabricating a MEA. The electrode was impregnated with ionomer (5 wt.% Nafion® solution, Aldrich) after cutting the area of 50 cm^2, and then it was dried in the oven at 80°C for 2 h. The electrolyte membrane was pretreated by boiling in 3 wt.% H_2O_2 and H_2SO_4, respectively, to remove impurities and to transform into the H^+ form. The MEA was fabricated by hot-pressing method at 120°C and 2 tons for 5 min.

2.2. Operating condition of cell

Pure hydrogen and oxygen were used as reactant gases, and their flow rate was automatically controlled with respect to current density keeping a stoichiometry of hydrogen and oxygen of 2. The cell was operated at 70°C and 1 atm. The reactant gases were humidified by flowing through the humidifier that was kept at constant temperature and level. These were supplied for the cell with a saturated water vapor from the humidifier. The potential-current characteristic curves of the cell were measured at constant current using DC Electronic Load connected to the cell.

2.3. Measurement of water flux

Fig. 1 shows a schematic diagram of the cell for mass balance of water at anode and cathode. For simplicity, it was assumed that movement of water was influenced by an electro-osmotic drag due to potential difference and a back diffusion due to concentration gradient, and that the cell was operated in the steady state. To solve this mass balance, we measured four quantities empirically at constant current density: (i) the flux of water supplied for anode, (ii) the flux of water supplied for cathode, (iii) the
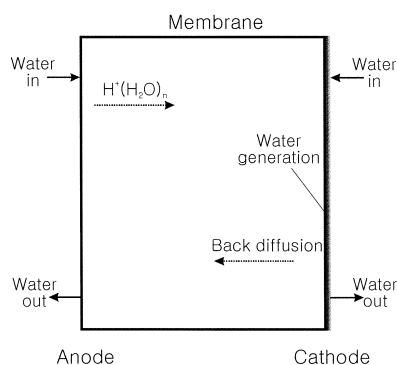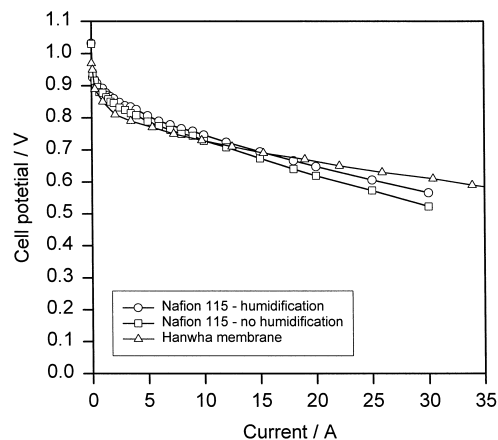
Fig. 2. The comparison of performances of cell using different membranes (cell area: 50 cm^2, operating condition: 70°C, 1 atm, reactant gases: H_2/O_2).

flux of water discharged from anode, and (iv) the flux of water discharged from cathode.

Net electro-osmotic drag coefficient is defined as the number of net water molecules transported from anode to cathode per proton, which was calculated from mass balance of water with above data. That is, net electro-osmotic drag coefficient is equivalent to the electro-osmotic effect minus the effect of back diffusion of water due to concentration gradient.

3. Results and discussion

All experiments were performed at 70°C (1 atm) and an electrolyte membrane was humidified by reactant gases passing through a humidifier. In PEMFC, continuous water supply for membrane is required to retain the membrane's conductivity. Excessive water supply, however, can cause a drop of performance due to flooding in the electrode, especially at cathode. In addition, water generation at cathode is intended to provide additional water for the membrane. Therefore, water management of the cathode is very important.

Fig. 2 shows the performance of cells using different membranes. The performance of cells using Hanwha membrane was lower at high potentials, but it showed better performance at low potentials. It is considered that Hanwha membrane showed better performance due to its good conductivity because the thickness of Hanwha membrane (70 μm) was thinner compared with Nafion® 115 (127 μm). In the case of cells using Nafion® 115, there was no large difference in performance ignoring cathode humidification, but it was thought that water supply for cathode was more favorable for cell performance at low potentials.

Fig. 3 shows the fluxes of water discharged from anode and cathode as a function of current density when the cathode is humidified (Nafion® 115). The fluxes of water discharged from anode and cathode at 0 mA cm^{-2} (open circuit voltage) refer to the fluxes of water supplied for

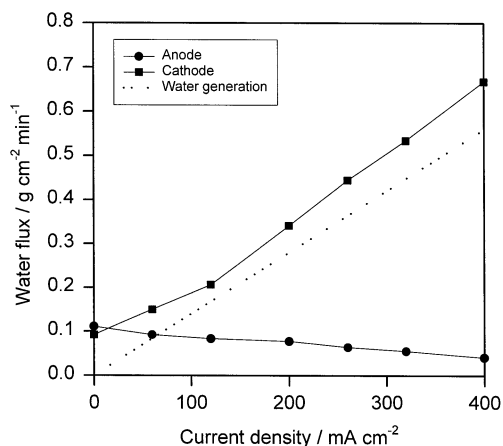Fig. 1. Schematic diagram of the cell for the mass balance of water at anode and cathode.

Fig. 3. The variations of water flux discharged from anode and cathode with current density when cathode is humidified (electrolyte: Nafion® 115, operating condition: 70°C, 1 atm, reactant gases: H_2/O_2).
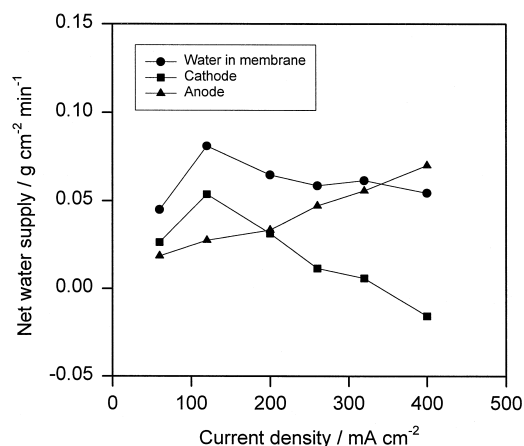

Fig. 4. The comparison of contribution of water supply from anode and cathode with current density when cathode is humidified (electrolyte: Nafion® 115, operating condition: 70°C, 1 atm, reactant gases: H_2/O_2).

anode and cathode, respectively. The flux of water discharged from anode decreased gradually with current density. The reason is that a portion of the water provided for the anode was transported from anode to cathode as a component of the hydrated proton, $H^+ (H_2O)_n$. On the other hand, the flux of water discharged from the cathode increased sharply with current density. It was considered that water generated by the electrochemical reaction was added to water transported from anode.

Data and the calculated results of the base case for water supply of Nafion® 115 at 200 mA cm^{-2} are shown in Table 1. A net water supply flux for membrane from anode was determined from the difference between supply flux and the water discharged at the anode. A net water supply flux from cathode was obtained by the difference of discharge flux from a sum of supply flux and water generated at the cathode. The amount of water generation was calculated mathematically using Faraday's law using the measured current density. Then, net electro-osmotic drag coefficient was determined with net water supply flux from anode divided by the number of protons transferred. This value indicates the number of water molecules actually transported from anode to cathode by one proton. In

the base case, the net electro-osmotic drag coefficient was about 0.3 [H_2O/H^+].

Net water supply fluxes for membranes from anode and cathode at various current densities are shown in Fig. 4 (Nafion® 115), which were calculated from the result of Fig. 3 as in the base case. These results implied that, at low current densities water supply for membranes was achieved mainly via the cathode. The reason was that water supply by absorption from cathode was greater than that by electro-osmotic drag force from anode even if the two forces operate simultaneously. As current density increased, the anode's contribution for water supply became gradually more important, but that for the cathode decreased. This is because water transport by an electro-osmotic drag from the anode increased considerably with current density, compared with the water generation at the cathode. Electro-osmotic drag is a force driven by the movement of protons, while water absorption is a physical force arising from a concentration difference. Therefore, the former overwhelms the latter even if both electro-osmotic drag and water absorption are considerable at high current densities. According to the result of Fig. 4, it is concluded that the cathode does not require a supply of additional water for humidification because it is sufficient to keep the conductivity of the electrolyte with water transported from anode and water generated by reaction at the cathode.

Table 2 shows the net electro-osmotic drag coefficients calculated at each current density with the above data. The net electro-osmotic drag coefficient decreased sharply with current density, but it had a nearly constant value over 200 mA cm^{-2}. The reason it has large values at low current densities is that the number of proton moving from anode to cathode was smaller compared with the amount of water, and so it was easier for protons to carry water molecules. However, as the current density increased, the number of water molecules carried per proton decreased because the number of protons increased linearly with

Table 1
Data and results of base case for water supply at 200 mA cm^{-2} (electrolyte: Nafion® 115, operating condition: 70°C, 1 atm, reactant gases: H_2/O_2)

	Values (g cm^{-2} min^{-1})
Flux of water supplied for anode	0.1108
Flux of water discharged from anode	0.0775
Net water supply flux from anode	0.0333
Flux of water supplied for cathode	0.0921
Flux of water discharged from cathode	0.3406
Water generation	0.2798
Net water supply flux from cathode	0.0313
Net electro-osmotic drag coefficient	0.30 H_2O/H^+

Table 2
Net electro-osmotic drag coefficient at various current densities when cathode is humidified (electrolyte: Nafion® 115, operating condition: 70°C, 1 atm, reactant gases: H_2/O_2)

Current density (mA cm^{-2})	Net electro-osmotic drag coefficient [H_2O/H^+]
60	0.55
120	0.41
200	0.30
260	0.32
320	0.31
400	0.31

current density and protons compete for transport of water molecules.

Derouin et al. [10] reported that electro-osmotic drag coefficient was 2.5 ± 0.2 for a fully hydrated Nafion® 117 membrane in equilibrium with liquid water at 30°C or 50°C. Our research results, however, showed very low values in Table 2. The reason is that the net electro-osmotic drag coefficient was determined from net water transport, including back diffusion of water and self-diffusion of protons. This means that even though water transport by electro-osmotic drag is large, the net flux of water transported to cathode is less because the back diffusion of water by the concentration gradient is also large.

Table 3 shows the net electro-osmotic drag coefficient of Hanwha membrane measured in the same way. Like Nafion® 115, the net electro-osmotic drag coefficients of Hanwha membrane decreased with current density, and these values were larger compared with Nafion® 115. This means that water transport in Hanwha membrane is easier because the thickness of Hanwha membrane is thinner than Nafion® 115.

Fig. 5 displays the relation between current density and the flux of water discharged from anode and cathode when the cathode is not humidified. The flux of water discharged from the cathode was less than that of water generated by electrochemical reaction. The difference between two values gives the amount of water absorbed into membrane from the cathode. Above 200 mA cm^{-2}, the steep increase of water discharged from the cathode suggests that the water supplied to the membrane decreased.

Table 3
Net electro-osmotic drag coefficient at various current densities when cathode is humidified (electrolyte: Hanwha membrane, operating condition: 70°C, 1 atm, reactant gases: H_2/O_2)

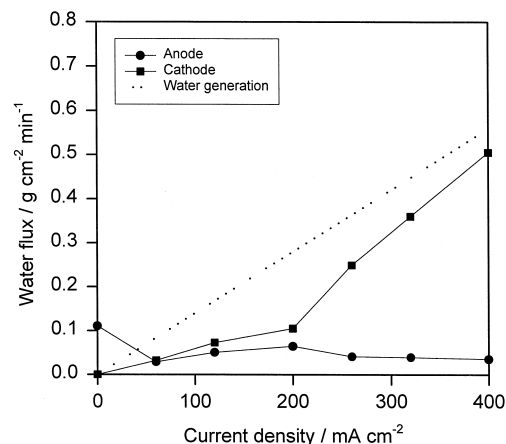| Current density (mA cm^{-2})	Net electro-osmotic drag coefficient [H_2O/H^+]
200	1.02
400	0.88
600	0.67
800	0.58

Fig. 5. The variations of water flux discharged from anode and cathode with current density when cathode is humidified (electrolyte: Nafion® 115, operating condition: 70°C, 1 atm, reactant gases: H_2/O_2).

Net water fluxes from anode and cathode at various current densities are shown in Fig. 6, which were calculated from the result of Fig. 5. Water from the cathode increased sharply up to 200 mA cm^{-2}, but, above this, it declined. At low current densities, most of water generated at the cathode could be absorbed by the membrane because water transport from the anode was small. On the other hand, water supplied from the cathode at high current densities appeared to decrease because water transport by an electro-osmotic drag increased considerably with current density.

Table 4 shows the net electro-osmotic drag coefficients calculated at each current density from the above data. These values were larger compared with Table 2. That is, the net electro-osmotic drag coefficient was larger when the cathode was not humidified. It is thought that water transport by protons from the anode was easier because there was no water supplied at the cathode. An increase of
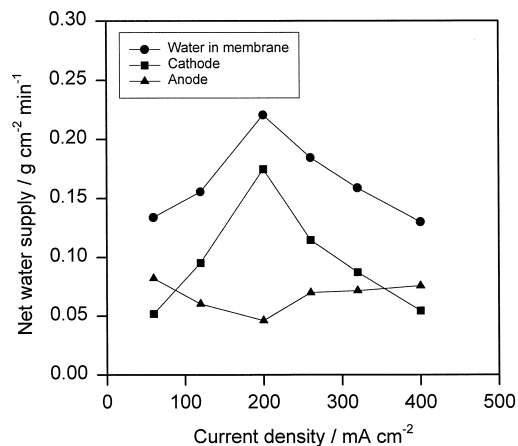

Fig. 6. The comparison of contribution for water supply from anode and cathode with current density when cathode is not humidified (electrolyte: Nafion® 115, operating condition: 70°C, 1 atm, reactant gases: H_2/O_2).

Table 4

Net electro-osmotic drag coefficient at various current densities when cathode is not humidified (electrolyte: Nafion$^®$ 115, operating condition: 70°C, 1 atm, reactant gases: H_2/O_2)

Current density ($mA\ cm^{-2}$)	Net electro-osmotic drag coefficient [H_2O/H^+]
60	2.4431
120	0.8961
200	0.4110
260	0.4799
320	0.3990
400	0.3375

current density reduced the net electro-osmotic drag coefficient considerably.

4. Conclusions

Water management is essential for the performance enhancement of PEMFC, and an analysis of water transport in the membrane and water supply to the membrane are necessary to evaluate the effect of humidification on cell performance.

In this study, water transport within the membrane and the water supply for the membrane (Nafion$^®$ 115 and Hanwha membrane) were investigated by measuring the fluxes of water discharged from anode and cathode at different current densities. When the cathode was humidified, a water supply for the membrane at low current densities was achieved mainly from the cathode because the water supplied by absorption from cathode was larger than that by electro-osmotic drag from the anode. How-

ever, the contribution of the anode became more important as current density increased. The net electro-osmotic drag coefficient decreased sharply with current density, but it had a nearly constant value above 200 mA cm^{-2}. In Hanwha membrane, the net electro-osmotic drag coefficients decreased with current density, and these values were larger compared with Nafion$^®$ 115.

When the cathode was not humidified, at low current densities, most of the water generated at the cathode was supplied to the membrane, because water transport from the anode was small. On the other hand, water supplied from the cathode at high current densities decreased because water transport by electro-osmotic drag increased with current density. The net electro-osmotic drag coefficient showed analogously large values because water transport by protons from anode was easier.

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