Effects and properties of various molecular weights of poly(propylene oxide) oligomers/Nafion® acid–base blend membranes for direct methanol fuel cells

Chen-Chi M. Ma[a,*], Yi-Hsiu Hsiao[a], Yu-Feng Lin[a], Chuan-Yu Yen[a], Shu-Hang Liao[a], Cheng-Chin Weng[a], Ming-Yu Yen[a], Min-Chien Hsiao[a], Fang-Bor Weng[b]

[a] Department of Chemical Engineering, National Tsing Hua University, Hsin-Chu 30043, Taiwan, ROC
[b] Fuel Cell Center, Yuan Ze University, Tao-Yuan 32003, Taiwan, ROC

ABSTRACT

Various molecular weights of poly(propylene oxide) diamines oligomers/Nafion® acid–base blend membranes were prepared to improve the performance of Nafion® membranes in direct methanol fuel cells (DMFCs). The acid–base interactions were studied by Fourier transform infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC). The performance of the blend membranes was evaluated in terms of methanol permeability, proton conductivity and cell performance. The proton conductivity was slightly reduced by acid–base interaction. The methanol permeability of the blend D2000/Nafion® was $8.61 \times 10^{-7} \, cm^2 \, S^{-1}$, which was reduced 60% compared to that of pristine Nafion®. The cell performance of D2000/Nafion® blend membranes was enhanced significantly compared to pristine Nafion®. The current densities that were measured with Nafion® and 3.5 wt% D2000/Nafion® blend membranes were 62.5 and 103.5 mA cm^{-2}, respectively, at a potential of 0.2 V. Consequently, the blend poly(propylene oxide) diamines oligomers/Nafion® membranes critically improved the single-cell performance of DMFC.

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1. Introduction

The direct methanol fuel cell (DMFC) is an attractive candidate for the mobile energy source due to its unique properties such as easy fuel storage, low operating temperature, and high design flexibility [1]. As the key part of DMFC, the polymer electrolyte membrane (PEM) is used between the anode and cathode to provide proton conductivity and to prevent the internal electronic current between the two electrodes [2].

Nafion®, a perfluorosulfonic acid polymer developed by DuPont Co., is the most frequently used PEM in fuel cells. Nafion® exhibits sufficient proton conductivity at optimal water content and is thermally, chemically and oxidatively stable. However, it suffers from high methanol crossover [3]. This drawback leads to decrease not only in the entire cell performance but also in the fuel efficiency. Two different methods can be utilized to solve this problem of methanol crossover. The first method is developing new synthetic polymeric membranes that have ionic cluster with a small percolation size [4], such as sulfonated poly(ether ether ketone) (PEEK) [5,6], poly(arylene ether sulfone) [7,8], and their blends or copolymerizations with other polymeric materials

[9–11]. The second method is modifying the Nafion® membranes by surface treatment or by blending them with other polymer materials [12,13].

Currently, a wide variety of polymer blends have been developed to produce materials with enhanced chemical and physical properties [14]. However, the development of blends is severely limited by the incompatibility of different polymers [15]. Thus, when blending dissimilar polymers, the miscibility is governed by some specific molecular interactions, such as hydrogen-bonding interaction [3] and acid–base interaction [15]. Wycisk et al. [16] prepared Nafion®/polybenzimidazole (Nafion®/PBI) membrane blends, and found that the membrane selectivity was up to four times greater than that of Nafion® 117.

In order to search the optimized condition of the proton exchange membrane for DMFC application, Nafion® polymer has been modified with various molecular weights of poly(oxypropylene) diamines (abbreviated as POP-diamines). The optimization between proton conductivity (C) and methanol permeability (P), i.e. the C/P ratio (Δ), is still a challenging task, since the hydrated proton and methanol have similar transport phenomenon through membrane. In the present work, a series of poly(oxypropylene) diamines (Mw = 230, 400, and 2000) were used to blend with Nafion® as proton exchange membranes. Good compatibility of the components was evident because of following two reasons: (i) the acid–base interactions between amines and sulfonic

acid protons; (ii) the backbone of poly(oxypropylene) diamines has the same structure as the side chain of poly(oxypropylene) as Nafion®. Indeed, in our previous work [18], hydrophilic region of the backbone of poly(oxypropylene) diamines was highly compatible with the side chain of Nafion®. It means that the acid–base interaction occurs in the cluster of Nafion®. This phenomenon would possibly reduce the channel size of Nafion® and restrict the mobility of the molecules in the channel; consequently, methanol crossover will be decreased due to smaller cluster of Nafion®.

In addition, the influence of the molecules with different chain lengths (D230, D400, and D2000) is also notable. The blend membranes were analyzed by Fourier transform infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC). The effect of poly(oxypropylene) diamines blending with Nafion® membranes on the methanol permeability and proton conductivity has been investigated. The performance of these blend membranes in DMFC has been evaluated and the results will be discussed.

2. Experimental

2.1. Preparation of composite membrane

Poly(oxypropylene)-backbone diamines with the weight average molecular weight, $M_w = 230$, 400, and 2000, were abbreviated as D230, D400, and D2000, which were received from Huntsman Chemical Co., Philadelphia, Pennsylvania (USA). To prepare the composite membranes, D230, D400 and D2000 were blended with 5 wt% Nafion® solution (DuPont Co., USA), and then stirred and degassed by ultrasonication. The quantities of POP-diamines were 1.98, 2.54, 3.50, and 5.73 wt%. Then the blends were slowly poured into a glass dish in an amount that would provide a thickness of ca. 120 μm of the formed blend membrane. The filled glass dish was placed on the leveled plate of a vacuum-dry oven, and then was dried at 50 °C to evaporate most of the solvent. Finally, the residual solvent in the membrane was completely removed by evacuation at 120 °C for 12 h.

2.2. FT-IR measurement

FT-IR spectra of the composite membranes were recorded between 1400 and 500 cm^{-1}, on a Nicolet Avatar 320 FT-IR spectrometer (USA). The polymer solutions were casted onto the KBr pellet, and then dried about 5 min to evaporate the solvent. A minimum of 32 scans was signal-averaged with a resolution of 1 cm^{-1} at the 1400–500 cm^{-1} range.

2.3. Differential scanning calorimeter measurement

A differential scanning calorimeter (Q10, TA Instruments, USA) was utilized to study the thermal properties of the composite blend membrane. The heating rate was 10 °C min^{-1} within a temperature range of 50–250 °C.

2.4. SEM

Scanning electron microphotographs (HITACHI S-4700 SEM) were used to analyze the morphology of the cross-section of the blending membranes. The cross-sections were sputter coated with gold prior to scanning.

2.5. Proton conductivity and methanol permeability measurement

Proton conductivities of membranes were measured at room temperature by AC impedance method, a Solartron Interface 1260 gain phase analyzer, Hampshire, UK, over the frequency range of 1 Hz–10 kHz. The sample was sandwiched between two circular platinum electrodes of 1.0 mm diameter in an open cell in air. A spring linked to one of the electrodes kept the membrane under a constant pressure, thereby providing good contact between the electrodes and the membrane. The conductivity was calculated from the following equation: $\sigma = L/RA$, where L is the membrane thickness, A is the surface area of the electrodes and R is the resistance.

Methanol permeability was determined and calculated by using two connected compartment cells as described in our previous papers [17–19]. In the beginning, one compartment was filled with 10 M methanol solution, and the other compartment was filled with deionized water. Each of the compartment was kept stirring during experiment to ensure the uniformity of the cell concentration. The refractive index of methanol solution was recorded with time and was converted to the methanol concentration. Methanol permeability was obtained by analyzing the methanol concentration with time.

2.6. Membrane–electrode assembly (MEA) fabrication and fuel cell evaluation

The membranes were immersed in sulfuric acid (0.5 M) for 1 day and then washed out to remove the remaining sulfuric acid with distilled water for assuring of the hydrogen form of the blend membranes. Fuel cell experiments were carried out in a 4-cm^2 self-designed single cell [19–21]. The single-cell was tested with 5 M methanol solution and air breathing after equilibrium at 40 °C for 4 h. A layer of 20 wt% of PtRu (1:1, a/o) on carbon black (anode) and 20 wt% of Pt on carbon black (cathode) were applied on two gas diffusion layers. The content of catalyst loading was approximately 0.2 and 0.4 mg cm^{-2} for anode and cathode, respectively.
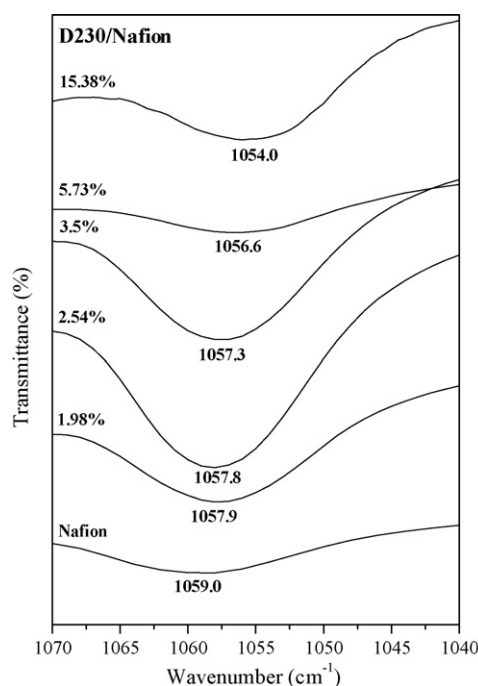

Fig. 1. FT-IR spectra of the 1070–1040 cm^{-1} region of D230/Nafion® blend membranes.

Table 1
Comparison of –SO$_3$H stretching bands of D230/Nafion®, D400/Nafion®, and D2000/Nafion®

| Content (wt%)	D230/Nafion® (cm^{-1})	D400/Nafion® (cm^{-1})	D2000/Nafion® (cm^{-1})
0	1059.0	1059.0	1059.0
1.98	1057.9	1058.1	1058.8
2.54	1057.8	1058.0	1058.2
3.50	1057.3	1057.4	1058.1
5.73	1056.6	1056.9	1058.0
15.38	1054.0	1054.2	1056.1

3. Results and discussion

3.1. FT-IR spectroscopy of blend membranes

Fig. 1 presents the symmetric –SO$_3$H stretching bands of the blend D230/Nafion® membranes at approximately 1060 cm^{-1}. The –SO$_3$H stretching band (1059 cm^{-1}) of pristine Nafion® membrane shifts when a change in polarization of the S–O dipole is caused by its ionic environment. More shift is observed for higher contents of D230, suggesting that the large quantities of positively charged groups are interacting with the SO$_3^-$ groups. Tannenbaum et al. [22] observed a SO$_3^-$ band shifted from 1059 cm^{-1} for Nafion® to 1052 cm^{-1} for Nafion® in the presence of poly(ethylacrylate-*co*-4-vinylpryridine). They explained this shift as being caused a decline in polarization of the S–O dipole due to the increase in the separation between SO$_3^-$ and H$^+$. The FT-IR spectra of Fig. 2b–d depict 3.5 wt% of oligomer contents for D230/Nafion®, D400/Nafion®, and D2000/Nafion®, respectively. Table 1 compares the position of –SO$_3$H stretching bands for D230/Nafion®, D400/Nafion®, and
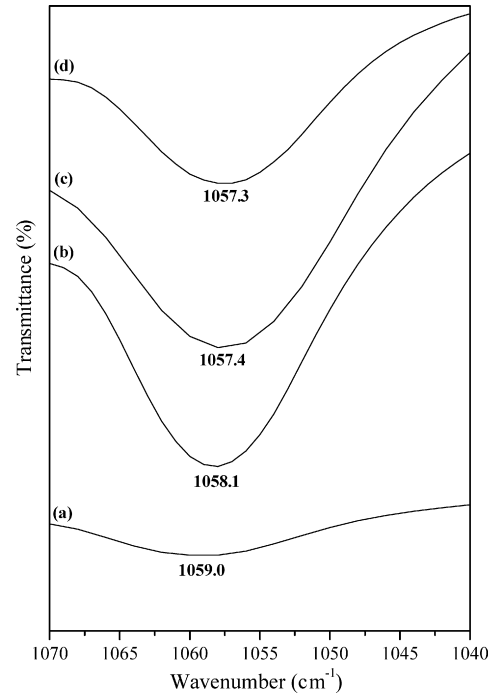
Fig. 2. FT-IR spectra of the 1070–1040 cm^{-1} region of (a) Nafion®, (b) D2000/Nafion®, (c) D400/Nafion®, and (d) D230/Nafion® blend membranes (3.5 wt%).
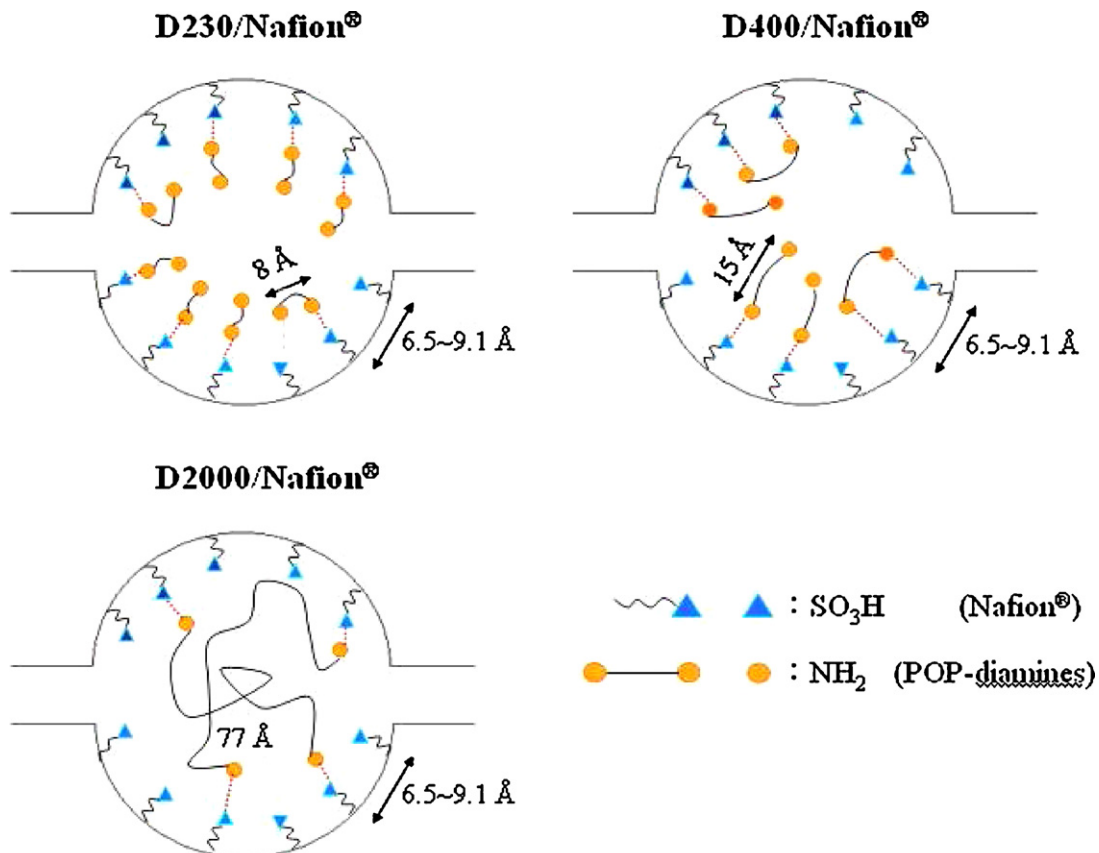
Scheme 1. The interaction between –SO$_3$H (Nafion®) and –NH$_2$ (D230, D400 or D2000) in the cluster network of Nafion® blend membranes.

D2000/Nafion®. As can be seen in Fig. 2 of the –SO$_3$H peaks of FT-IR spectra, D230/Nafion® (curve d) shifts to the lowest frequency (1057.3 cm^{-1}) due to the strongest acid–base interaction. Although the same amounts of POP-diamines were added to the blend membranes, however, the quantities of the amine functional groups generated will be different, i.e. D230 > D400 > D2000. Therefore, the observation of the shift from 1059 to 1054 cm^{-1} in 15.38 wt% D230/Nafion® will be higher than others, as proposed by Tan and Bélanger that a stronger electrostatic polarization is associated with a higher peak shift [23].

Scheme 1 presents the interaction between –SO$_3$H (Nafion®) and –NH$_2$ (POP-diamines) in the cluster of Nafion® blend membranes. The average SO$_3$$^-$–SO$_3$$^-$ group spacing of Nafion® is in the range 6.5–9.1 Å [24], and D230, D400, and D2000 materials have chain lengths of 8, 15, and 77 Å, respectively [25]. Therefore, a weak acid–base interaction may occur in the D2000/Nafion® blend membranes. Additionally, the amine groups of D230 in Nafion® exhibits the strongest acid–base interaction, and this result is consistent with that of FT-IR.

3.2. Differential scanning calorimetry

A typical DSC curve of Nafion® has two endothermic peaks. The first endothermic peak appears at about 110 °C which may be interpreted as the cluster transition temperature. That can be accompanied by polymer contraction due to the loss of water with an increase in entropy [26]. The second peak is a weak and broad endothermic peak which is presented at around 200 °C, is assigned to the melting peak of the nonpolar crystallite backbone [27]. Fig. 3 compares the DSC curves of pristine Nafion® and 5.73 wt% D230/Nafion®, D400/Nafion®, and D2000/Nafion®, respectively. Incorporating POP-diamines into the Nafion® matrix decreased the melting temperature of the nonpolar crystallite and increased the cluster transition temperature, as shown in Fig. 3. The
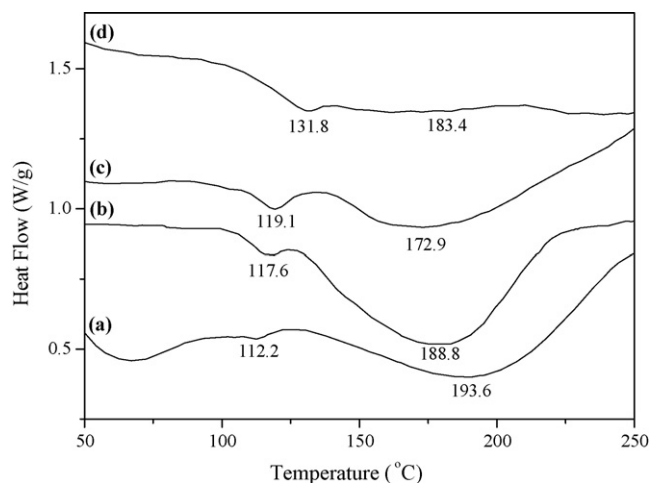

Fig. 3. DSC thermograms of (a) Nafion®, and 5.73 wt% (b) D2000/Nafion® (c) D400/Nafion® and (d) D230/Nafion® blend membranes.

invasion of polypyrrole particles into the cluster could stabilize the polar phase by means of the interaction between POP-diamines and Nafion®, and decrease the crystallinity of the backbone indirectly due to the disruptive effect of swelled clusters on the lamellar ordering of nonpolar backbone [28]. Therefore, the decreasing of melting temperature of the nonpolar crystallite indicates that the strongly interacting POP-diamines component of the blended films perturbed the crystallization process of Nafion® during annealing [16].

Table 2 compares the cluster transition temperature of D230/Nafion®, D400/Nafion®, and D2000/Nafion®, and it can be seen that the temperature of D230/Nafion® is the highest among the samples. These results are consistent with those observed by
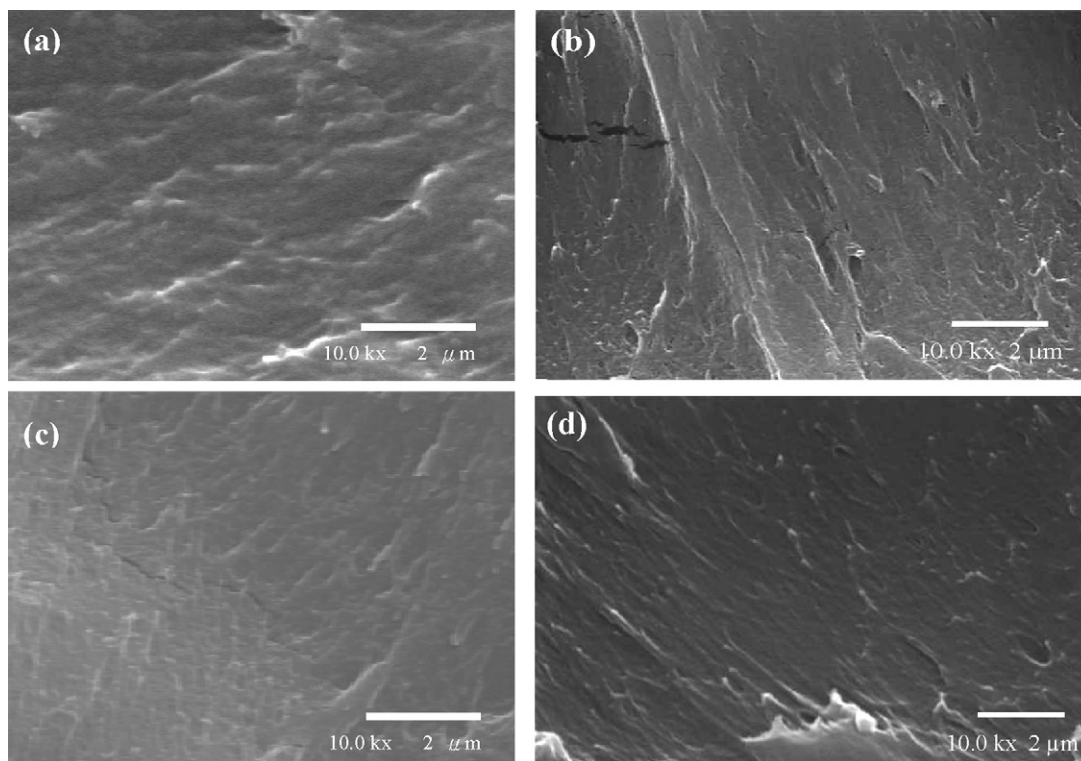

Fig. 4. SEM cross-section of (a) Nafion®, and 3.5 wt% (b) D230/Nafion®, (c) D400/Nafion®, and (d) D2000/Nafion®.

Table 2
Comparison of cluster transition temperature of D230/Nafion®, D400/Nafion®, and D2000/Nafion®

Content (wt%)	D230/Nafion® (°C)	D400/Nafion® (°C)	D2000/Nafion® (°C)
0	112.2	112.2	112.2
1.98	125.5	113.3	112.5
2.54	126.3	113.6	113.0
3.50	127.2	115.8	117.3
5.73	131.8	119.1	117.6

Park et al. [29] for Nafion® membranes that have been modified with polypyrrole and by Tan and Bélanger [23] for Nafion® membranes that have been modified with polyaniline. The presence of POP-diamines forces the Nafion® polymer chains to re-organize themselves and to form a more cross-linked structure within the clusters, which would increase the cluster transition temperature. Moreover, the stronger interaction between the ammonium groups of D230 and the sulfonate groups of Nafion® may cause the cluster transition temperature to shift to higher temperature than that of the D400/Nafion® and D2000/Nafion® blend membranes, this result is also consistent with the FT-IR data [18].

3.3. SEM microphotographs

Scanning electron microscopy is a very convenient tool for investigating the properties and morphology of the electrodes, and it can also be used for studying the surface structure of the membranes. The SEM images in Fig. 4a–d show the cross-section of the pristine Nafion®, the 3.5 wt% blend membranes of D230/Nafion®, D400/Nafion®, and D2000/Nafion®, respectively. No pores were detected in all membranes, and all membranes possessed dense structures. The presence of dense structures can be explained in terms of the interactions between the sulfonic acid groups of Nafion® and the amine units of D230 (or D400 and D2000). Due to the strong acid–base interactions, no phase separation occurred during solvent evaporation; hence homogeneous, transparent films were formed [18].

3.4. Proton conductivity

Fig. 5 compares the proton conductivities of various compositions of D230/Nafion®, D400/Nafion®, and D2000/Nafion®. In the proton conductivity experiment, each sample was measured more

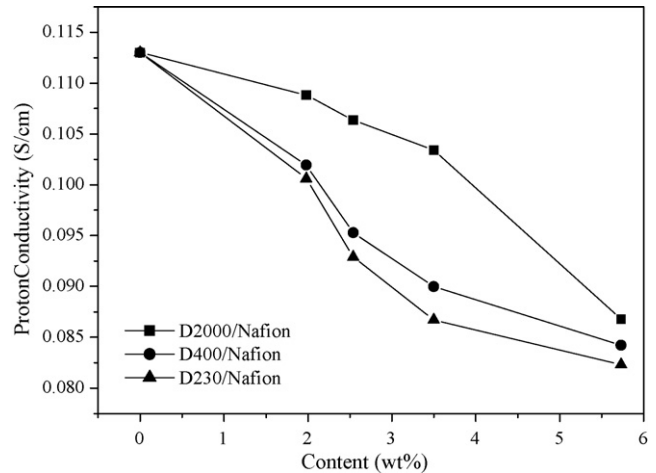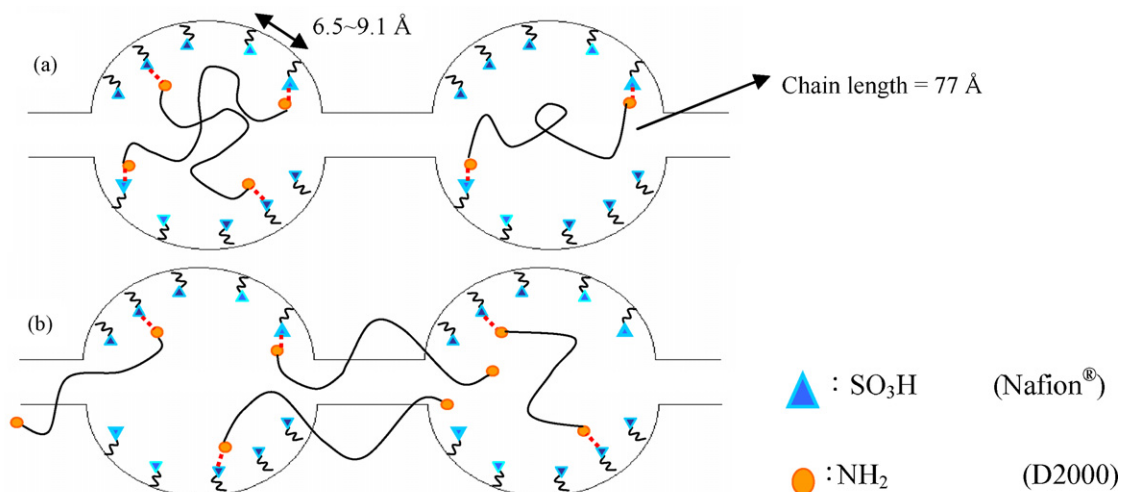**Fig. 5.** Proton conductivity of D230/Nafion®, D400/Nafion®, and D2000/Nafion®.

than five times. Every result was averaged in the error range ±5%. Increasing the POP-diamines content tends to reduce the proton conductivity of the membranes [30–33].

The linear relationship between POP-diamines contents and proton conductivity suggests that the POP chains partially block the ionic cluster network by reducing the number of ion-exchange sites. Comparison of different chain lengths, the value of proton conductivity decreases with the decreasing of molecular weights, as in the following order: D230 < D400 < D2000. The treads are the same as the forces of acid–base interaction because the strong interaction will reduce the number of sulfonic acid groups in the cluster which can transform protons by hopping mechanism [21]. Therefore, the promotion of the hopping mechanism will be blocked by the acid–base interaction. In addition, it is worthy to observe that the rate of proton conductivity decrease slowly with D2000 content up to 3.5 wt%, but became more rapidly at higher loadings. The result may be caused by following reasons: (i) Although the acid–base interaction occurs in the cluster, D2000 may be separated homogeneously in the whole membrane at high D2000 content instead of dispersing in the cluster due to its long chain, as shown in Scheme 2. (ii) D2000 is more hydrophobic than D400 and D230, the electrical resistance (Ω) may be increased rapidly when the electrodes contact the lipophilic material; hence, the increasing resistance leads to decrease the proton conductivity.
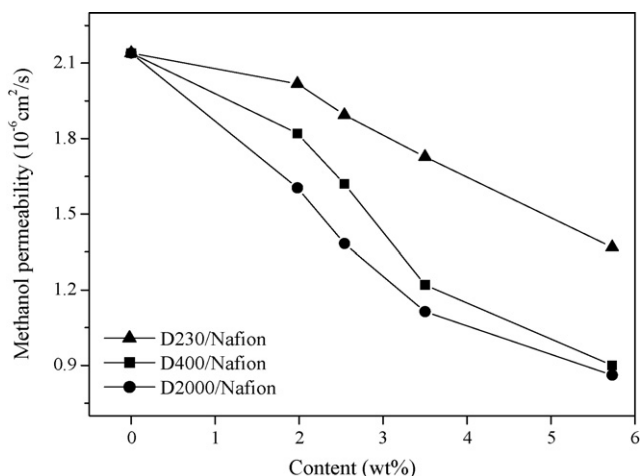

Scheme 2.

Fig. 6. Methanol permeability of D230/Nafion®, D400/Nafion®, and D2000/Nafion®.

Fig. 8. Polarization curves for the MEA made with pristine Nafion® membrane and 3.5 wt% POP-diamines/Nafion® operated at 323 K.

3.5. Methanol permeability

As shown in Fig. 6, the methanol permeability decreased with the increasing of POP-diamines, for two possible reasons. The first is the restricted mobility of the ionic clusters, even through swelling, as revealed by the DSC data; the second is the agglomeration of the structure by the ion–dipole interaction between the ammonium group (POP-diamines) and the sulfonate groups (Nafion®), as demonstrated by the FT-IR results as described above. Additionally, Fig. 6 indicates that the methanol permeability of D2000/Nafion® blend membranes is much lower than the other two. As the amount of D2000 is increased to 5.73 wt%, methanol permeability was decreased from 2.14×10^{-6} to 0.86×10^{-6}. Although the acid–base interaction between D2000 and Nafion® is weaker than D400 and D230, high molecular weight of D2000 can provide the long chain of backbone which will occupy almost space of cluster and, consequently, will block the methanol molecule more effectively, as shown in Scheme 1.

The proton conductivity and the methanol crossover dominate the cell performance in a DMFC. Good performance generally depends on high proton conductivity and low methanol crossover. Adding D2000 increases the ratio of proton conductivity to methanol permeability (C/P ratio), as presented in Fig. 7. Although the proton conductivity was still somewhat low, the compos-
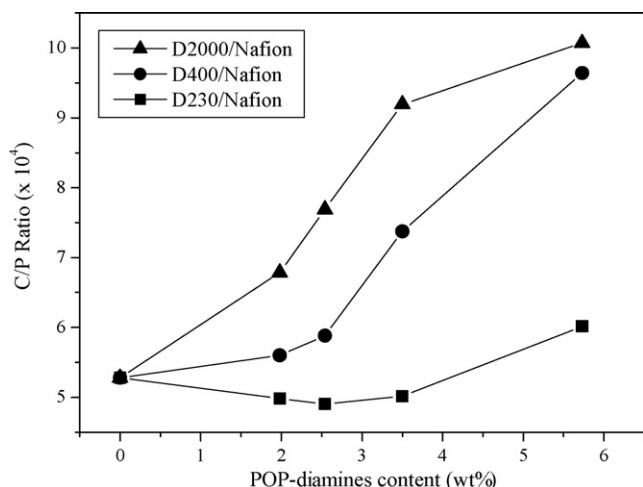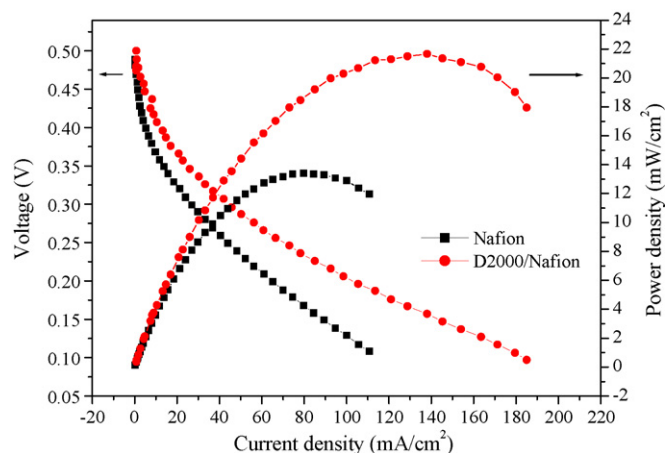
ite membranes that were tested in DMFC exhibited considerably improved performance by reducing the methanol crossover to much lower than that associated with the pristine Nafion® membrane.

3.6. Fuel cell performance

Due to the higher proton conductivity and lower methanol permeability of D2000/Nafion®, the performance of D2000/Nafion® blend membranes in a DMFC single cell was tested. Fig. 8 shows the plots of cell potential vs. current density (polarization curves) and power density vs. current density for the DMFC MEA with composite membranes of different contents. The blend membrane with 3.5 wt% of D2000/Nafion® outperformed pristine Nafion®. The suppression of the methanol crossover exhibits higher open circuit voltage (OCV) at lower current densities, as presented in Fig. 8. The current densities measured with the composite membranes with D2000 contents of 0 and 3.50 wt%, respectively, were 62.5, and 103.5 mA cm^{-2} at a potential of 0.2 V. The maximum power density of 21.6 mW cm^{-2} was obtained for the membrane with 3.5 wt% of D2000. Hence, the performance of the DMFC was improved by introducing D2000. The proposed D2000/Nafion® system provides promising results for following reasons: acid–base interaction and the longest chain length of D2000 restrict both the mobility of the ionic clusters and decrease the methanol permeability efficiently.

4. Conclusion

Various molecular weights of poly(propylene oxide) diamines oligomers/Nafion® acid–base blend membranes were prepared to improve the performance of Nafion® membranes in DMFCs. The proton conductivity of D2000/Nafion® blend membrane was maintained by adding D2000 which possesses the lowest acid–base interaction with sulfonic acid groups of Nafion®. The methanol permeability of the blend membrane dramatically with increasing content of D2000 in the blend membrane for two reasonable factors: (i) the longest chain length of D2000, which can occupy the cluster of Nafion®, (ii) the agglomeration of the structure by the ion–dipole interaction between the ammonium group and the sulfonate groups, as demonstrated by the FT-IR results. The D2000/Nafion® blend membranes have a higher selectivity than pristine Nafion®, since the proton conductivity is maintained and the methanol permeability is reduced. The high selectivity confirms that the composite membrane is suitable for DMFC applications. The current densities that were measured with the D2000/Nafion®

Fig. 7. C/P ratio of D230/Nafion®, D400/Nafion®, and D2000/Nafion®.

blend membranes in the ratios, 0 and 3.5 wt% were 62.5 and 103.5 mA cm^{-2}, respectively, at a potential of 0.2 V. The combination of these effects significantly improved the performance of D2000/Nafion® blend membranes in DMFCs.

Acknowledgement

References

[1] H. Kim, H. Chang, J. Membr. Sci. 288 (2007) 188.
[2] J. Liu, H. Wang, S. Cheng, K.Y. Chan, J. Membr. Sci. 246 (2005) 95.
[3] N.W. DeLuca, Y.A. Elabd, J. Membr. Sci. 282 (2006) 217.
[4] B. Bae, H.Y. Ha, D. Kim, J. Membr. Sci. 276 (2006) 51.
[5] K.D. Kreuer, J. Membr. Sci. 185 (2001) 29.
[6] M. Rikukawa, K. Sanui, Prog. Polym. Soc. 25 (2000) 1463.
[7] J. Kerres, W. Cui, S. Reichle, J. Polym. Sci. Part A: Polym. Chem. 34 (1996) 2421.
[8] F. Wang, M. Hickner, Y.S. Kim, T.A. Zawodzinski, J.E. McGrath, J. Membr. Sci. 197 (2002) 231.
[9] K. Scott, W.M. Taama, P. Argyropoulos, J. Membr. Sci. 171 (2000) 119.
[10] T. Yamaguchi, F. Miyata, S. Nakao, J. Membr. Sci. 214 (2003) 283.
[11] J. Kerres, A. Ullrich, F. Meier, T. Haring, Solid State Ionics 125 (1999) 243.
[12] H.J. Kim, Y.G. Shul, H.S. Han, J. Power Sources 135 (2004) 66.
[13] K.Y. Cho, H.Y. Jung, N.S. Choi, S.J. Sung, J.K. Park, J.H. Choi, Y.E. Sung, Solid State Ionics 176 (2005) 3027.
[14] F.A. Landis, R.B. Moore, Macromolecules 33 (2000) 6031.
[15] V. Deimede, G.A. Voyiatzis, J.K. Kallitsis, L. Qingfeng, N.Y. Bjerrum, Macromolecules 33 (2000) 7609.
[16] R. Wycisk, J. Chisholm, J. Lee, J. Lin, P.N. Pintauro, J. Power Sources 163 (2006) 9.
[17] Y.F. Lin, C.Y. Yen, C.C.M. Ma, S.H. Liao, C.H. Lee, Y.H. Hsiao, H.P. Lin, J. Power Sources 171 (2007) 388.
[18] Y.F. Lin, Y.H. Hsiao, C.Y. Yen, C.L. Chiang, C.H. Lee, C.C. Huang, C.C.M. Ma, J. Power Sources 172 (2007) 570.
[19] Y.F. Lin, C.Y. Yen, C.C.M. Ma, S.H. Liao, C.H. Hung, Y.H. Hsiao, J. Power Sources 165 (2007) 692.
[20] Y.F. Lin, C.Y. Yen, C.H. Hung, Y.H. Hsiao, C.C.M. Ma, J. Power Sources 168 (2007) 162.
[21] C.Y. Yen, C.H. Lee, Y.F. Lin, H.L. Lin, Y.H. Hsiao, S.H. Liao, C.Y. Chuang, C.C.M. Ma, J. Power Sources 173 (2007) 36.
[22] R. Tannenbaum, M. Rajagopalan, A. Eisnberg, J. Polym. Sci. Part B: Polym. Phys. 41 (2003) 1814.
[23] S. Tan, D. Bélanger, J. Phys. Chem. B 109 (2005) 23480.
[24] S. Dokmaisrijan, E. Spohr, J. Mol. Liq. 129 (2006) 92.
[25] H.Y. Huang, W.F. Chen, P.L. Kuo, J. Phys. Chem. B 109 (2005) 24288.
[26] L.G. Lage, P.G. Delgado, Y. Kawano, Polym. J. 40 (2004) 1309.
[27] I.D. Stefanithis, K.A. Mauritz, Macromolecules 23 (1990) 2397.
[28] B.R. Moore El, C.R. Martin, Macromolecules 22 (1989) 3549.
[29] H.S. Park, Y.J. Kim, W.H. Hong, Y.S. Choi, H.K. Lee, Macromolecules 38 (2005) 2289.
[30] H.S. Park, Y.J. Kim, W.H. Hong, H.K. Lee, J. Membr. Sci. 272 (2006) 28.
[31] L.J. Hobson, Y. Nakano, H. Ozu, S. Hayase, J. Power Sources 104 (2002) 79.
[32] I.T. Kim, J. Choi, S. Chul Kim, J. Membr. Sci. 300 (2007) 28.
[33] N.W. DeLuca, Y.A. Elabd, J. Power Sources 163 (2006) 386.