Short communication

Structural optimization of the direct methanol fuel cell passively fed with a high-concentration methanol solution

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ABSTRACT

In a high-concentration direct methanol fuel cell (HC-DMFC), the methanol crossover is typically decreased to an acceptable level by two main mechanisms: high methanol transport resistance between the anode reservoir and the membrane electrode assembly (MEA), and high water back flow from the cathode to the anode. Based on the semi-passive HC-DMFC fabricated in this work, the effects of methanol barrier layer (MBL) thickness and electrolyte membrane thickness on cell performance, methanol and water crossover, and fuel efficiency have been studied. The results showed that a thicker MBL could significantly decrease the methanol and water crossover by increasing the mass transport resistance between the anode reservoir and the MEA, while a thinner Nafion® membrane could also significantly decrease the methanol and water crossover by enhancing the water back flow from the cathode through the electrolyte membrane to the anode. Using Nafion® 212 as the electrolyte membrane, and a 6.4 mm porous PTFE plate as the MBL, a semi-passive HC-DMFC operating at 70 °C produced the maximum power density of 115.8 mW cm^{-2} when 20 M methanol solution was fed as the fuel.

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1. Introduction

The direct methanol fuel cell (DMFC) is a promising power source for portable electronic devices because of the high theoretical energy density (6100 kWh kg^{-1}) of methanol [1–5]. As a key component of the DMFC, the electrolyte membrane should have both high-proton conductivity and low methanol crossover in order to gain good cell performance and high-fuel efficiency. Nafion® membranes are widely used in DMFCs as the electrolyte membrane because they have high-proton conductivity and mechanical strength. However, Nafion® membranes also have high-methanol permeability and thus, lead to the inevitable methanol crossover in DMFCs, which limits the cell performance, decreases the fuel efficiency, and restricts the extensive application of DMFCs.

In the past decade, the effects of Nafion® membrane thickness on methanol crossover have been studied [6,7], and results showed that a thicker membrane led to a higher conductive resistance and lower methanol crossover. The effect of the Nafion® membrane on the cell performance and fuel efficiency was also studied in conventional DMFCs, actively or passively fed with diluted methanol solutions (usually less than 3 M) [8–12]. In general, the methanol crossover can be decreased by increasing the thickness of the Nafion® membranes. However, thicker Nafion®

membranes lead to higher conductive resistances. Therefore, when highly concentrated methanol or pure methanol is fed as fuel, it is not practical to decrease the methanol crossover to an expected level by simply increasing the thickness of the Nafion® membrane, because of the simultaneous sharp rise in conductive resistance. In order to achieve low methanol crossover and stable performance at high-methanol concentrations, different approaches including improving the electrolyte membranes [13–15], improving the fuel-feed system [16–18], and altering the cell structure [19–22] have been proposed. Among these approaches, changing the cell structure to get a stable cell performance is the easiest strategy to implement.

Kim [19] developed a passive DMFC fed with methanol vapor at room temperature. In this device, liquid methanol was absorbed in the fuel chamber by a porous pulp with 0.2 cm thickness, and was vaporized by a Nafion® 112 membrane. A hydrophobic barrier layer, made from porous Teflon, and a buffer layer, made from fired alumina, were added between the vaporizer and the membrane electrode assembly (MEA) to restrict the diffusion rate of the methanol vapor. Furthermore, their gas diffusion layers (GDL) were made from carbon papers modified by a mixture of nano-silica particles and polyvinylidene fluoride (PVDF). 57% fuel efficiency and 0.145 Wh cm^{-3} energy density were reported when pure methanol was supplied as the fuel.

Abdelkareem and Nakagawa [20] tested a passive DMFC operated with 1 M to neat methanol at room temperature. A hydrophobic porous carbon plate was employed between the fuel

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reservoir and anode current collector in their device. This porous layer, together with the CO_2 layer formed between the porous layer and MEA, acted as a methanol barrier layer (MBL) to decrease the diffusive rate of methanol. Results showed that the MBL could significantly decrease methanol crossover and increase fuel efficiency. A peak power density of 24 mW cm^{-2} was achieved using 16 M methanol solution at room temperature.

Eccarius et al. [21] studied the vapor-feed, semi-passive DMFC using 25–100 wt% methanol solutions. Polydimethyl siloxane (PDMS) membranes were used as phase change barriers between liquid and gaseous methanol. Anode and cathode over-potentials were measured separately with the help of reference electrodes. The effects of the methanol concentration, air flow rate, structure of the gas diffusion layer (GDL), operating temperature, and evaporator open ratio on the overall performance and over-potentials were studied. The peak power density was about 24 mW cm^{-2} at 50 °C using 50 wt% methanol solution.

Li et al. [22] studied the water management in a semi-passive DMFC fed by concentrated methanol solution with a 3.2-mm thick porous polytetrafluoroethylene (PTFE) plate adopted as the MBL. Methanol solutions varying from 4 M to neat methanol were passively supplied from the anode reservoir, while oxygen with different flow rates and relative humidities was actively blown into the cathode. Results showed that after adopting a MBL, the insufficient supply of water to the electrolyte membrane significantly decreased the cell performance. When oxygen with 100% relative humidity was actively supplied to the cathode, the peak power density was 75.9 mW cm^{-2} at 70 °C using 16 M methanol solution as fuel.

According to the literature review, the structure of the high-concentration direct methanol fuel cell (HC-DMFC) is typically different from the conventional DMFC with the addition of MBLs between the anode fuel reservoir and the MEA to control the methanol crossover rate. Only limited studies were conducted concerning the effect of MBLs on overall methanol crossover in HC-DMFCs [20]. The effects of the physical properties of Nafion® membranes on the methanol and water crossover in HC-DMFCs and cell performances have not been reported. Therefore, methanol and water crossover in the HC-DMFC using different MBLs and different Nafion® membranes, such as Nafion® 212, Nafion® 115, and Nafion® 117, were experimentally studied in this work. Cell performance, internal resistance, and fuel efficiency of the HC-DMFCs were also measured and calculated.

2. Experiment

2.1. Fuel cell assembly

The semi-passive DMFC shown in Fig. 1 is the same as described by Li et al. [22]. A highly concentrated methanol solution was passively stored in the anode fuel reservoir with a volume of 18 ml, while oxygen was actively provided through various serpentine channels with 1×1 mm^2 cross-sectional areas at the cathode. A porous PTFE plate was implemented directly below the anode fuel reservoir as a MBL in order to increase methanol transport resistance and decrease the methanol crossover through the membrane. Three different PTFE plates were used with thicknesses of 1.6, 3.2, and 6.4 mm. All these PTFE plates had an average pore size of 30 μm.

The active area of the MEA was 3×3 cm^2. It consisted of anode and cathode ELAT gas diffusion electrodes (GDE) from E-TEK and a Nafion® membrane. The anode GDE had a 5 mg cm^{-2} Pt loading using unsupported Pt: Ru alloy (1:1, a/o), while the cathode GDE had a 5 mg cm^{-2} Pt loading using unsupported Pt black. The MEA was fabricated by hot-pressing the anode and cathode GDEs on opposite sides of the Nafion® membrane at 130 °C and 4 MPa
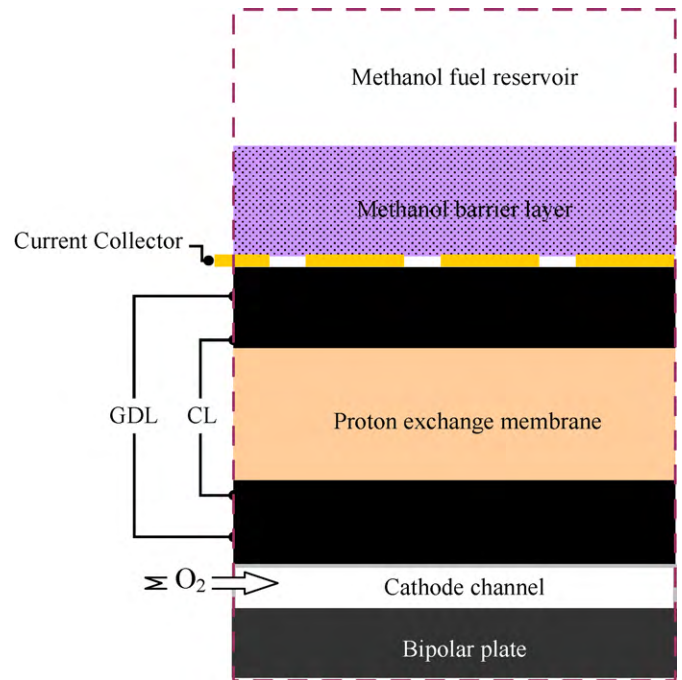

Fig. 1. Schematic diagram of a high-concentration direct methanol fuel cell (HC-DMFC) passively fed by a high-concentration methanol solution from the anode fuel reservoir [22].

for 20 min. Three different polymer electrolyte membranes (i.e., Nafion® 212, Nafion® 115, and Nafion® 117) from Ion Power, each with a different thickness, were pre-treated using a common cleaning procedure [22] before hot pressing.

2.2. Cell test

The current, voltage, power, and resistance of the fuel cell were measured using the Compact Fuel Cell Test system (Model 850C) from Scribner Associates Inc. The performance of the HC-DMFC with different MBLs and Nafion® membranes was evaluated by the commonly used voltage–current density, internal resistance–current density, and power density–current density curves. After each initial voltage scan, the cell, filled with 10 ml of 16 M methanol, was discharged at 70 °C at a constant current density of 200 mA cm^{-2} for 3 h. The fuel efficiency as well as the methanol and water crossover coefficients were calculated in the same way as described elsewhere [22].

2.3. Determination of methanol and water crossover coefficients

Several mechanisms contribute to the loss of methanol and water from the anode fuel reservoir: evaporation, Δm_{evap}, consumption by the anode electrochemical reaction, Δm_{cons}, and crossover from the anode to the cathode, Δm_{cross} Consequently, the weight change of methanol and water due to crossover can be calculated by subtracting the methanol and water loss by evaporation and the electrochemical reaction from the total weight change, Δm_{tot}:

$$\Delta m_{corss,i} = \Delta m_{tot,i} - (\Delta m_{evap,i} + \Delta m_{cons,i}). \tag{1}$$

The methanol and water crossover coefficients, α, are determined by:

$$\alpha_i = \frac{\Delta m_{cross,i}}{\left(\int I.dt/F\right) M_i} \tag{2}$$

where the subscript i can be either methanol or water, I is the current applied to the cell, F is the Faradic constant (96487 C mol^{-1}), and M_i is the molecular weight of species i.

The total weight changes of methanol and water, Δm_{tot}, were determined by measuring the weight and concentration of the methanol solution in the anode fuel reservoir before and after each 3 h test:

$$\Delta m_{tot,MeOH} = m_{init}\omega_{init} - m_{final}\omega_{final'} \tag{3}$$

$$\Delta m_{tot,H_2O} = m_{init}(1 - \omega_{init}) - m_{final}(1 - \omega_{final}). \tag{4}$$

The initial weight, m_{init}, and final weight, m_{final}, of the methanol solution in the fuel reservoir were measured using an analytical balance with 0.1 mg accuracy. The concentrations of the methanol solutions before and after each test were calculated by finding their densities. Subsequently, the initial and final mass fractions of the methanol solutions, ω_{init} and ω_{final}, were determined.

Since a hole with a 2-mm diameter was drilled on the top of the anode reservoir to expel the generated carbon dioxide gas, the methanol and water vapor in the reservoir would be lost to the atmosphere together with the carbon dioxide. It was assumed that all the carbon dioxide generated in the anode catalyst layer (ACL) was expelled from the anode reservoir and that the carbon dioxide, water vapor, and methanol vapor were mixed uniformly in the reservoir. The amounts of water and methanol lost by evaporation, $\Delta m_{evap,i}$, are determined by their partial pressures, P_i, and the amount of generated carbon dioxide:

$$\Delta m_{evap,i} = \frac{\int I.dt}{6F} \cdot \frac{P_i}{P_{CO_2}} \cdot M_i \tag{5}$$

in which i can be methanol or water, and P_{CO_2} is the partial pressure of carbon dioxide. The partial pressures of water and methanol are related to the composition of the solution by Raoult's law: the vapor pressure of each component, P_i, will be equal to the saturation vapor pressure of the pure substance, P_i^{sat}, times the mole fraction in the solution, x_i:

$$P_i = x_i P_i^{sat} \tag{6}$$

Since the methanol concentration varied with time during operation, an averaged mole fraction of species i in the solution was utilized by finding the average molar fraction in the solution before and after the test:

$$x_i = \frac{x_{i,int} + x_{i,final}}{2} \tag{7}$$

Then, the partial pressure of carbon dioxide, P_{CO_2}, will be:

$$P_{CO_2} = P_0 - P_{MeOH} - P_{H_2O} \tag{8}$$

in which P_0 is the atmospheric pressure.

The amount of consumed methanol and water by the reaction, $\Delta m_{cons,i}$, is related to the discharge electric quality by:

$$\Delta m_{cons,i} = \frac{\int I \cdot dt}{6F} M_i, \tag{9}$$

The fuel efficiency is defined as the methanol consumed by the reaction divided by the total weight change of methanol in the fuel reservoir:

$$\eta = \frac{\Delta m_{cons,MeOH}}{\Delta m_{tot,MeOH}} \tag{10}$$

3. Results and discussion

3.1. Effect of the methanol barrier layer (MBL) thickness

Three porous PTFE plates with different thicknesses, 1.6, 3.2, and 6.4 mm, were tested as the MBLs. A Nafion® 117 membrane
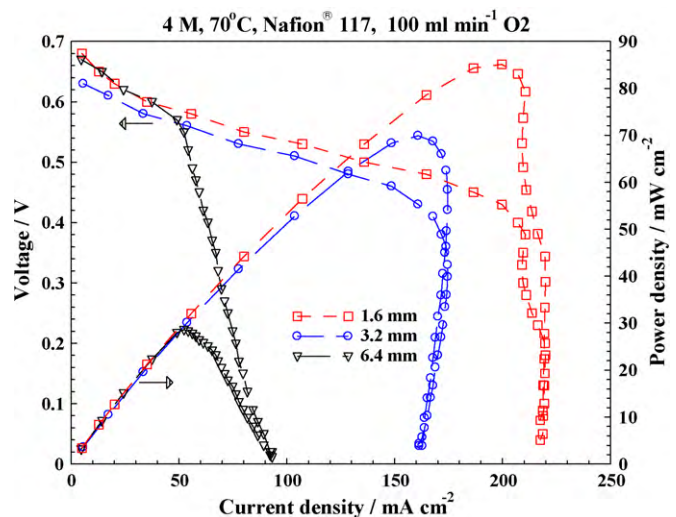

Fig. 2. Performances of a DMFC with different MBLs (Nafion® 117 membrane, 70 °C temperature, 4 M methanol, 100 ml min^{-1} oxygen, and 100% cathode relative humidity).

was used as the electrolyte membrane, and 4 and 16 M methanol solutions were tested.

Fig. 2 shows the fuel cell performance when the cell was fed with the low concentration of 4 M. It is seen that the limiting current density decreased from 217.7 to 169.7 mA cm^{-2} and then to 93.2 mA cm^{-2} when the thickness of the MBL increased from 1.6 to 3.2 mm and then to 6.4 mm. This indicates that, at this low concentration, the methanol crossover from the anode to the cathode was not a big concern, but the insufficient supply of methanol to the anode catalyst layer (ACL) led to concentration polarization at a limiting current density. Therefore, it is clear that the methanol transport resistance from the anode fuel reservoir to the MEA was increased by increasing the thickness of the MBL.

Fig. 3 shows the fuel cell performance when the cell was fed with the high concentration of 16 M. As is shown in Fig. 3, when the MBL thickness increased from 1.6 to 3.2 mm, and then to 6.4 mm, the open circuit voltage (OCV) increased from 0.56 to 0.58 V and then to 0.65 V due to the decrease of methanol crossover, which is shown in Fig. 5(a). Also, the decreased methanol crossover rate led to a
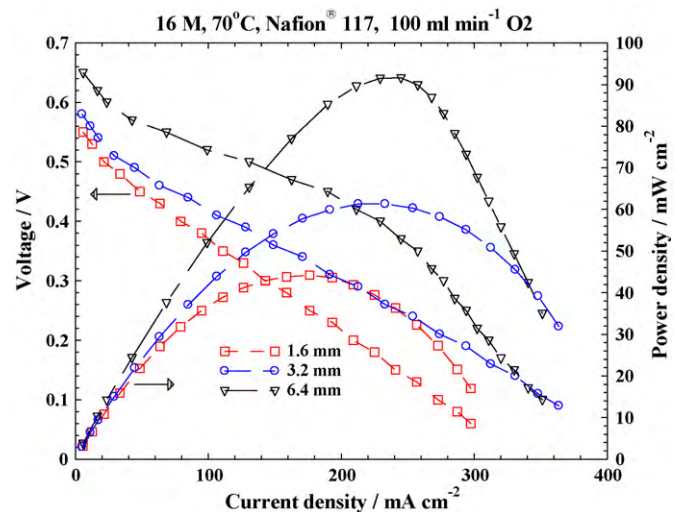

Fig. 3. Performances of a DMFC with different MBLs (Nafion® 117 membrane, 70 °C temperature, 16 M methanol, 100 ml min^{-1} oxygen, and 100% cathode relative humidity).

higher peak power density: the peak power density increased from 44.2 to 61.3 mW cm^{-2}, and then to 91.6 mW cm^{-2} as thicker MBLs were implemented. The limiting current density first increased from 297.4 to 363.6 mA cm^{-2} when the MBL thickness increased from 1.6 to 3.2 mm because of the decreased methanol crossover; and then slightly decreased to 351.3 mA cm^{-2} when the MBL thickness was further increased to 6.4 mm due to the combined effect of lower methanol crossover and insufficient methanol supply to the ACL. The insufficient supply of methanol to the ACL with the 6.4 mm MBL, shown in Fig. 3, indicated that the fuel cell could produce higher performance if the methanol concentration in the anode fuel reservoir was further increased.

Fig. 4 shows the power densities of the HC-DMFC fed with 16 M methanol and the fuel cell discharged at a constant current density of 200 mA cm^{-2}. It is seen that the fuel cell with a thicker MBL yielded a higher average power density; the average power density increased from 44.6 to 60.3 mW cm^{-2}, and then to 81.8 mW cm^{-2} when the MBL thickness increased from 1.6 to 3.2 mm, and then to 6.4 mm. When the MBL thickness was 1.6 mm, a sharp decrease of power density was observed after about 150 min, which indicated that the methanol crossovered faster with a thinner MBL. The corresponding fuel efficiencies and the methanol and water crossover coefficients are shown in Fig. 5. The coefficients of the methanol and water crossover in Fig. 5(a) indicate that the methanol and water crossover decreased with an increased MBL thickness. The methanol crossover coefficient decreased from 0.352 to 0.325 and then to 0.056, and the water crossover coefficient decreased from 0.400 to 0.291, and then to −0.081 when the MBL thickness increased from 1.6 to 3.2 mm and then to 6.4 mm. A negative water crossover coefficient with the 6.4 mm MBL indicated that the overall water flow was from the cathode through the electrolyte membrane and back to the anode.

The methanol and water crossover from the anode catalyst layer, through the membrane, to the cathode is due to three mechanisms: electro-osmotic drag; diffusion by a concentration gradient, ∇C; and convection by the hydraulic pressure gradient, ∇P_1 [22]:

$$\alpha_i = n_{d,i} + \Psi_{C,i}\nabla C_i + \Psi_{P,i}\nabla P_1; \qquad (11)$$

where species i can be methanol or water, the coefficients ψ_C and ψ_P are all positive and related to the Faradic constant, current density, diffusion coefficient, permeability of liquid, density and

Fig. 5. Coefficients of water and methanol crossover and fuel efficiency with different MBLs (Nafion® 117 membrane, 70 °C temperature, 16 M methanol, 100 ml min^{-1} oxygen, and 100% cathode relative humidity, 200 mA cm^{-2} discharging current density).

viscosity of liquid, and the molecular weight of species i. The liquid pressure, P_l, is related to the gas pressure, P_g, and liquid volume fraction, s, by the Leverett Function [23]:

$$P_1 = P_g - P_C = P_g - \phi(1.417s - 2.12s^2 + 1.263s^3) \qquad (12)$$

In which, the effective coefficient of capillary pressure, ϕ, is determined by the surface tension, contact angle, porosity, and permeability of the porous media, and ϕ is negative if the porous medium is hydrophobic. If the gas pressure is assumed to be a constant, a decrease of liquid volume fraction, s, will lead to a lower liquid pressure.

Because the transport resistance of liquid from the anode reservoir to the ACL, and the transport resistance of carbon dioxide gas from the ACL to the anode reservoir were increased by increasing the MBL thickness, the overall liquid saturation in the anode was decreased. Consequently, the water content in the electrolyte membrane, λ, was decreased, which led to a smaller electro-osmotic drag coefficient, n_d [24]. Moreover, the liquid pressure in the ACL was decreased, and the liquid pressure gradient between the cathode and the anode was increased which led to a higher back flow of water to the anode. Both a lower electro-osmotic drag coefficient and a higher water back flow rate caused a lower methanol and water crossover with a thicker MBL. At the same time, the lower methanol and water crossover led to a higher fuel efficiency with a thicker MBL. As is shown in Fig. 5(b), the fuel efficiency increased from 24.2% with a 1.6-mm MBL to 25.2% with a 3.2-mm MBL, and then to 39.3% with a 6.4 mm MBL.
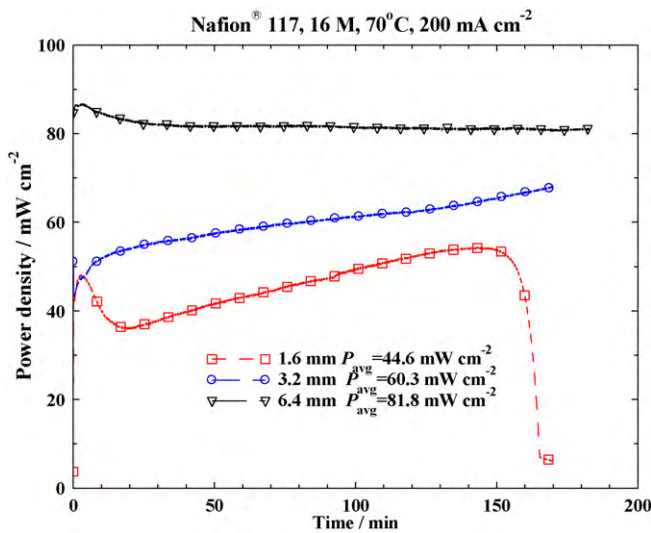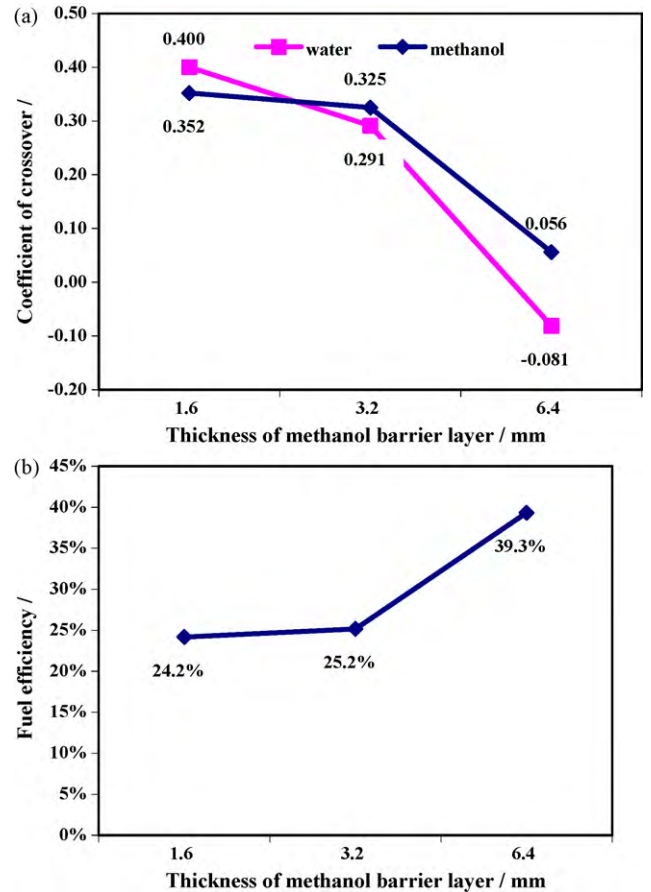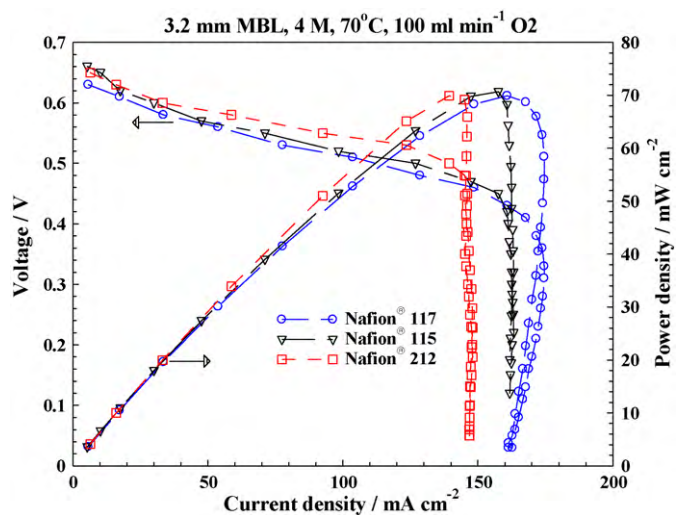
Fig. 4. Power densities of the cell with different MBLs during the constant discharge current density (Nafion® 117 membrane, 70 °C temperature, 16 M methanol, 100 ml min^{-1} oxygen, and 100% cathode relative humidity, 200 mA cm^{-2} discharging current density).

Fig. 6. Performances of a DMFC with different electrolyte membranes (3.2 mm MBL, 70 °C temperature, 4 M methanol, 100 ml min⁻¹ oxygen, and 100% cathode relative humidity).

3.2. Effect of Nafion® membrane thickness

The performances of the DMFC fed with 4 M methanol, utilizing a 3.2-mm thick MBL, and using different electrolyte membranes are compared in Fig. 6. As is shown in Fig. 6, the performances of the DMFC were similar with different electrolyte membranes at a low current density, and the OCV remained approximately 0.68 V. Since the thickness of the MBL, 3.175 mm, is much higher than that of the electrolyte membrane, 50–175 μm, the resistance to methanol diffusion was not significantly affected by changing the electrolyte membrane thickness, which led to similar DMFC performance through the low current density region. However, the limiting current densities slightly increased from 148.0 to 163.3 mA cm⁻² and then to 174.6 mA cm⁻² when the electrolyte membrane changed from Nafion® 212 to Nafion® 115 and then to Nafion® 117. Since the mass transfer resistance was higher with a thicker Nafion® membrane, the water back flow driven by the liquid pressure gradient between the cathode and the anode was lower. Consequently, the methanol supplied from the anode reservoir was less diluted in the ACL by the back flow of water, which led to a higher limiting current density with a thicker Nafion® membrane.

The limiting current density was relatively low with 4 M methanol, which resulted in less water generation at the cathode, and the water back flow rate from the cathode to the anode was small. As a result, the thickness of the electrolyte membrane did not show a significant impact on the methanol crossover and limiting current density. When the methanol concentration was high, such as 16 M, the sufficient supply of methanol to the ACL generated a higher limiting current density. When the DMFC was operated with high-concentration methanol, the electrolyte membrane thickness would have a much more significant effect on the methanol and water crossover, limiting current density, and the overall performance.

The performances of the DMFC fed with 16 M methanol, utilizing a 3.2-mm MBL, and using different electrolyte membranes are compared in Fig. 7(a). The OCV of the fuel cell with different electrolyte membranes remained around 0.55 V, indicating once again, that the methanol crossover rate was almost not affected by the thickness of the electrolyte membrane under open circuit condition. When the current density increased, the difference between the fuel cell performances with different electrolyte membranes increased. First, the voltage dropped faster with a thicker electrolyte membrane due
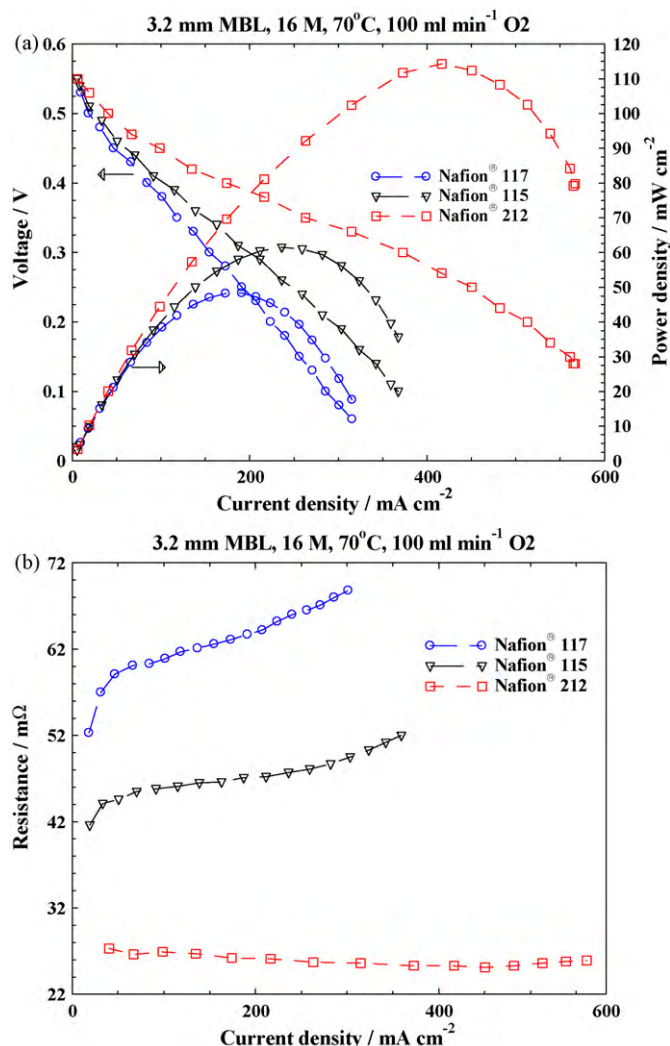

Fig. 7. Performances and internal resistance of a DMFC with different electrolyte membranes (70 °C temperature, 16 M methanol, 100 ml min⁻¹ oxygen, and 100% cathode relative humidity).

to its higher conductive resistance, which is shown in Fig. 7(b). Second, the methanol and water back flow had more significant effects on the overall methanol and water crossover at a higher current density. Consequently, the peak power density sharply decreased from 114.3 mW cm⁻² with Nafion® 212 to 61.0 mW cm⁻² with Nafion® 115, and then to 48.3 mW cm⁻² with Nafion® 117 as shown in Fig. 7(a). The current–resistance curves in Fig. 7(b) showed that the internal resistance increased from 25.7 mΩ with Nafion® 212 to 48.7 mΩ with Nafion® 115, and then to 68.8 mΩ with Nafion® 117, at the current density of 300 mA cm⁻². As was reported in the previous work [22], hydration of the Nafion® membrane was the key factor that determined the performance of the HC-DMFC fed with highly concentrated methanol. The change in internal resistances shown in Fig. 7(b) also proved that more water was required to hydrate the thicker Nafion® membranes because the conductive resistance of the thicker electrolyte membranes, such as Nafion® 115 and Nafion® 117, quickly increased as the current density was increased, while the conductive resistance of the thinner electrolyte membranes, Nafion® 212, remained almost constant while the current density was increased.

In Fig. 8, the power densities during the 3-h test are compared for different Nafion® membranes. As can be seen from the figure, the average power density decreased with an increased Nafion®
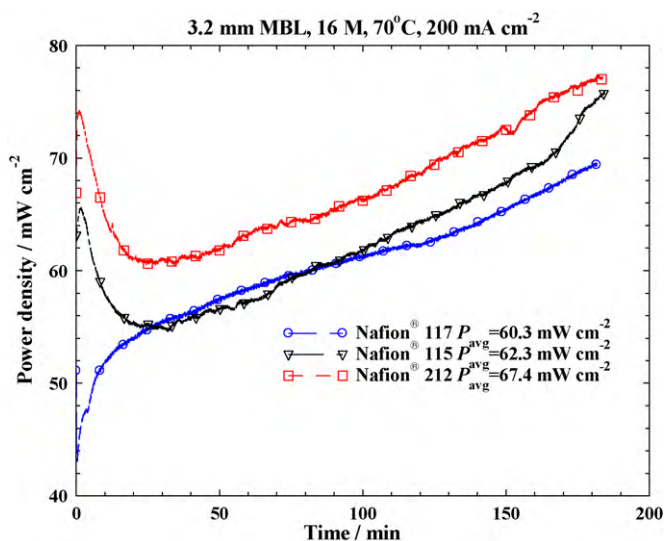
Fig. 8. Power densities of the cells with different Nafion® membranes during the constant discharge current density (3.2 mm MBL, 70 °C temperature, 16 M methanol, 100 ml min⁻¹ oxygen, and 100% cathode relative humidity, 200 mA cm⁻² discharging current density).

Fig. 9. Water and methanol crossover coefficients and fuel efficiencies with different electrolyte membranes (3.2 mm MBL, 70 °C temperature, 16 M methanol, 100 ml min⁻¹ oxygen, and 100% cathode relative humidity, 200 mA cm⁻² discharging current density).

membrane thickness. The average power density decreased from 67.4 mW cm⁻² with Nafion® 212 to 62.3 mW cm⁻² with Nafion® 115, and then to 60.3 mW cm⁻² with Nafion® 117. The water and methanol crossover coefficients, compared in Fig. 9(a), show that the water crossover coefficient increased from −0.126 to −0.101, and then significantly to 0.29, while the methanol crossover coefficient increased from 0.153 to 0.175, and then significantly to 0.325 when the electrolyte membrane changed from Nafion® 212 to Nafion® 115, and then to Nafion® 117. Since a thicker electrolyte membrane causes a higher transport resistance between the anode and the cathode, the effect of water back flow, due to the liquid pressure gradient, was smaller. Subsequently, the decrease of water back flow, associated with a thicker Nafion® membrane, increased the overall water and methanol crossover coefficient, according to Eq. (11). The increase of methanol and water crossover not only limited the cell performance but also lowered the fuel efficiency. The fuel efficiencies of DMFCs with different Nafion® membranes, shown in Fig. 9(b), show that the fuel efficiency decreased from 49.2% with Nafion® 212 to 40.9% with Nafion® 115, and then to 20.6% with Nafion® 117.

The above results indicate that when highly concentrated methanol is fed as fuel, a thicker MBL mainly reduces methanol crossover at the open circuit condition, or low current density, by increasing the mass transport resistance between the anode reservoir and the MEA. A thinner Nafion® membrane will also decrease the methanol and water crossover by enhancing water back flow, especially at high-current densities. Therefore, in an effort to develop the best semi-passive HC-DMFC, a 6.4-mm PTFE as the MBL and Nafion® 212 as the electrolyte membrane was built, and methanol solutions ranging from 4 M to neat methanol were passively supplied from the anode reservoir. The fuel cell operated at 70 °C, and 100 ml min⁻¹ oxygen with 100% relative humidity actively supplied through the cathode serpentine channel.

3.3. HC-DMFCs fed with different concentrations of methanol

The current–voltage curves of the DMFC fed with different methanol solutions are compared in Fig. 10. The OCV decreased from 0.67 to 0.50 V when the methanol concentration increased from 4 M to neat methanol due to the increased methanol
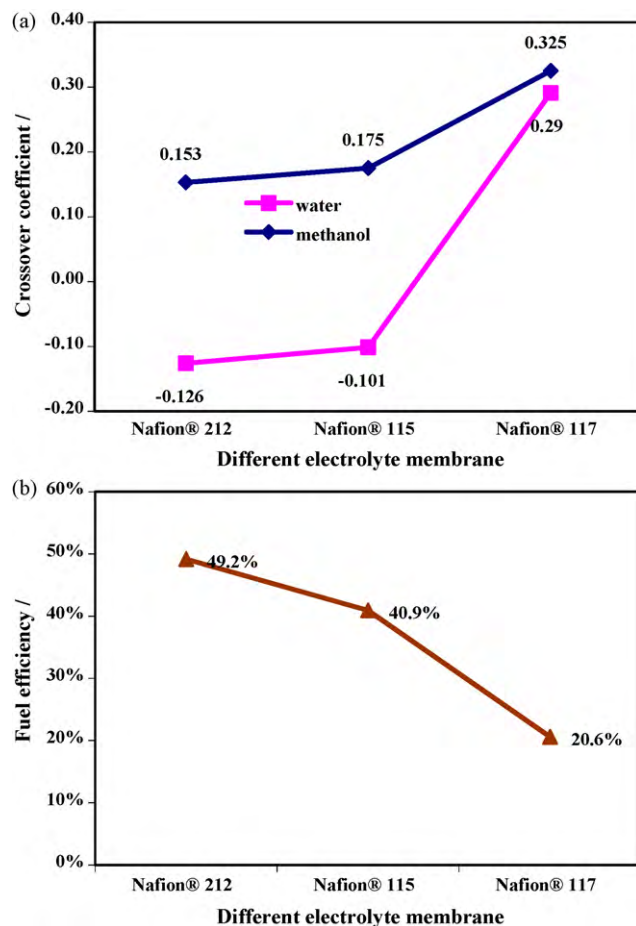
crossover. The limiting current density continuously increased from 84.7 to 494.7 mA cm⁻² and the peak power density continuously increased from 32.9 to 115.8 mW cm⁻² when the methanol concentration increased from 4 to 20 M. When the methanol con-
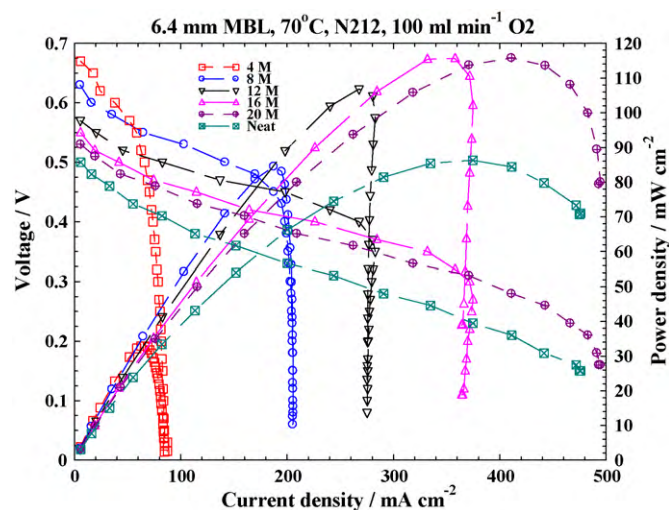

Fig. 10. Performances of a DMFC with Nafion® 212 and 6.4 mm methanol barrier layers (70 °C temperature, 100 ml min⁻¹ oxygen, and 100% cathode relative humidity).

centration increased further from 20 M to neat methanol, the resulting methanol crossover was so high that the limiting current density slightly decreased from 494.7 to 476.0 mA cm^{-2} and the peak power density also decreased from 115.8 to 86.3 mW cm^{-2}. The decreases in the limiting current density and peak power density were caused by insufficient water back flow from the cathode and/or too much methanol crossover, which could be solved by further increasing the anode mass transport resistance or decreasing the back flow resistance.

4. Conclusions

A semi-passive HC-DMFC using porous PTFE plates with different MBL thicknesses, and Nafion® membranes with different thicknesses as the electrolyte membrane was experimentally studied in this work. The effects of the MBL thickness and Nafion® membrane thickness on the cell performance, methanol and water crossover, and fuel efficiency were evaluated. The results are summarized as follows:

(1) Since the thickness of the MBL, 1–6 mm, is much higher than that of the electrolyte membrane, 50–175 μm, the total methanol crossover was mainly determined by the thickness of the MBL rather than the electrolyte membrane under open circuit current or low current density conditions;
(2) a thicker MBL was preferred when highly concentrated methanol was supplied as the fuel to decrease the mass transport resistance between the anode reservoir and the MEA. In our study, the fuel cell adopting a 6.4 mm porous PTFE plate as the MBL gained the best cell performance and highest fuel efficiency when 16 M methanol was supplied to the cell;
(3) a thinner electrolyte membrane, such as Nafion® 212, was preferred in HC-DMFC construction because a thinner Nafion® membrane had a lower conductive resistance, and more importantly, a thinner electrolyte membrane had a lower water back flow resistance from the cathode to the anode and could decrease the overall methanol and water crossover; and

(4) with a 6.4-mm porous PTFE plate as the MBL, and Nafion® 212 as the electrolyte membrane, a semi-passive HC-DMFC produced a maximum power density of 115.8 mW cm^{-2} with 20 M methanol solution passively supplied in the fuel reservoir.

Acknowledgement

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