Effect of membrane thickness on the performance and efficiency of passive direct methanol fuel cells

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Abstract

The use of various Nafion membranes, including Nafion 117, 115 and 112 with respective thicknesses of 175 μm, 125 μm and 50 μm, in a passive direct methanol fuel cell (DMFC) was investigated experimentally. The results show that when the passive DMFC operated with a lower methanol concentration (2.0 M), a thicker membrane led to better performance at lower current densities, but exhibited lower performance at higher current densities. When the methanol concentration was increased to 4.0 M, however, the three membranes exhibited similar cell voltages over a wide range of current densities. In contrast, this work also shows the polarization behaviors in an active DMFC when the three membranes were substantially different. Finally, the test of fuel utilization indicates that the passive DMFC with a thicker membrane exhibited higher efficiency.
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1. Introduction

Compared with hydrogen, methanol, as a liquid non-fossil fuel for fuel cells, offers many advantages, such as high energy density (6100 Wh kg^{-1} at 25 °C), ease in storage and transport, as well as low cost. Therefore, direct methanol fuel cells (DMFCs) based on Nafion membranes are more suitable for powering small portable devices such as telecommunications, laptop and other consumable electronic devices. Over the past decade, DMFCs have been extensively studied [1–7]. More recently, a so-called passive DMFC has been proposed and investigated [8–15]. In passive-feed DMFCs, since external pumps and other ancillary devices are completely removed, the fuel supply relies on the diffusion from a built-in fuel reservoir only, while the oxidant is supplied from the ambient air. Therefore, the most striking feature of the passive DMFC is that it has much simpler structure and more compact system design than active DMFCs. Moreover, the

parasitic power loss from ancillary devices, which is significant in active DMFCs, is eliminated in passive DMFCs. For these reasons, the passive DMFC has been considered as a more promising power source for future advanced electronic devices.

Presently, one of the most challenging issues for DMFCs (both active and passive) that employ Nafion membranes is methanol crossover, which results not only in a fuel loss, but also a decrease in the overall cell voltage due to the mixed potential on the cathode. Methanol crossover from the anode compartment through the membrane to the cathode compartment occurs in part because of molecular diffusion and in part because of the electro-osmotic drag. It has been shown that the former mechanism dominates under the open circuit condition and at low current densities, whereas the latter one becomes more important at high current densities [16]. Methanol crossover depends on a number of factors; the most important ones are the membrane permeability/thickness, the concentration of methanol in the fuel feed, the operating temperature and the performance of the anode itself. The membrane is a very important factor regarding the methanol

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crossover problem. Thicker membranes give a lower rate of methanol crossover but tend to have higher resistances, degrading the cell performance. Therefore, there exists an optimal thickness for the current Nafion membranes, which gives the best performance.

The use of three kinds of commercially available Nafion membranes, including Nafion 117, 115 and 112 with respective thicknesses of 175 μm, 125 μm and 50 μm, in active DMFCs has been extensively studied [17–21]. Ren et al. [19] and Jung et al. [20] tested these membranes in an active DMFC operating at 110–130 °C. Their experiments revealed that the cell performance increased with decreasing membrane thickness as a result of lower resistances. The best performance was obtained using the Nafion 112 membrane. They also found that at higher operating temperatures, the performance difference between the different membranes became much larger. An improvement in more than $100\,mW\,cm^{-2}$ at 0.5 V could be achieved when Nafion 112 replaced Nafion 117 at 130 °C. Hikita et al. [21] found that the rate of methanol crossover decreased with increasing current density, indicating that the influence of methanol crossover becomes less important at high current densities.

To the best of our knowledge, the effect of Nafion membrane thickness on the performance of passive DMFCs has never been reported in the literature. Most recently, we tested Nafion 115 in a passive DMFC operated with different methanol concentrations [15] and found that the cell performance was improved substantially with the increased methanol concentration. We further found that the better performance with higher methanol concentrations was mainly attributed to the increased cell operating temperature as a result of the exothermic reaction between the permeated methanol and oxygen on the cathode. Therefore, it can be speculated that the effect of membrane thickness on the performance of a passive DMFC is different from that on an active DMFC, as the cell operating temperature is inherently coupled with the rate of methanol crossover in the passive DMFC. In this work, we tested the effect of membrane thickness on the performance of a passive DMFC and show how the rates of methanol crossover and the cell operating temperatures associated with different membranes affect the polarization behavior of the cell. Moreover, we also show the effect of membrane thickness on fuel utilization.

2. Experimental

2.1. Membrane and electrode assembly (MEA)

Three Nafion membranes, including Nafion 117, 115 and 112, whose thicknesses in the dry state are 175 μm, 125 μm and 50 μm, respectively, were used in this work. These membranes were pretreated before final fabrication in 5 vol.% H_2O_2, DI water, 0.5 M H_2SO_4 and DI water for 1 h in turn, and were kept in DI water prior to the fabrication of MEAs. Single-side ELAT electrodes, by E-TEK Corp., were em-

ployed in both the anode and the cathode. The catalyst loading on the anode was $4.0\,mg\,cm^{-2}$ with PtRu black (1:1, a/o), while the catalyst loading on the cathode was $2.0\,mg\,cm^{-2}$ using 40 wt.% Pt on Vulcan XC-72. In addition, the loading of dry Nafion® ionomer on the surface of each electrode was $0.8\,mg\,cm^{-2}$. MEAs with an active area of $4.0\,cm^2$ were fabricated by hot pressing at 135 °C and 8 MPa for 3.0 min. More detailed information about the MEA fabrication can be found elsewhere [2].

2.2. Single cell fixture

As shown in Fig. 1, the MEA mentioned above was sandwiched between two electrical current collectors, which were made of 316 stainless steel plates of 1.0 mm in thickness. A plurality of parallel channels was machined by a wire cutting technique for both current collectors, serving as the passages of fuel and oxidant, which resulted in an open ratio of 48%. A 200-nm platinum layer was sputtered onto the surface of 316 stainless steel plates to reduce the contact resistance with the electrodes. The cell was held together between an anode and a cathode fixture, both of which were made of transparent acrylic plates. A 3.0 mL methanol solution reservoir was built in the anode fixture. 2.0 M or 4.0 M methanol was diffused into the catalyst layer from the built-in reservoir, while oxygen, from the surrounding air, was diffused into the cathode catalyst layer through the opening of the cathode fixture. The cell temperature was measured by a miniature thermocouple (0.0005-in. thick, CO-1T, OMEGA), which was installed between the anode current collector and the MEA.

The limiting current density method [22] in the permeation cell was employed to evaluate methanol crossover of the three membranes in this work. Humidified nitrogen at room temperature was passed through the cathode side in the permeation cell at a rate of $100\,mL\,min^{-1}$, while 2.0 M or 4.0 M methanol was passed through the anode side at $1.0\,mL\,min^{-1}$. An external voltage of polarization at $1\,mV\,s^{-1}$ by 273A EG&G potentiostat was imposed on the cell. The value of current density at 0.9 V was chosen to represent the limiting current density.

2.3. Electrochemical instrumentation and test conditions

An Arbin BT2000 electrical load interfaced to a computer was employed to control the condition of discharging and record the voltage–current curves. For each discharging current point along the I–V curve, a more than 40-s waiting time was used to obtain the stable voltage. The internal resistance of the cell was measured by the Arbin BT2000 built-in function. To this end, ten continuous current pulses with amplitude of 0.2 A were applied to the cell; the internal resistance reported in this work are the average data over the ten pulses.

All the experiments of the passive DMFCs were performed at room temperatures of 20–22 °C and the relative humidity of 50–70%. Prior to the passive DMFC performance test,
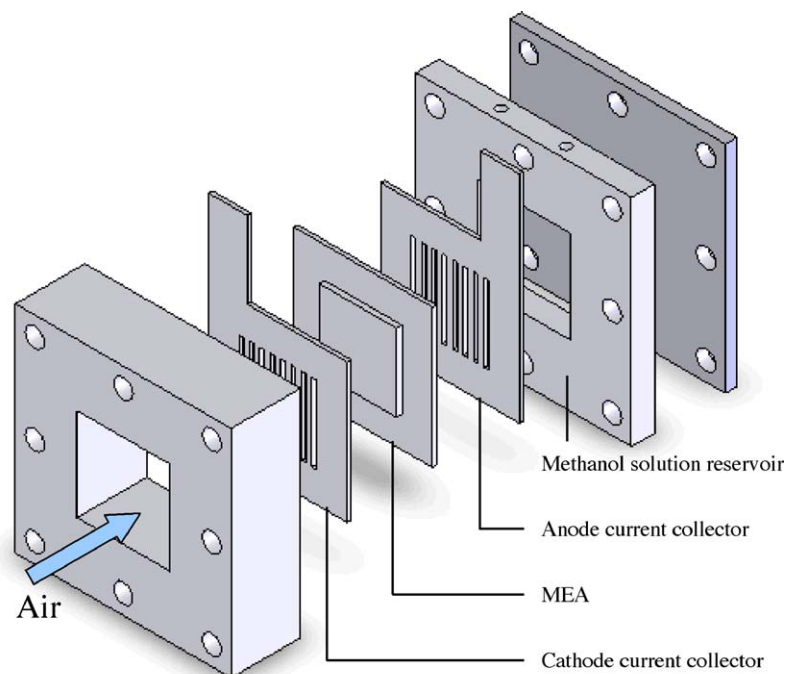
Fig. 1. Schematic of the passive DMFC.

the MEA was installed in an active cell fixture and was activated by discharging at $100\,mA\,cm^{-2}$ at $75\,^{\circ}C$ for about 5 h. During the activation period, 1.0 M methanol was fed at $1.0\,mL\,min^{-1}$, while oxygen was supplied under atmospheric pressure at a flow rate of $50\,mL\,min^{-1}$.

## 3. Results and discussion

3.1. Cell performance

In a typical DMFC (regardless of active or passive feed mode), in addition to electrochemical reactions of methanol oxidation on the anode and oxygen reduction on the cathode, the permeated methanol from the anode to the cathode also reacts directly with oxygen on the cathode, i.e.:

$$CH_3OH_{(l)} + \tfrac{3}{2}O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}. \qquad (1)$$
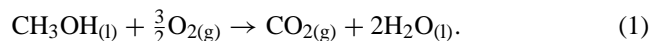
Reaction (1) is accompanied with a heat value of $\Delta H^{\circ}_{298\,K} = 726\,kJ\,mol^{-1}$, which is usually much larger than the heat generated from the voltage polarizations of the anode and cathode as well as Joule heating from the different components of the MEA. Therefore, reaction (1) has an important impact on the cell operating temperature and the cell performance. In an active-feed DMFC, the cell operating temperature is virtually controlled by forced convection of the circulated methanol solution and oxygen/air flowing through the flow fields of a cell/stack. In a passive DMFC, however, the cell operating temperature varies passively, primarily depending on the ambient conditions. Thus, once a passive DMFC starts

to operate, its operating temperature is expected to rise, primarily caused by reaction (1). In this work, the cell operating temperature was monitored with a tiny thermocouple, which was installed between the current collector and the anode. Fig. 2 presents the transient operating temperature of the passive DMFCs with different membranes (Nafion 117, 115 and 112) with either 2.0 M (Fig. 2a) or 4.0 M (Fig. 2b) methanol injected into the fuel tank. It is seen that the operating temperature increased rapidly once the fuel cell started to operate; the thinnest membrane (Nafion 112) yielded the rapidest temperature rise, indicating that the heat generation rate with this membrane is the highest. After the rapid rise in the initial operation, the cell operating temperature rise became slower and eventually reached a steady value corresponding to each membrane, when the heat generated in the cell and the heat loss to the surrounding air was balanced. The thinnest membrane (Nafion 112) yielded the highest operating temperature. A comparison between Fig. 2a and b indicates that a higher methanol concentration led to a higher cell operating temperature. As shown in Fig. 2b, with 4.0 M methanol solution, the cell operating temperatures corresponding to Nafion 117, 115 and 112 were $28.3\,^{\circ}C$, $31.6\,^{\circ}C$ and $34.0\,^{\circ}C$, respectively, which were $5\,^{\circ}C$ higher than those corresponding to each membrane when 2.0 M methanol solution was used.

To confirm that the higher operating temperature with a thinner membrane was primarily caused by the higher rate of methanol crossover through the thinner membrane, we measured the rates of methanol crossover through the different membranes in the permeation cell. The results are shown in Fig. 3, which shows that the limiting current density with each methanol concentration increased with decreasing membrane
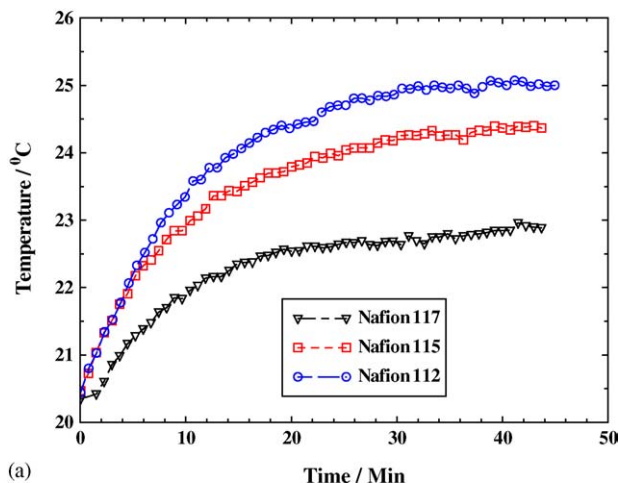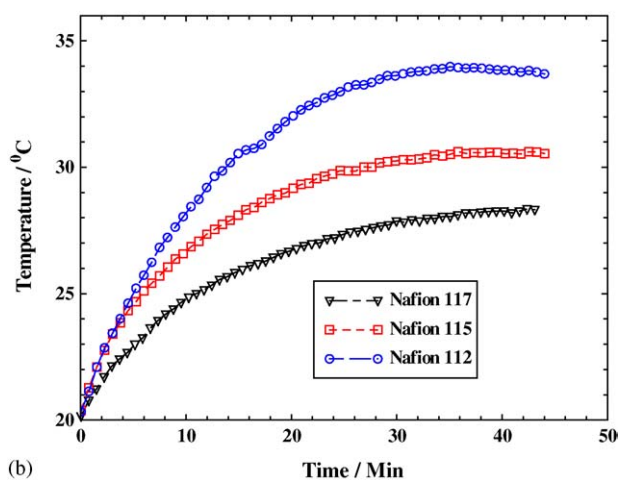
Fig. 2. Variation in cell operating temperature when the cell started to operate under the open circuit condition with: (a) 2.0 M methanol and (b) 4.0 M methanol.

thickness; the limiting current density for Nafion 112 is almost the double of that for Nafion 117. Fig. 3 also indicates that a higher methanol concentration led to a higher limiting current density or a higher rate of methanol crossover. The results presented in Fig. 3 verify that the higher operating tem-
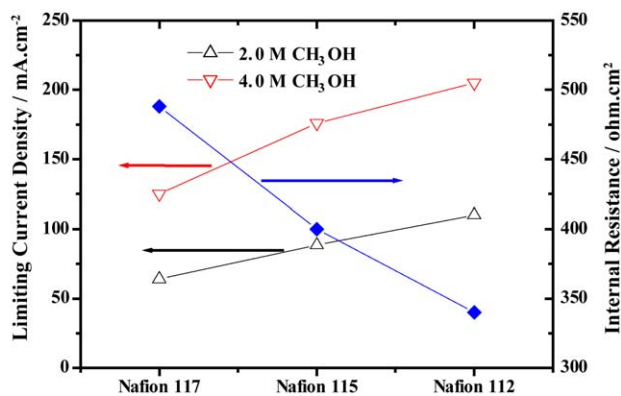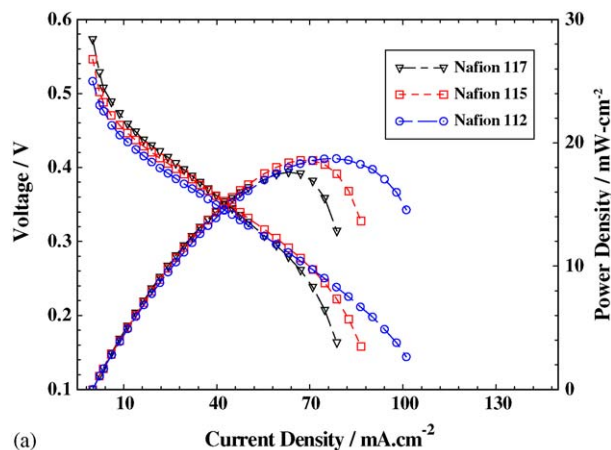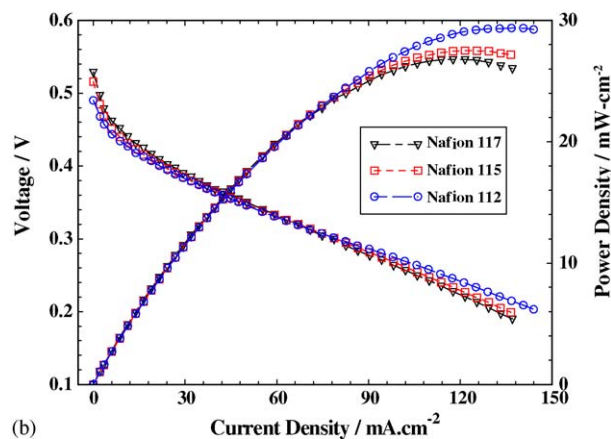

Fig. 3. Limiting current density and internal resistance of the cell with various membranes.

Fig. 4. Polarization and power density curves of the passive DMFC with various membranes operated with: (a) 2.0 M methanol and (b) 4.0 M methanol.

perature associated with a thinner membrane was caused by the corresponding higher rate of methanol crossover, which resulted in a higher exothermic reaction rate between the permeated methanol and oxygen on the cathode.

Fig. 4 presents polarization and power density curves of the passive DMFCs with Nafion 117, 115 and 112 operated with 2.0 M and 4.0 M methanol. The data were collected when the cell temperature reached the steady-state value corresponding to each membrane under the open circuit condition. As seen from Fig. 4a for the case of 2.0 M methanol, the open circuit voltage (OCV) dropped from 0.573 V to 0.546 V and 0.516 V when Nafion 117 was replaced by Nafion 115 and 112, respectively. When the cell discharged (current density higher than zero), the effect of the membrane thickness on cell performance can be divided into two distinct regions. In the low current density region ($<40\,\mathrm{mA\,cm^{-2}}$), the cell with a thicker membrane gave a better performance, whereas in the high current density region, the cell with a thinner membrane yielded a better performance. As shown in Fig. 3, the membrane change leads not only to a change in the rate of methanol crossover, but also to a change in the internal resistance of the cell. On one hand, due to the higher rate of methanol crossover, a thinner membrane tends to cause a larger mixed potential on the cathode, degrading the cell

performance. On the other hand, the use of a thinner membrane will yield a smaller internal cell resistance and a higher operating temperature, both of which tend to increase the cell performance. The results presented in Fig. 4a suggest that the predominant factor affecting the cell performance of the passive DMFC varied with current density. Under the OCV and low current density conditions, Fig. 4a indicates that the mixed potential problem associated with the thinner membrane (Nafion 112) is more significant than the improved kinetics of electrochemical reactions as a result of the increased temperature with the use of the thinner membrane. At moderate and higher current densities, however, the effect of the internal resistance becomes predominant; thus, the use of the thinner membrane yielded a higher cell performance. It should also be mentioned that the rate of methanol crossover decreases with increasing current density [21]. This might also contribute to the improved performance with the use of the thinner membrane at higher current densities.

We now turn our attention to the polarization and power density curves shown in Fig. 4b when methanol concentration was increased from 2.0 M to 4.0 M. The OCV corresponding to Nafion 117, 115 and 112 were 0.529 V, 0.516 V and 0.490 V, which are significantly lower than those with 2.0 M methanol. The polarization behavior corresponding to each membrane was basically similar to that with lower methanol concentration. For example, as compared with the thicker membranes (Nafion 115 and 117), the thinner membrane (Nafion 112) still exhibited lower performance at lower current densities, but higher performance at higher current densities. A peak power density of 29.5 mW cm^{-2} was achieved for the cell with Nafion 112 to operate with 4.0 M methanol, which is significantly higher than the value (18.7 mW cm^{-2}) with 2.0 M methanol operation. In particular, it is interesting to note that the significant difference in polarization behavior between the lower and higher methanol concentrations is that with higher methanol concentration, the performance difference caused by the various membranes became much smaller within the entire current density range; the three membranes exhibited similar performance. This behavior suggests that membrane thickness has little effect on the performance of passive DMFCs that operate with higher methanol concentrations. To compare the effects of membrane thickness on passive and active DMFCs, we also tested the three Nafion membranes in an active DMFC that operated with 4.0 M methanol fed at 1.0 mL min^{-1} at 40 °C and at an oxygen flow rate of 50 mL min^{-1}. The results are shown in Fig. 5, which clearly shows that the use of the different membranes made substantial differences in the performance of the active DMFC that operated with higher methanol concentrations, particularly at high current densities; the difference in the peak power density between Nafion 117 and 112 is more than 10 mW cm^{-2}. Therefore, the passive DMFCs operated with higher methanol concentrations are relatively less sensitive to the change in membrane thickness than active DMFCs. This unique feature of the passive DMFCs can be explained as follows.
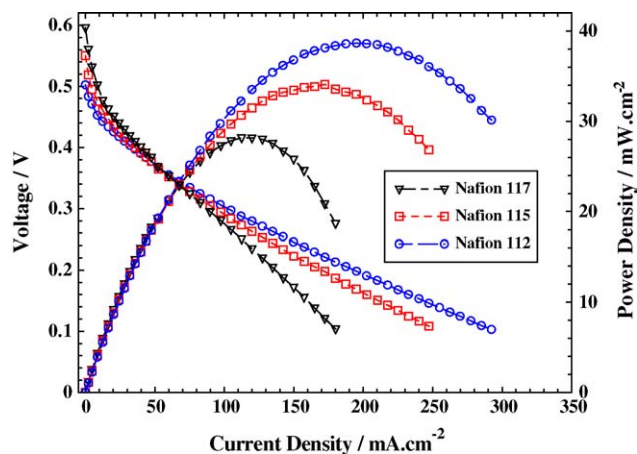

Fig. 5. Polarization and power density curves of the active DMFC with various membranes operated with 4.0 M methanol at 1.0 mL min^{-1} at 40 °C and with an oxygen flow rate of 50 mL min^{-1}.

Under the OCV condition and at low current densities, the improved kinetics of electrochemical reactions as a result of the increased operating temperature with the use of Nafion 112 becomes comparable to the voltage decline caused by the mixed potential. As a result, at low current densities, the cell voltage with Nafion 112 becomes closer to that with Nafion 117. At higher current densities, although Nafion 112 will yield a better performance due to the smaller internal cell resistance and the increased operating temperature associated with the higher rate of methanol crossover, the enlarged mixed potential on the cathode with this thinner membrane tends to bring the cell voltage to that with Nafion 117. In the active DMFCs, since the operating temperature was fixed, the distinctive polarization behaviors with the different membranes were caused by the difference in the cell internal resistance and the variation in the mixed potential as a result of different rates of methanol crossover in the different membranes.

3.2. Fuel utilization

Fig. 6 shows the transient discharge current of the passive DMFCs with the various membranes at a constant voltage (0.35 V) with a start from the cell to be fueled with 3.0 mL methanol solution at 2.0 M (Fig. 5a) and 4.0 M (Fig. 5b). It is seen that the discharging current for all the membranes increased rapidly in the early stage, reached a peak and decreased gradually toward zero as the methanol concentration in the fuel tank decreased. The corresponding transient operating temperatures are shown in Fig. 7. It is found that the transient cell operating temperature varied with a trend similar to the transient discharging current shown in Fig. 6. This behavior indicates that the current differences among the different membranes can be attributed to the differences in the temperature variation and mixture potential caused by the different rates of methanol crossover. The discharge capacity
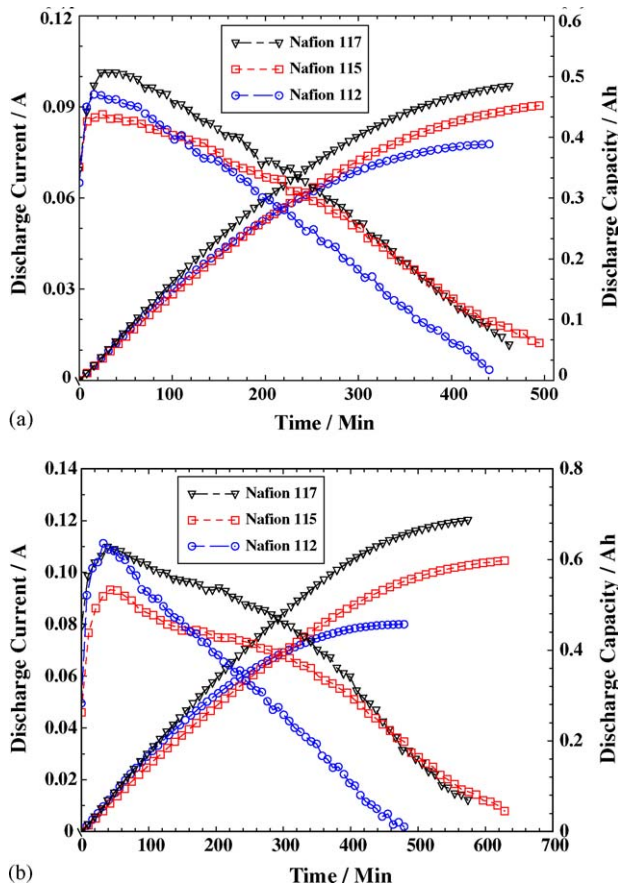
Fig. 6. Transient discharging current and discharge capacity at a constant voltage (0.35 V) with a start from the cell to be fueled with 3.0 mL methanol solutions with various membranes: (a) 2.0 M methanol and (b) 4.0 M methanol.
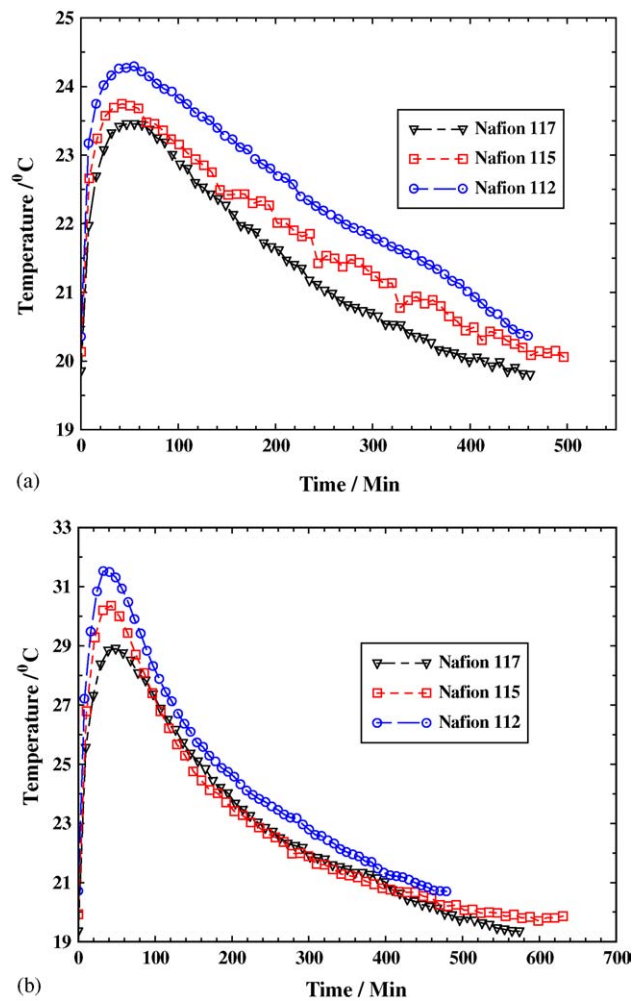

Fig. 7. Transient operating temperature of the cell with different membranes to be discharged at a constant voltage (0.35 V) with a start from the cell to be fueled with 3.0 mL methanol solutions: (a) 2.0 M methanol and (b) 4.0 M methanol.

of the passive DMFCs with various membranes is also shown in Fig. 6. Although all the discharge capacity increased with time, the final value after methanol in the built-in reservoir was exhausted drastically depends on the membrane thickness. The passive DMFCs with the Nafion 117 that have less methanol crossover rate give the largest discharge capacity whether in 2.0 M or 4.0 M methanol.

To investigate the fuel utilization, we define the Faradic efficiency as:

$$\eta = \frac{\text{discharging capacity (Ah)}}{\text{theoretical discharging capacity (Ah)}} = \frac{\int_0^t i(t)\,dt}{6C_M V_M F} \tag{2}$$

where t is the time of the discharging process, $i(t)$ the transient discharging current, C_M the initial methanol concentration, V_M the methanol solution volume and F is the Faraday constant. The Faradic efficiency defined in Eq. (2) indicates the ratio of the actual discharging capacity to the theoretical discharging capacity.

The Faradic efficiencies of the passive DMFCs with the different membranes at 2.0 M and 4.0 M calculated by Eq. (2) are shown in Fig. 8. It is observed that there exist substantial
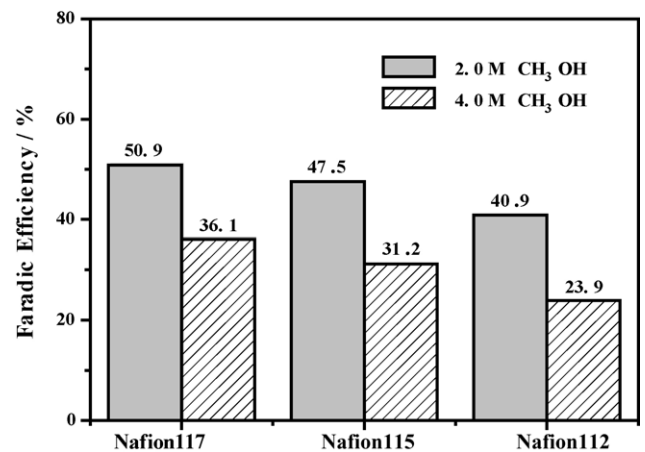

Fig. 8. Faradic efficiency of the passive DMFCs with various membranes fueled with 3.0 mL, 2.0 M and 4.0 M methanol solutions and discharged at a constant voltage (0.35 V).

differences in the cell efficiency among the different membranes; the thickest membrane (Nafion 117) exhibited the highest efficiency, whereas the thinnest membrane (Nafion 112) yielded the worst efficiency. The Faradic efficiencies of the cells with all the membranes were decreased by about 15% when methanol concentration was increased from 2.0 M to 4.0 M. In particular, only 23.9% methanol was utilized in the cell with Nafion 112 and 4.0 M methanol, while the remaining of the fuel permeated to the cathode and reacted with oxygen directly, generating heat, as indicated by Eq. (1). The results presented in Fig. 8 indicate that to achieve higher efficiency, a thicker membrane for passive DMFCs would be recommended. In addition, the thicker membrane yields cell voltages similar to those of thinner membranes over a wide range of current densities as described in Section 3.1. Therefore, the thicker Nafion membrane in passive DMFCs operated with higher methanol concentration is preferable as higher cell performance and higher methanol utilization are required simultaneously.

4. Concluding remarks

The use of various membranes, including Nafion 117, 115 and 112, in a passive DMFC has been evaluated in this work. The results have revealed that there exists a complicated relationship between the cell operating temperature and the mixed potential on the cathode caused by different rates of methanol crossover through the different membranes. It has been shown that when the passive DMFC operated with a lower methanol concentration (2.0 M), at lower current densities, the cell with a thicker membrane gave better performance, whereas at higher current densities, the cell with a thinner membrane yielded better performance. In particular, it has been demonstrated that at higher methanol concentrations, the three membranes yielded similar cell voltages over a wide range of current densities; a maximum power density of about 29.5 mW cm^{-2} was achieved with 4.0 M methanol operation. Therefore, the passive DMFCs operated with higher methanol concentrations are relatively less sensitive to the change in membrane thickness than active DMFCs. The fuel utilization tests have shown that the thickest membrane (Nafion 117) exhibited the highest efficiency, whereas the thinnest membrane (Nafion 112) yielded the lowest efficiency. Since using a thicker membrane would yield higher cell efficiency and yet would exhibit more or less the same cell performance as that using thinner membranes, a thicker

membrane is recommended for passive DMFCs that operate with high methanol concentrations.

References

[1] R. Dillon, S. Srinivasan, A.S. Arico, V. Antonucci, J. Power Sources 127 (2004) 112–126.
[2] H. Yang, T.S. Zhao, Q. Ye, J. Power Sources 139 (2005) 79–90.
[3] Q. Ye, T.S. Zhao, H. Yang, J. Prabhuram, Electrochem. Solid-State Lett. 8 (2005) A52–A54.
[4] Q. Ye, T.S. Zhao, Electrochem. Solid-State Lett. 8 (2005) A211–A214.
[5] H. Yang, T.S. Zhao, Q. Ye, J. Power Sources 142 (2005) 117–124.
[6] H. Yang, T.S. Zhao, Q. Ye, Electrochim. Commun. 6 (2004) 1098–1103.
[7] J.G. Liu, Z.H. Zhou, X.S. Zhao, Q. Xin, G.Q. Sun, B.L. Yi, Phys. Chem. Chem. Phys. 6 (2004) 134–137.
[8] H. Chang, J.R. Kim, J.H. Cho, H.K. Kim, K.H. Choi, Solid State Ionics 148 (2002) 601–606.
[9] A. Bulm, T. Duvdevani, M. Philosoph, N. Rudoy, E. Pled, J. Power Sources 117 (2003) 22–25.
[10] C.Y. Chen, P. Yang, J. Power Sources 123 (2003) 37–42.
[11] G.G. Park, T.H. Yang, Y.G. Yoon, W.Y. Lee, C.S. Kim, Int. J. Hydrogen Energy 28 (2003) 645–650.
[12] J. Han, E.S. Park, J. Power Sources 112 (2002) 477–483.
[13] D. Kim, E.A. Cho, S.A. Hong, I.H. Oh, H.Y. Ha, J. Power Sources 130 (2004) 172–177.
[14] J.G. Liu, G.G. Sun, F.L. Zhao, G.X. Wang, G. Zhao, L.K. Chen, B.L. Yi, Q. Xin, J. Power Sources 133 (2004) 175–180.
[15] J.G. Liu, T.S. Zhao, R. Chen, C.W. Wong, Electrochem. Commun. 7 (2005) 288–294.
[16] R.Z. Jiang, D. Chu, J. Electrochem. Soc. 151 (2004) A69–A76.
[17] S. Slade, S.A. Campbell, T.R. Ralph, F.C. Walsh, J. Electrochem. Soc. 149 (2002) A1556–A1564.
[18] J. Ling, O. Savadogo, J. Electrochem. Soc. 151 (2004) A1604–A1610.
[19] X.M. Ren, M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 143 (1996) L12–L15.
[20] D.H. Jung, C.H. Lee, C.S. Kim, D.R. Shin, J. Power Sources 71 (1998) 169–173.
[21] S. Hikita, K. Yamane, Y. Nakajima, JSAE Rev. 22 (2001) 151–156.
[22] X.M. Ren, T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, J. Electrochem. Soc. 147 (2000) 466–474.