# Characteristics of the Nafion ionomer-impregnated composite membrane for polymer electrolyte fuel cells

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## Abstract

Composite polymer electrolyte membranes were prepared by impregnating Nafion solution into the porous expanded PTFE (ePTFE) films as a substrate and their single cell performance, gas permeability, water flux, and water uptake were investigated. Although the nitrogen permeability of the composite membrane was higher than that of Nafion 112, there was not the serious cross-over of gases to diminish cell performance and it was seen that the cell performance could be improved by reduced thickness of the composite membrane. It was also seen that water uptake and water flux of the composite membrane were dependent on the Nafion loading amount on the substrate and, therefore, the thickness of the membrane. The water uptake as well as the water flux of the composite membrane increased as the Nafion loading amount increased and the increase rate of water uptake with temperature for the composite membranes was found to be larger than Nafion 112.
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*Keywords:* Polymer electrolyte fuel cell; Composite membrane; Nafion; Water uptake; Water flux

## 1. Introduction

Fuel cells are very promising power sources for electric vehicles (EVs) to replace combustion engines using hydrocarbon fuel in the future [1–3]. The polymer electrolyte fuel cell (PEFC) is a strong candidate for EVs. The advantages of PEFC are a high power output convenience for fuel supply, long lifetime, etc. However, the relatively high cost of manufacture of PEFC stacks has restricted their commercialization for EVs [4]. The polymer electrolyte in PEFC plays an important role in cell performance, by increasing the power density (kW/l) based on the total volume of the stack, and therefore, reducing the overall stack manufacturing cost.

If cheaper, thinner, and more durable polymer electrolyte can be made, it would be possible to improve the performance of polymer electrolyte fuel cells easily. Martin and coworkers prepared composite membranes by impregnating ionomer into porous PTFE membranes, to investigate the transport properties of the composite membranes [5,6]. Verbrugge et al. [7] reported the equilibrium and transport characteristics of the composite membranes for a fuel cell

application. Unfortunately, however, they did not report any fuel cell performance for the composite membranes. Recently, W. L. Gore & Associates, Inc., and Los Alamos National Laboratories reported that the fuel cell performance was improved by composite membranes with a thickness of 5–20 μm [8].

Although some researchers have reported fuel cell performances, ionic conductivities, and mechanical properties of the composite membranes, there were few investigations on the variation of fuel cell performance and water properties of the composite membranes related to the change in Nafion loading. In this work, therefore, composite membranes with the various thickness were prepared by impregnating Nafion solution as ionomer into the porous ePTFE films. The effect of hot-pressing and humidifying temperature for the composite membrane on the cell performance were examined, and the variation of water uptake and flux along with the Nafion loading amount and, therefore, the membrane thickness were also investigated.

## 2. Experimental

### 2.1. Preparation of the composite membranes

The ePTFE sheets with a thickness of 13 μm (Tetratex) were used as a substrate for the composite polymer electro-

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lyte membranes. To remove any impurities before use, the ePTFE sheets were cleaned in acetone at 50–60 °C for 2 h. Nafion solution (5 wt.%, Du Pont), diluted in a mixture of water and alcohol, with an equivalent weight (EW) of 1100 g/mol was then sprayed on both sides of the ePTFE sheet, followed by drying at 80 °C for 5 min. The procedure was repeated several times to fully impregnate Nafion into the pores of the ePTFE sheet and to achieve the desired thickness. The resulting composite membranes were not pretreated, before any physical and electrochemical testing. Nafion 112 with 1100 EW was used as the standard sample for a comparison with the composite polymer electrolyte membranes. Nafion 112 was pretreated using hydrogen peroxide and sulfuric acid to remove the impurities in the membrane before the physical and electrochemical testing [9,10].

### 2.2. Preparation of the membrane-electrode assembly (MEA)

The catalyst inks were prepared by mixing catalyst powders (20 wt.% Pt/C, E-TEK), Nafion solution (5 wt.%, EW 1100 g/mol, Du Pont), and solvent (isopropyl alcohol). The obtained catalyst inks were sprayed on the wet-proofed carbon paper until platinum was loaded to 0.4 mg/cm$^2$, and then dried at 60 °C in an air atmosphere to remove solvent. Two gas diffusion electrodes prepared as above were hot-pressed with the composite membrane at a pressure of 200 atm and a temperature of 140 °C for 90 s to make a sandwich type MEA [11].

### 2.3. Electrochemical and physical characterization

The prepared MEA was held between two graphite plates to make a single cell. The test station for operating the single cell and measuring its performance consisted of a temperature controller, humidification chamber, flowmeter, back pressure regulator, and electronic load box (10 V, 40 A). The single cell was connected with the electronic load box under galvanostatic load and cell potentials were recorded periodically.

Nitrogen permeability was measured to check the presence of pinholes or pores in the Nafion-impregnated composite membranes. The cell frames of the single cell were used to measure permeability of the composite membranes. The upstream pressure difference was 10 psi or more and a digital flow meter was located at the gas outlet to record the permeated gas volumes. Permeability was calculated from the permeated gas volumes according to [12].

Water uptake of the composite membranes were measured by immersing membranes in liquid water and by weighing them before and after immersion. First, the composite membrane was hot-pressed at 120 °C for 60 s to remove pinholes or pores in the membrane, to prepare homogeneous composite membranes, and to dry the membrane. Nafion 112 was also dried at 80 °C for 1 h in ambient

atmosphere before testing. The dried membranes were weighed, and then immersed in liquid water at the various temperatures for at least 6 h to equilibrate them with water, then weighed again.

The net transport of water across the composite membrane during cell operation was measured by collecting water at the cathode side under current load. Hydrogen gas humidified at 60 °C was supplied to the anode side, but dried oxygen gas was used at the cathode side. The operating temperature of the single cell for measurement of water flux was fixed at 50 °C. Water that diffused from the anode to the cathode was trapped for 3 h, and then the water flux was calculated from the amount of the water trapped.

## 3. Results and discussion

When composite polymer electrolyte membranes were prepared by impregnating Nafion ionomer solution into the thin porous ePTFE substrates using air spraying, the pores in the substrate have to be blocked by the Nafion films to prevent the crossover of the reactant gases, hydrogen and oxygen. However, measurement of the nitrogen permeability of the composite membranes thinner than Nafion 112 indicated some pores or pinholes remained. Table 1 shows the change in the nitrogen permeability of composite membranes along with the Nafion loading amount. As the Nafion loading amount in the substrate increased, the nitrogen permeability significantly decreased. It is seen that, however, at 85% of Nafion loading, the permeability was still higher than that of Nafion 112 ($5.1 \times 10^{-11}$ cm$^2$/s cmHg) [12]. Although the permeability above a 75% Nafion loading was not satisfactory apparently, it is believed that most of the pores in the substrate could be filled by Nafion ionomer at such loading levels confirmed by the cell performance.

Nafion with the Teflon-like backbone structure is made by copolymerization of perfluorovinly ether sulfonyl fluoride with tetrafluoroethylene. When the Nafion ionomer solution is air-sprayed on the ePTFE substrate, Nafion impregnation may be facilitated, because Nafion and ePTFE have a similar structure based on fluorocarbon molecules. However, the possibility for the presence of pinholes or pores that are not filled by Nafion still exists. To reduce this, the composite

Table 1
Nitrogen permeability of the composite membranes at 25 °C

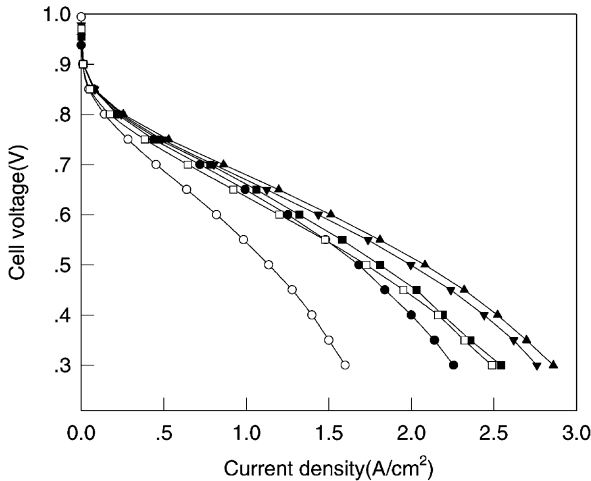| Nafion loading (wt.%) | Thickness (μm) | Nitrogen permeability (cm$^2$/s cmHg) |
| --- | --- | --- |
| 71 | 20 | $5.3 \times 10^{-5}$ |
| 75 | 22 | $5.5 \times 10^{-6}$ |
| 78 | 25 | $3.2 \times 10^{-6}$ |
| 82 | 30 | $1.8 \times 10^{-6}$ |
| 85 | 35 | $5.4 \times 10^{-8}$ |
| 100[a] | 51 | $5.1 \times 10^{-11}$[b] |

[a] Nafion 112.
[b] [12].

Fig. 1. Effect of hot pressing pressure on the cell performance of composite membranes: (●) 1 t; (■) 2 t; (▲) 3 t; (▼) 4 t; (○) Nafion 115; (□) Nafion 112. Composite membrane thickness, 30 μm; Nafion loading, 82%; cell temperature, 80 °C; $H_2/O_2 = 1/1$ atm.



Fig. 2. Variation of the cell voltage with the hot pressing pressure for the different current densities: (●) OCV; (■) 0.2 A/cm$^2$; (▲) 1.0 A/cm$^2$; (▼) 2.0 A/cm$^2$.

membranes with impregnated Nafion were hot-pressed before the cell performance test. Hot pressing may increase the adhesion of Nafion within the substrate and the pinholes or pores in the membrane may decrease, resulting in a decrease in membrane thickness and improvement in cell performance.

Fig. 1 shows the effect of hot pressing on the cell performance for the composite membranes. It is seen from Fig. 1 that the cell performance increased with increasing pressure, probably for the reasons mentioned above. However, at a higher pressure of 4 t, the cell performance was seen to then decrease. If membranes are pressed too much, molecular chains of Nafion may become too close. Consequently, water may not easily diffuse into Nafion and the resulting in the lower ion conductance may be the cause of decreased cell performance.

The cell voltage variation with hot pressing pressure for different current densities is shown in Fig. 2. The trend in cell voltage with the hot pressing pressure is consistent with Fig. 1, but the open circuit voltage (OCV) of the cell showed no diminution at a higher pressure of 4 t. If there were large spaces between molecular chains, after low pressure, the reactant gases could easily diffuse to the opposite electrode through the electrolyte and OCV would decrease. High pressures protect against crossover of the reactant gases.

Fig. 3 shows the variation of cell performance along with the Nafion loading amount in the substrate. At low current density, there was little difference in the cell performance for the various loading amounts. At the high current densities, however, it is seen that as the Nafion loading amount and, therefore, the membrane thickness increased, the cell performance decreased. In the low current density region where activation polarization prevails, the intrinsic property of the catalysts in the electrode is an important factor, whereas in the ohmic polarization region at high current density, he ionic conductivity of polymer electrolyte or the surface
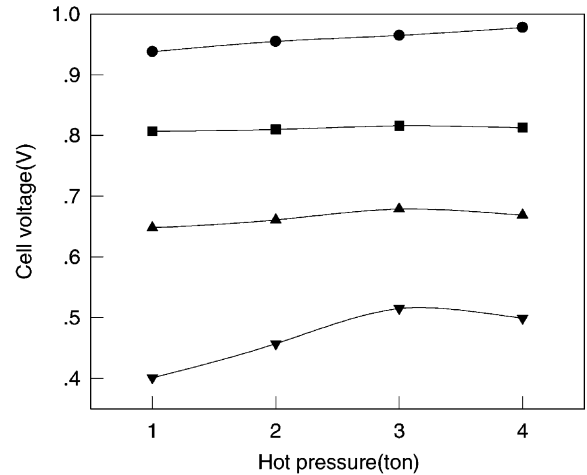
area of catalysts is more important. Therefore, the thick membranes with the higher loading amounts, which would have a high conductance, showed lower cell performance than the thin membranes at high current density.

In Table 1, slightly higher nitrogen permeability was observed for the thin composite membranes with a Nafion loading amount of 75%, which may imply that higher gas permeability will result in lower performance. However, it is seen from Fig. 3 that it showed a good cell performance without a decrease in cell voltage caused by gas cross-over, although the OCV of the cell was slightly lower than the others. Although a nitrogen permeability of $5.5 \times 10^{-6}$ cm$^2$/s cmHg for the 75% Nafion-loaded composite membrane was high in comparison to $5.1 \times 10^{-11}$ cm$^2$/s cmHg for Nafion 112, the cell performance showed a current density of 2.65 A/cm$^2$ at 0.4 V. This shows that the cell performance
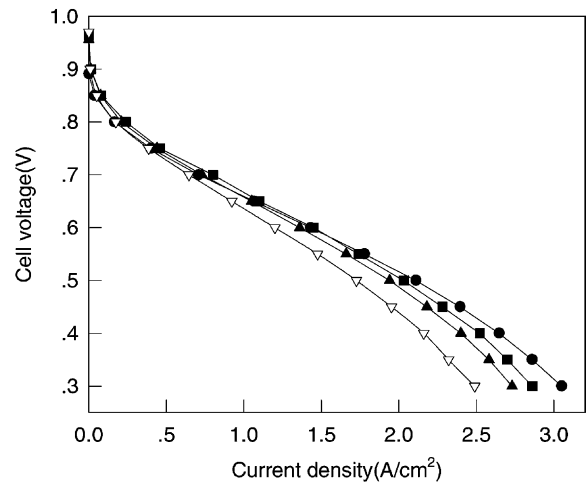


Fig. 3. Effect of the Nafion loading amount on the cell performance: (●) 75% Nafion loading (thickness 22 μm); (■) 82% Nafion loading (thickness 30 μm); (▲) 85% Nafion loading (thickness 35 μm); (▽) Nafion 112. Cell temperature, 80 °C; $H_2/O_2 = 1/1$ atm.
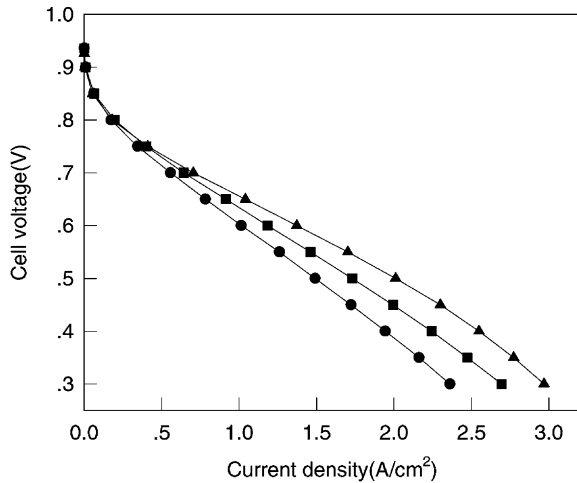
Fig. 4. Effect of the operating temperature on the cell performance for the composite membrane with a thickness of 25 μm and a Nafion loading amount of 78% $H_2/O_2 = 1/1$ atm: (●) 50 °C; (■) 60 °C; (▲) 80 °C.



Fig. 5. Effect of the oxidants on the cell performance for the different operating pressures at 80 °C; (a) $H_2/O_2$ and (b) $H_2$/air; composite membrane (35 μm) (●) 1/1 atm and (■) 2/2 atm; Nafion 112 (○) 1/1 atm and (□) 2/2 atm.

could be improved significantly by decreasing the thickness of composite membranes. However, when thin composite membranes were prepared with less than 75% of Nafion loading, the cell showed a very low OCV due to a high crossover of reactant gases, and therefore, the cell performance for such cells could not be evaluated.

Fig. 4 shows the effect of the operating temperature on cell performance for the composite membrane with a Nafion loading amount of 78%. As the temperature increased, the performance increased correspondingly. It is also seen from the figure that there was no mass transport limitation from 50 to 80 °C in the cell temperature, because the reactant gases were pure hydrogen and oxygen [13]. When air is used as an oxidant, nitrogen will be accumulated in the gas diffusion layer of the cathode, resulting in a retardation of the oxygen diffusion through the gas diffusion layer of the cathode. Oxygen gain is defined as the amount of voltage drop of the cell when the cathode gas is changed from pure oxygen to air with the same oxygen molarity and it is regarded as an index of the mass transfer resistance of oxygen in the cathode. Fig. 5 shows such an effect of the oxidants on the cell performance for the different operating pressures at 80 °C. It is seen that mass transfer limitation for air was severe compared with the pure oxygen case and, therefore, the effect of raising the operating pressure from 1 to 2 atm for the air case was not as effective in the pure oxygen case.

If the reactant gas is air, the flux of air should be five times higher than pure oxygen because of the lower oxygen concentration of air. Also, the flux of water, which is supplied by humidified air into the electrode, would increase. Therefore, the humidification temperature of air and the hydrophobic property of the air electrode play a very important role on the cell performance in addition to the oxygen gain caused by the oxidant change from oxygen to air. If water supply is too high for the electrode, the reactant gas would be prevented from diffusing into the active sites
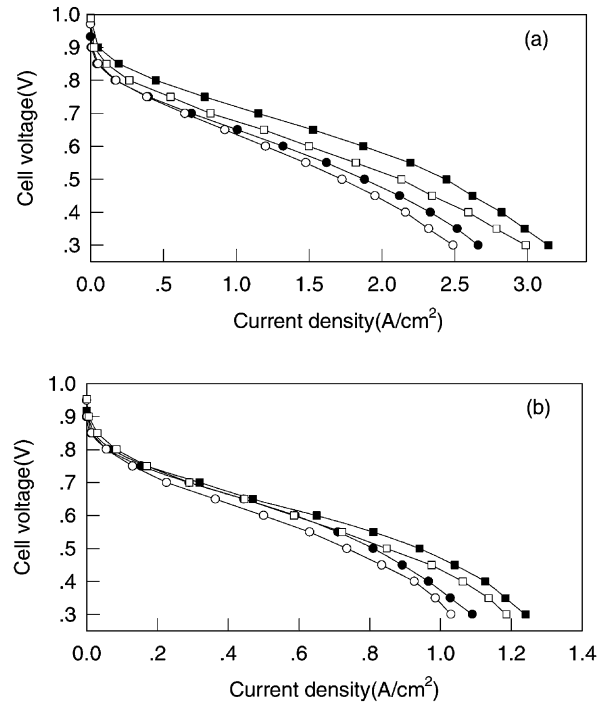
by the flooding of water within the electrode, resulting in a sudden decay of cell performance. Usually, the cell performance at low hydrogen and air pressure (~1 atm) shows a mass transfer limitation in the high current region [14,15]. Fig. 6 shows the effect of the humidification temperature on the cathode side on cell performance, when fuel cells are operated with hydrogen and air. The operating temperature of the cell was 80 °C and the humidification temperature at the anode side was kept constant at 90 °C. It is apparent from
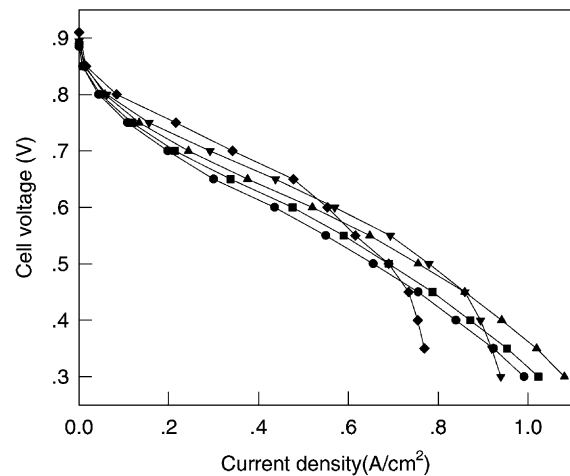


Fig. 6. Effect of the humidification temperature at the cathode side on cell performance: (●) 50 °C; (■) 60 °C; (▲) 65 °C; (▼) 70 °C; and (◆) 80 °C. Cell temperature, 80 °C; anode humidification temperature, 90 °C; $H_2$/air = 1/1 atm.

the figure, that the cell performance above 70 °C for the humidification temperature suffers from severe mass transfer limitation in the high current region. This means that water flooded the cathode and, therefore, the reactant gas could not diffuse into the electrode easily. However, the cell performance below 65 °C does not show signs of mass transfer limitation down to 0.3 V. It is also apparent that the cell performance increased with increasing humidification temperature in the low current region, which implies that the water flux for the humidification of the polymer electrolyte is more important than the diffusion of the reactant gas at the low current region.

The water uptake of polymer electrolyte is very important for its ionic conductivity. The diffusion of protons through the polymer electrolyte is directly related to the extent of the hydration of membrane. Fig. 7 shows the water uptake of Nafion 112 and the composite membranes immersed in liquid water at the various temperatures. It is seen that the water uptake of the composite membranes increased with the temperature of liquid water as well as the Nafion loading level. The rate of water uptake with temperature for the composite membranes was higher than for Nafion 112. For the composite membrane with 82% Nafion loading, its water uptake below 50 °C was lower than Nafion 112. But, at high temperatures, the composite membrane took up more water than Nafion 112. This may be because the recast Nafion films from the Nafion solution have different mechanical and chemical properties compared with Nafion films such as Nafion 115 or 112 [16]. The water uptake of membranes dried at room temperature is also twice as much as that of the membrane dried at elevated temperature [17,18]. This implies that the drying temperature of membranes during fuel cell assembly is very important in rehydration of membranes. In the usual method of preparing the membrane-electrode assembly, the electrodes and membrane are hot-pressed above 100 °C to attach the
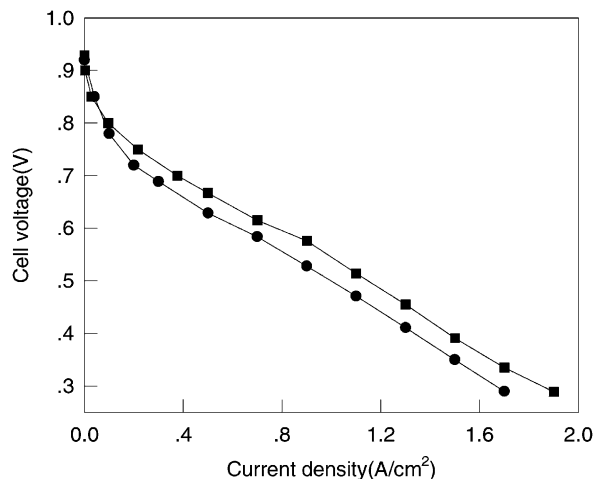
Fig. 8. Cell performance in a water flux measurement of the composite membranes: (●) 78% Nafion loading and (■) 82%. Cell temperature, 50 °C; anode humidification temperature, 60 °C; $O_2$, non-humidified.

electrodes to the membrane. Most of water is evaporated from the membrane during this process. As shown in Fig. 7, after drying at the elevated temperatures, the composite membrane will have a higher rehydrateability than the commercial Nafion membrane. This could be one of the reasons for the performance improvement of fuel cells with the composite membrane.

To measure the net transport of water across the composite membrane, a fuel cell was operated with humidified hydrogen and dried oxygen at 50 °C. Fig. 8 shows the cell performance for a water flux measurement. The thicknesses of composite membranes were 25 and 30 μm, respectively. Before the water flux test, cells were preoperated to equilibrate the polymer electrolyte with water for 2 h, because the polymer electrolyte and the cathode side were dried slightly by dry oxygen gas. If humidified oxygen gas is used, the cell performance with a thin composite membrane is usually higher than a thick one as shown in Fig. 3. However, Fig. 8 shows better performance for the cell with a thick polymer electrolyte than with a thin one, when non-humidified oxygen gas was used.

Fig. 9 shows the water flux across the composite membrane at the various current densities and how the water flux coefficients for the composite membranes were calculated from the fuel cell test and the water trap [19]. The water flux coefficient, 0.14 $H_2O/H^+$, for the 82% Nafion-loaded thicker composite membrane, was seen to be higher than that for the 78% Nafion-loaded one, 0.10 $H_2O/H^+$. These values are lower than the water flux of Nafion 117 reported by Zawodzinski et al. [18] because they tested them at 80 °C. As shown in Fig. 7, the water uptake of composite membranes increases as the Nafion loading amount in the substrate increases. This can explain the results of Figs. 8 and 9, because the thicker membranes can absorb more water. The cell performance with humidified oxygen usually increases with decreasing the thickness of the composite membrane because of the higher ionic conductance of membrane. But
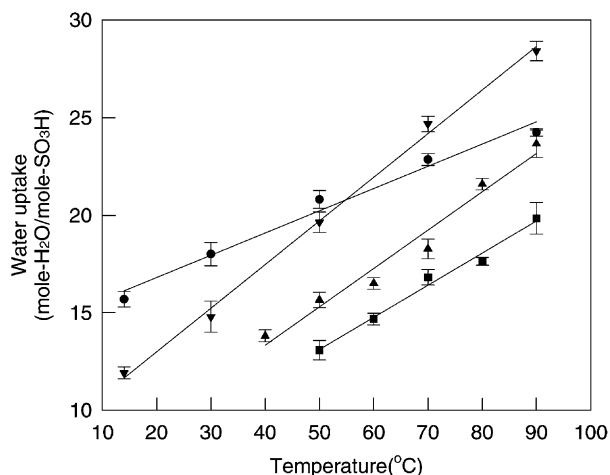
Fig. 7. Water uptake of Nafion 112 and the composite membranes immersed in liquid water at the various temperatures: (●) Nafion 112; (■) composite membrane with 67% Nafion loading, (▲) 78%, and (▼) 82%.
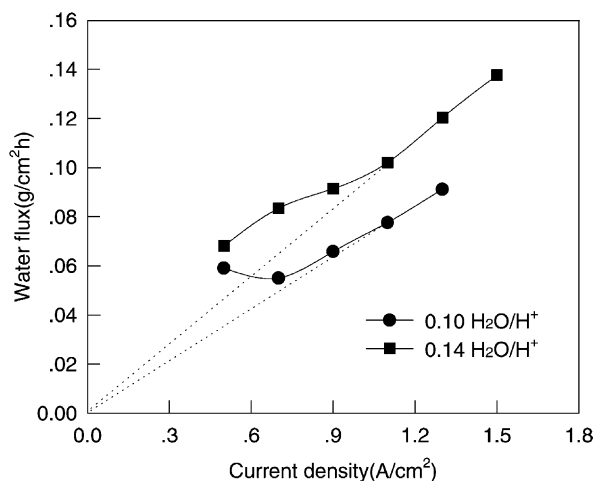
Fig. 9. Water flux across the composite membrane at the various current densities: (●) 78% Nafion loading and (■) 82%. Cell temperature, 50 °C; anode humidification temperature, 60 °C; O₂, non-humidified.

with non-humidified oxygen, the thicker membrane gives higher cell performance due to its higher water uptake capability. That is, the water uptake and the flux of composite membranes are proportionally dependent on the Nafion loading amount in the substrate. The specific properties of the recast Nafion films with regard to water may be unchanged after impregnation. However, the recast Nafion in the composite membrane may show different properties because this Nafion is held by a rigid support such as ePTFE films.

## 4. Conclusion

Composite polymer electrolyte membranes were prepared by impregnating Nafion ionomer solution into the thin porous ePTFE substrates by air spraying. Measurement of the nitrogen permeability revealed that all the pores of the composite membranes were not blocked entirely, but with loading amounts above 75% there was no gas cross-over and a good cell performance. Although nitrogen permeability of $5.5 \times 10^{-6}$ cm$^2$/s cmHg for the 75% Nafion-loaded composite membrane (22 µm) was high in comparison to that of $5.1 \times 10^{-11}$ cm$^2$/s cmHg for Nafion 112 (51 µm), the cell performance gave a current density of 2.65 A/cm$^2$ at 0.4 V. Therefore, the cell performance could be improved greatly by decreasing the thickness of composite membranes. Hot pressing may increase the adhesion of Nafion in the substrate and diminish the number of pinholes or pores in the

membrane, resulting in a decrease in the membrane thickness and improvement in cell performance. However, too high, a pressure resulted in a detriments effect on cell performance.

Membranes with a higher loading amount and, therefore, thicker membrane showed poorer cell performance than thinner membranes particularly at high current density. As the operating temperature increased, the performance increased accordingly, as expected. It was seen that mass transfer limitations in air was severe compared with pure oxygen case and cathode side humidification temperatures above 70 °C also resulted in the severe mass transfer limitations in the high current region. The water uptake of the composite membrane increased with the temperature of liquid water as well as the Nafion loading amount and the increased rate of water uptake with temperature for the composite membranes was larger compared with Nafion 112. The water flux coefficient for a thick composite membranes with a Nafion loading of 82%, 0.14 H₂O/H⁺, was found to be higher than that for a thin one with 78%, 0.10 H₂O/H⁺.

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