

Short communication

Low methanol crossover and high performance of DMFCs achieved with a pore-filling polymer electrolyte membrane

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Abstract

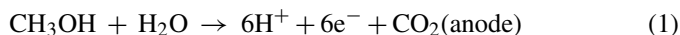
We compared the performance of the membrane electrode assembly for direct methanol fuel cells (DMFCs) composed of a pore-filling polymer electrolyte membrane (PF membrane) with that composed of a commercial Nafion-117 membrane. In DMFC tests, the methanol crossover flux was 23% lower in the PF membrane than in the Nafion-117 membrane even though the thickness of the PF membrane was 43% that of Nafion-117. This led to a higher DMFC performance and the lower overpotential of the cathode of the PF membrane. Feeding an aqueous 10 M methanol solution at 50 °C produced a low cathode overpotential, as low as 0.40 V at 0.2 A in the PF membrane, whereas the potential was 0.65 V at 0.2 A in the Nafion-117 membrane. In contrast, the ohmic loss and anode overpotential were almost the same in the two membranes. We confirmed that a reduction in methanol crossover using the PF membrane results in lower cathode overpotential and higher DMFC performance. In addition, the electro-osmotic coefficient was estimated as 1.3 in the PF membrane and 2.6 in Nafion-117, based on a water mass-balance model and values showing that the PF membrane prevents the flooding of the cathode at a low gas flow rate using. A highly concentrated methanol solution can be applied as a fuel without decreasing DMFC performance using PF membranes.

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Keywords: Direct methanol fuel cell; Polymer electrolyte membrane; Pore-filling; Methanol crossover; Cathode overpotential

1. Introduction

Direct methanol fuel cells (DMFCs) have potential to provide portable power sources because of their high energy density compared with the Li ion battery [1]. DMFCs use methanol as a fuel by the following reactions.



A membrane electrode assembly (MEA) is the most frequently used type of DMFC. One of the keys to the MEA is the methanol permeability of polymer electrolyte membranes. Nafion-117 supplied by DuPont is now a standard membrane [2,3], but its methanol permeability is quite high, and so methanol passes through the membranes and causes the serious problem of “methanol crossover” [1], which induces the follow-

ing problems: (i) poisoning of cathode catalysis, (ii) increased reaction overpotential because of the mixed potential, (iii) loss of fuel and reduction of energy density, and (iv) emission of low-concentration toxic materials such as formic acid. In addition, a highly concentrated methanol solution is not allowed, and (v) energy density remains at a low level. Some problems including (i) the poisoning of cathode catalysis and (iv) emission of low-concentration toxic gases can be solved to some degree by increasing the amount of Pt catalysts of the cathode. However, some problems, especially the fuel loss in the cathode, cannot be avoided. Achieving high proton conductivity and low methanol permeability through the polyelectrolyte membranes at the same time should greatly reduce all the problems mentioned above and decrease the amount of loaded Pt catalysts.

Many researchers have attempted to reduce methanol permeability through polymer electrolyte membranes [2–9,11,12]. Some researchers have tried to change the system [10] or operating manner [10] of DMFCs. We have reported that a pore-filling polymer electrolyte membrane (PF membrane) achieves both a higher proton conductivity and lower methanol permeability than does the Nafion membrane [11,12]. DMFCs composed of

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a PF membrane have higher cell performance than membranes composed of Nafion [13]. More recently, we developed an all-aromatic-type PF membrane, which has 300 times less methanol crossover permeability than the Nafion-117 membrane [11].

The relationship between DMFC performance and methanol crossover has been reported [14–25]. Ren et al. [14] measured the methanol crossover flux and overpotential of both Nafion-117 and 120 membranes. Hikita et al. [15] also measured and compared methanol crossover flux and DMFC performance between three Nafion membranes of varying thickness in 3–9 vol% aqueous methanol solutions. Thicker membranes showed slightly higher voltage in the low current density range but lower voltage at a high current density because of diffusion limiting. Liu et al. [16] changed the operating temperatures from 40 to 80 °C and found that increasing the temperature decreased the anode potential but did not decrease the cathode potential because both the methanol crossover flux and reaction rate increased. Ren et al. [17] and Jiang and Chu [18] measured the methanol crossover flux in DMFCs and discussed the relationship between DMFC performance and methanol crossover.

We investigated in detail how the reduction of methanol permeability through the use of the PF membrane improves the total cell performance of DMFCs. We measured the concentration of CO₂ and methanol generated in the cathode, and we estimated the methanol flux through the membrane during the operation of DMFCs. At that time, the effects of preconditioning of MEA before measurements, operating temperature, and flow rate of O₂ in the cathode [26] on methanol crossover flux measurements were evaluated to make a fair comparison of the PF and Nafion membranes. We also measured ohmic loss and anode overpotential using the current-interruption method and overpotential of the anode by electrolysis of methanol. By subtracting the ohmic loss and anode overpotential from the total overpotential, we estimated the cathode overpotential. We measured water flux and determined the electro-osmotic coefficient. We discuss the relationship between cathode overpotential and methanol crossover, the relationship between water transport and flooding phenomena, and the effect of the membranes on the DMFC performance.

2. Experimental methods

2.1. Preparation of PF membranes

We prepared the membranes using our previous method [12]. Briefly, acrylamide *tert*-butyl sulfonate sodium salt (supplied by Toa Gosei Co. Ltd.) and *N,N'*-methylene bisacrylamide were polymerized in the porous cross-linked high-density polyethylene (supplied by Nitto Denko Co. Ltd.; 58 μm thickness, 100 nm pore diameter, and 28% porosity). The pore-filling ratio was 50.0% and the thickness was 86 μm after polymerization.

The proton conductivity of the PF membrane was measured by an impedance analyzer (Hewlett Packard 4192A), which value was 7.0 S cm⁻², while that of Nafion-117 membrane was 4.1 S cm⁻². When the membrane thickness was considered, proton conductivity of the PF membrane and Nafion-117 membrane was 0.060 S and 0.082 S cm⁻¹, respectively.

2.2. Measurements of CO₂ permeability through the Nafion-117 membrane

CO₂ permeability through the Nafion-117 membrane was measured at 50 °C by GTR-20XF (GRT Tech Co.). The permeation side and feed side were humidified at 95% relative humidity.

2.3. Preparation of membrane–electrode assemblies

The electrodes comprised a backing layer, a gas diffusion layer, and a catalyst layer. Toray's graphite fiber paper was used as the backing layer. The catalyst layer was formed [13] on the gas diffusion layer (GDL) by painting on a mixture of metal supported on a carbon black catalyst, a 5 wt% Nafion solution (Aldrich Chemicals Inc., USA), and a polymer binder. The catalysts used on the anode and cathode were 49.4 wt% PtRu/Ketjenblack (TEC60E50E, Tanaka Kikinzo Kogyo KK, Japan) and 55.3 wt% Pt/Ketjenblack (TEC10E60E, Tanaka Kikinzo Kogyo KK), respectively. The geometric area of the each electrode was 5 cm². MEAs were prepared using the hotpress method. The anode, membrane, and cathode were stacked in that order and then treated at a pressure of 2 MPa and a temperature of 130 °C. The amount of PtRu in the anode was 1.16 mg cm⁻² in MEAs using the Nafion-117 membrane and 1.13 mg cm⁻² in MEAs using the PF membrane. The amount of Pt in the cathode was 1.10 mg cm⁻² in MEAs with the Nafion-117 membrane and 1.20 mg cm⁻² in MEAs with the PF membrane.

2.4. DMFC performance measurements

The performance of the MEAs with PF membranes or Nafion-117 membranes was examined using a single cell with the same electrodes used in the fixed operating condition. Preconditioning method was tested for a fair comparison between PF membrane and Nafion-117 membrane as shown in [Supplementary data](#). As a result, the cells were pretreated with N₂ gas. The operating temperature of 50 °C was chosen, because DMFCs were expected for portable use. An aqueous methanol solution and O₂ gas at ambient pressure were used as the fuel and oxidizing reagents, respectively. The flow rate of the methanol solution was set at 10 mL min⁻¹. Only the O₂ gas flow rate differed: 500 mL min⁻¹ in Nafion-117 membranes and 360 mL min⁻¹ in PF membranes.

Fuel cell performance was measured and the current–potential (*I*–*E*) curve was recorded under galvanostatic control using a charge–discharge unit (Hokuto Denko Co., HJ1010SM8A). The current density was increased stepwise from zero to a given current density at 50 mA/10 s and then decreased to zero again at the same rate. This cycle was repeated until no difference between the forward curve and the backward curve was observed.

2.5. Methanol crossover flux and water transport measurements

CO₂ discharged through the cathode was introduced directly into gas chromatography (GC) (Shimadzu Co., GAS

CHROMATOGRAPH GC-14B) to measure its concentration. Methanol discharged through the cathode was trapped once in dry ice–acetone, and analyzed by GC. The measurements were performed in the open-circuit condition before the DMFC tests.

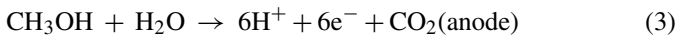
Water discharged through the cathode was also trapped in dry acetone at various current densities using 2.5 M methanol solution, and analyzed by GC.

2.6. Measurements of Ohmic loss by a current-interruption method

To measure ohmic loss (η_{IR}), a current-interruption method [15] was applied during the DMFC cell tests using a current pulse generator (Hokuto Denko Co., HC-112) and oscilloscope (Riken Denshi Co., Ltd., TCDS-8000). Current density was varied from 100 mA cm⁻² to around the limiting current density at 50 mA cm⁻² intervals.

2.7. Measurements of anode overpotential by methanol electrolysis in the anode and calculation of the cathode overpotential

An aqueous methanol solution and hydrogen gas were fed to the anode and cathode, respectively. The following reactions occurred in the anode and cathode [18].



The hydrogen gas flow rate was 300 or 500 mL min⁻¹, and the methanol solution flow rate was 10 mL min⁻¹ at 50 or 60 °C. The current–potential (I – E') curve was recorded using the same method as in the DMFC cell test. The ohmic loss (η'_{IR}) of the above reaction was measured by the current-interruption method using the same methods as in the DMFC cell test. The overpotential of the hydrogen-reduction reaction in the cathode was negligible in the DMFC operating condition range, and the overpotential of the anode (η_{anode}) was estimated by the following equations.

$$\eta_{\text{anode}} = E' - \eta'_{IR} - E_{0\text{anode}} \quad (5)$$

where $E_{0\text{anode}}$ is the equilibrium potential of these methanol electrolysis reactions. The total cathode overpotential (η_{cathode}) was determined by the following equation

$$\eta_{\text{cathode}} = E_0 - E - \eta_{IR} - \eta_{\text{anode}} \quad (6)$$

where E_0 is the theoretical electromotive force of DMFC.

2.8. Estimation of relative humidity in the cathode

Water management [27–29] is very important in the DMFC. Buchi and Srinivasan [27] reported that DMFCs can operate without humidification at temperatures <60 °C. Ren et al. [29] concluded that all water flux from anode to cathode is driven by electro-osmosis only. In the case of the liquid-fed DMFC, diffusion of water is negligible, and the mass balance of water

in the cathode depends on the generation by O₂ reduction in the cathode, electro-osmosis through the membrane, and elimination by gas flow. Assuming that: (i) the operation is stable and that the electric current is constant, (ii) the effect of the diffusion of water through the membrane is negligible, (iii) the effect of the water generation by the oxidation of crossover methanol is negligible, (iv) the relative humidity is homogeneous in the cathode layer, and (v) all the water evaporates and can be expressed as >100% relative humidity, water (n_w) and O₂ (n_O) mol flux can be described by the following equations.

$$J_w = \frac{I}{2F} + \frac{nI}{F} \quad (7)$$

$$J_O = \frac{I}{4F} \times \lambda - \frac{I}{4F} \quad (8)$$

where F is the Faraday constant, n is the electro-osmotic coefficient of protons through the membranes, and λ is the stoichiometric coefficient of the O₂ flow to O₂ gas consumed in the cathode reaction. Here we fixed the current density at 200 mA cm⁻², so consumed O₂ gas by reaction was a constant value. Fed O₂ gas was equaled to O₂ flow. Thus, λ can be calculated. For instance, fed O₂ gas is 100 times higher than consumed O₂ gas (i.e. $\lambda = 100$) when O₂ flow rate was 360 mL min⁻¹ as shown in horizontal axes of Fig. 5.

n was determined by the fitting of Eq. (7) to experimental data of Fig. 4. Based on the ideal gas equation, water (P_w) and O₂ (P_O) partial pressures follow the relationship

$$\frac{P_w}{P_O} = \frac{J_w}{J_O} \quad (9)$$

O₂ gas is consumed on the cathode, so the O₂ partial pressure in the entrance of the cathode (P_{O0}) is as follows.

$$P_O = \frac{\lambda - 1}{\lambda} \times P_{O0} \quad (10)$$

Summing up the above equations gives the following equation.

$$P_w = \frac{2 + 4n}{\lambda} \times P_{O0} \quad (11)$$

Relative humidity (φ) is calculated using the saturated humidity at each temperature as follows.

$$\varphi = \frac{P_w}{P_{\text{sat}}} \times 100[\%] \quad (12)$$

3. Results and discussion

3.1. The effect of CO₂ crossover on the accuracy of methanol crossover measurement

Part of the permeated methanol was converted to CO₂ by cathode catalysis, and the total methanol crossover from the anode is detected as the sum of CO₂ and nonreacted methanol. However, some of the generated CO₂ diffuses through the membrane from the cathode to the anode, and the measured methanol crossover value may underestimate the real value of this CO₂ crossover.

The methanol crossover flux was measured in an open-circuit condition and the values were converted to electrical current densities. The CO_2 permeation flux measured in the permeability tests was also converted to electrical current density. These values were 1.58 mA cm^{-2} in the Nafion-117 membrane and 0.33 mA cm^{-2} in the PF membrane, whereas the methanol flux was $>100 \text{ mA cm}^{-2}$ in the aqueous 2.5 M methanol solution. Therefore, we considered that CO_2 crossover was negligible and did not need to be considered in further research. This conclusion agrees with a previous report by Jiang and Chu [18].

3.2. Drastic decrease in methanol crossover by the PF membrane compared with the Nafion-117 membrane

We previously reported the low permeability of methanol through the PF membranes [11,12]. Here, we measured the methanol crossover flux in the MEAs (Fig. 1). All the pre-conditioning and operating conditions were the same in the MEAs using the Nafion-117 membrane and the PF membrane. The methanol crossover flux in the 10 M methanol solution was 162 mA cm^{-2} in the MEA with the PF membrane and 650 mA cm^{-2} in the MEA with the Nafion-117 membrane. The measured methanol permeability was $0.12 \text{ kg m}^{-2} \text{ h}$ in the MEA with the PF membrane and $0.37 \text{ kg m}^{-2} \text{ h}$ in the MEA with the Nafion-117 membrane. The relationship between methanol permeability and measured methanol crossover flux were almost the same in the two types of MEAs.

The other point in Fig. 1 is the shape of the curves. The methanol crossover through Nafion-117 membrane increased almost in proportion to the fed methanol concentration, while methanol crossover through PF membrane saturated at high methanol concentration. This is because the swelling of the filling polymer electrolyte of the PF membrane was prevented, and the solvent content of the PF membrane was kept lower than that of Nafion-117 membrane [12].

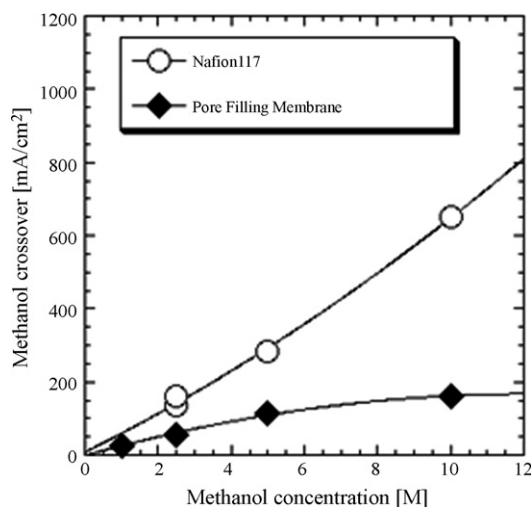


Fig. 1. The difference in methanol crossover flux between the MEAs using Nafion-117 or PF membranes. Methanol flux was converted to electrocurrent density.

3.3. High DMFC performance and low cathode overpotential achieved by the PF membrane

The low methanol crossover led to the high DMFC performance and low cathode overpotential, as shown in Fig. 2. In 10 M methanol solution, the OCV was 603 mV in the PF membrane and 400 mV in the Nafion-117 membrane. To focus on the breakdown of overpotentials (Fig. 3), the ohmic loss and anode overpotential were almost same in the MEAs using the PF membrane and Nafion-117 membrane, whereas cathode overpotential differed considerably. This means that the decrease in DMFC performance was caused mainly by the increase in cathode overpotential. The PF membrane prevented the methanol crossover and kept the cathode overpotential lower despite the low amount of cathode catalysis. In 2.5 M methanol solution, Nafion-117 showed slightly higher performance than the PF membrane at high current density, though the proton conductivity of the PF membrane is higher than that of Nafion-117. This is probably because the anode overpotential of the PF membrane is higher than that of Nafion-117 as shown in Fig. 3. Besides, the surface resistance between catalytic layers and the PF membrane may be slightly higher than that of Nafion-117 membrane. Meanwhile the OCV of the PF membrane is higher than that of Nafion-117 even in the 2.5 M methanol solution, because the PF membrane decreased methanol crossover. And again may we express, the point here is that the reduction of methanol crossover using the PF membrane decreased a cathode overpotential even in a high concentration of methanol solution, though cathode overpotential can be improved more or less by increasing Pt loading. For the further decrease of the cathode potential, the function of the current Pt catalysis needs to be improved.

Besides, methanol crossover flux through the PF membranes decreased to 23% of the value through Nafion-117. Which brings us to the point that fuel loss by methanol crossover decreased, and the PF membrane is better than Nafion-117 in terms of energy density. However, methanol equivalent to 162 mA cm^{-2} was still lost by methanol crossover even in the PF membranes used in this research. Ideally, the methanol crossover should decrease to almost zero to increase the power density of the DMFC in future.

We are studying about the mechanism of low methanol crossover through the PF membrane, and recently found it important to decrease free water in the membrane using low-temperature differential scanning calorimetry (DSC). This knowledge will lead to higher performance of the next-generation PF membranes [32].

3.4. The PF membrane leads to low electro-osmosis and can prevent flooding in the cathode

Flooding at high current density is one of the serious problems in DMFCs and is closely related to water transport through the polymer electrolyte membrane. In the case of DMFCs, most of the water flux comes from electro-osmosis, and diffusion is negligible because there is small water activity gradient through the membrane between the anode and the

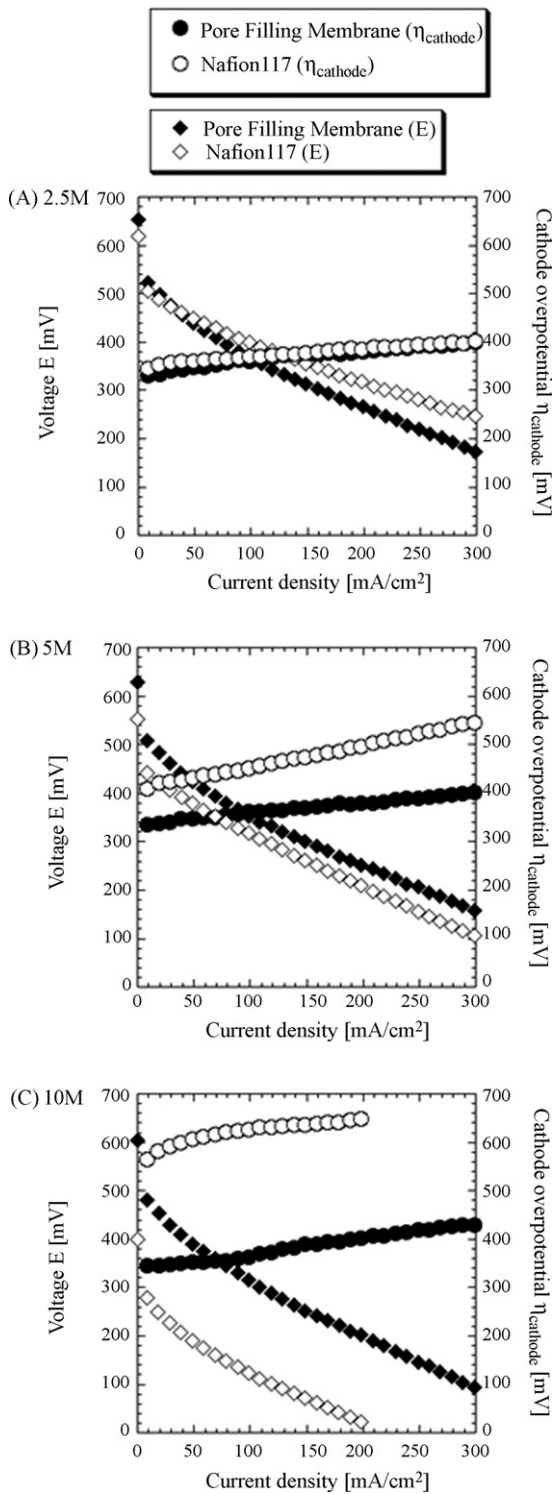


Fig. 2. The difference in DMFC performance and cathode overpotential between MEAs using Nafion-117 and PF membranes. The operating temperature was set at 50 or 60 °C, and N₂ gas was swept through the cathode. The concentration of the fed methanol solutions was (A) 2.5 M, (B) 5 M, or (C) 10 M. The Nafion-117 data were the plots shown in Figs. 2 and 3.

cathode. The anode is fed by an aqueous methanol solution. And the water generates in the cathode at high current density. Thus, water activity is high both in the cathode and in the anode.

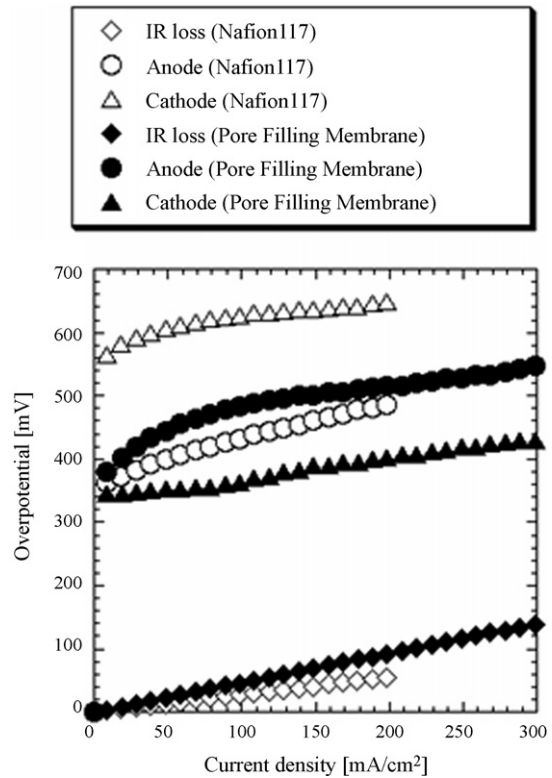


Fig. 3. The composition of overpotentials in the DMFC tests with MEAs using Nafion-117 and PF membranes. The cathode potential data were those presented in Fig. 2.

The PF membrane decreased water flux, J_w , through the membrane, as shown in Fig. 4. The electro-osmotic coefficient, n , can be determined by fitting Eq. (7) to the plots of Fig. 4. The determined n was 2.6 in Nafion-117, which coincided with reported values [29–31], whereas the value was 1.3 in the PF

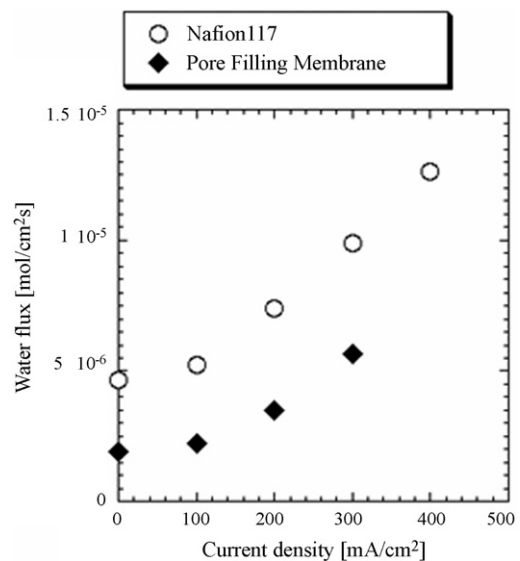


Fig. 4. The difference in water flux discharged from the cathode between MEAs using Nafion-117 and PF membranes during the DMFC test. The operating temperature was set at 50 °C. The concentration of the fed methanol solution was 2.5 M.

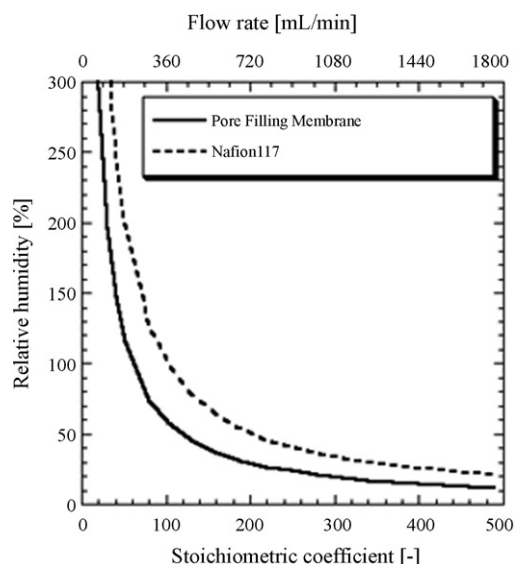


Fig. 5. Calculated relative humidity in the cathode based on the water mass-balance model. The humidity value of >100% is hypothetical, meaning that flooding can occur easily. The electro-osmosis coefficient was determined as 2.6 in Nafion-117 and 1.3 in the PF membrane by fitting the data presented in Fig. 4.

membrane. The PF membrane suppressed the swelling of the filling polymer, producing fewer free water molecules, which contribute to electro-osmosis [32]. We note that the effect of the water generation by the oxidation of crossover methanol is not more or less negligible in reality and caused the fitting error for n though the tendency does not change.

Based on the water mass-balance model in Eq. (12), the relative humidity in cathodes was calculated as the function of O_2 flow rate, as shown in Fig. 5. The humidity values >100% are hypothetical, indicating that flooding can occur easily. Because of the difference in the electro-osmotic coefficient, the O_2 flow rate was lower in the MEA using the PF membrane than in the MEA using the Nafion-117 membrane. A lower gas flow rate is desirable in terms of the compact system for portable use for DMFCs, and pore-filling membranes have an advantage in terms of preventing flooding in the cathode.

4. Conclusions

The methanol crossover flux in the PF membrane decreased to 23% of that in the Nafion-117 membrane in tests of the DMFCs using aqueous 10M methanol solution as a fuel, even though the thickness of the PF membrane was 43% that of the Nafion-117 membrane. This led to better DMFC performance and lower overpotential of the cathode of the PF membrane. Based on the DMFC operating data, the electro-osmotic coefficient was estimated as 1.3 in the MEA using the PF membrane and 2.6 in the MEA using the Nafion-117 membrane. The most important conclusion here is that, by using the PF membranes, a highly concentrated methanol solution can be applied as a fuel without decreasing either the DMFC performance or energy density. In

addition, the reduction of methanol crossover in the MEA using the PF membrane allows a lower amount of cathode catalyst to be used, and the low electro-osmosis of the PF membrane decreases the flow rate of the cathode gas without flooding, which also allows for a more compact DMFC system.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2007.08.081.

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