Sulfonated poly(propylene oxide) oligomers/Nafion® acid-base blend membranes for DMFC

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Abstract

A novel functional poly(propylene oxide)-backboned diamine of M_w 400 (abbreviated as D400) was grafted with sulfonic acid (abbreviated as D400-PS) to improve the performance of Nafion® membranes in direct methanol fuel cells (DMFCs). The interaction of the D400-PS with Nafion® was studied by Fourier transform infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC). The performance of the blend Nafion®/D400-PS membranes was evaluated in terms of methanol permeability, proton conductivity and cell performance. The proton conductivity of the blend membrane was slightly reduced by rendering proton conductivity to D400 by functionalized with an organic sulfonic acid. The methanol permeability of the blend membrane decreased with increasing of D400-PS content. The methanol permeability of the blend Nafion®/D400-PS with the composition 3/1 ($-SO_3H/-NH_2$) was 1.02×10^{-6} cm² S⁻¹, which was reduced 50% compared to that of pristine Nafion®. The current densities that were measured with Nafion®/D400-PS blend membranes in the ratio 1/0 and 5/1 ($-SO_3H/-NH_2$), were 51 and 72 mA cm⁻², respectively, at a potential of 0.2 V. Consequently, the blend Nafion®/D400-PS membranes critically improved the single-cell performance of DMFC.
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Keywords: Fuel cell; Nafion® acid-base blend membrane; 1,3-propane sultone; Poly(propylene oxide) oligomers; FT-IR

1. Introduction

Direct methanol fuel cells (DMFCs) are appropriate for portable devices or transportation applications because of their high energy density at low operating temperatures and the ease of handling liquid fuel [1]. A DMFC is equipped with a proton exchange membrane (PEM). The Nafion® (perfluorosulfonic acid) membrane is commonly used as electrolytes, due to its good chemical and thermal stability and high ionic conductivity in its hydrated state [2]. However, extensive methanol permeation through Nafion® membranes significantly lowers fuel efficiency and cell performance. This problem of methanol crossover must be solved.

Recently, numerous acid-base composite membranes have been focused, since the membranes exhibit a specific interaction between the components [3–16]. The acid-base composite membrane can be synthesized in two ways. The first is the development of ion-conductive membranes that are based on alternative polymers or polymer composites [3]. Fu et al. [4] prepared sulfonated poly(ether ether ketone)/polysulfon composite membrane, which exhibited higher proton conductivity and better performance in PEMFC at 90 and 100 °C than the SPEEK or Nafion® membranes. Similarly, Smitha et al. [7] demonstrated that the blend membrane consists of polyeletrolyte complexes and poly(acrylic acid) exhibited low methanol permeability (3.9×10^{-8} cm² s⁻¹) and high proton conductivity (0.038 S cm⁻¹). Furthermore, the fuel cell test demonstrated that the operational temperature at which polybenzimidazole/sulfonated polysulfone blends could be used as electrolytes was up to 200 °C [8].

The second synthetic approach involves the modification of the Nafion® membrane. For instance, Park et al. [10,11] reported that the Nafion®/polypyrrole composite membrane possesses higher mechanical and thermal stabilities than pristine Nafion® because of the interaction between the sulfonate groups in Nafion® and the secondary ammonium groups; it also reduces
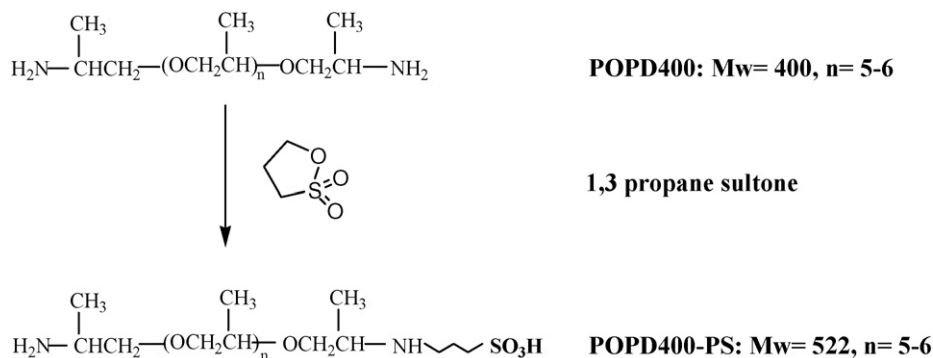
Scheme 1. Synthesis scheme of D400 bearing sulfonic acid side group.

the methanol crossover while maintaining proton conductivity. Another example, in PBI (polybenzimidazole)/Nafion®, the composite membranes show improved DMFC performance, an increased working current density, and an increase in maximum power output [14].

In this investigation, the Nafion®/D400 acid-base blend composite membranes were prepared. The backbone of D400, poly(oxypropylene) amines, has the same side chain of poly(oxypropylene) as of Nafion®. Accordingly, the hydrophilic region of the backbone of D400 is highly compatible with the side chain of Nafion®. Therefore, the acid-base interaction occurs in the cluster of Nafion®. This phenomenon may reduce the channel size of Nafion®, and then the smaller cluster of Nafion® lead to lower the methanol crossover. However, proton conductivity declines when D400 is added to Nafion® because the acid-base interaction between D400 and Nafion® yields less free sulfonic acid groups ($-SO_3H$) of Nafion®. Modified-D400 has been synthesized to overcome this problem. In this study, 1,3-propane sultone was utilized to modify D400 and then a novel material was formed by grafting sulfonic acid ($-SO_3H$) to D400. When the novel material blends with Nafion®, its sulfonice acid ($-SO_3H$) will solve the problem of low proton conductivity. The combination of these effects markedly improves the performance of a DMFC that has been made with the novel composite membrane.

2. Experimental

2.1. Synthesis of materials

The adduct of amine/1,3-propane sultone (abbreviated as –PS) was synthesized using poly(propylene oxide)-backboned diamines of M_w 400 as starting material and abbreviated as D400. The diamine was received from the Huntsman Chemical Co., Philadelphia, Pennsylvania (USA). The preparation of diamine bearing one sulfonic acid ($-SO_3H$), abbreviated as D400-PS was carried out in a glass reactor equipped with a stirrer. The designated amount of 1,3-propane sultone (12.2 g, 100 mmol) was slowly added to a reactor charged with D400 (40 g, 100 mmol). The progress of the reaction was characterized by FT-IR to confirm that the diamine bearing one sulfonic acid ($-SO_3H$) successfully.

2.2. Preparation of composite membrane

To prepare a composite membrane, D400 and D400-PS were blended with 5 wt.% Nafion® solution (DuPont), and then stirred and degassed by ultrasonication. The molar ratios of sulfonic acid (Nafion®) to amines (D400) and Nafion® to D400-PS ($-SO_3H$/$-NH_2$) are 9/1, 7/1, 5/1, 3/1 and 1/1. 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 levelled 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.

2.3. FT-IR measurement

FTIR spectra of the D400, D400-PS, and 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.
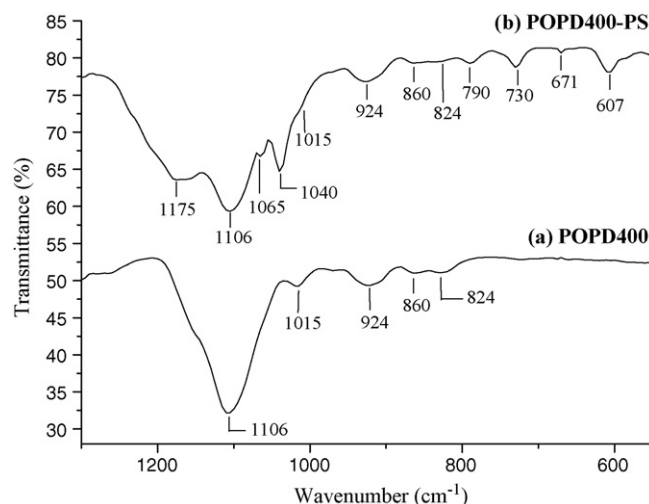

Fig. 1. FT-IR spectra of (a) D400 and (b) D400-PS.

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2.4. 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 $10\,^{\circ}\text{C}\,\text{min}^{-1}$ within a temperature range of 50–250 °C.

2.5. Proton conductivity and methanol permeability measurement

Proton conductivities of membranes were measured at room temperature by AC impedance method, using a Solartron Interface 1260 gain phase analyzer, Hampshire, UK over the frequency range of 1 Hz–10 kHz. The sample was place 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 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 [16,17]. 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

Table 1
Comparison of infrared frequencies (cm^{-1}) of D400 and D400-PS

D400-PS	D400	Assignment [ref. [18]]
607, 671		ν(C–S)
730		ρ(–CH$_2$–CH$_2$–CH$_2$–)
790		ω(Secondary amine, –NH–)
824, 860	824, 860	ν(Primary amine –NH$_2$)
924	924	ν(C–O–C)
1015	1015	ν(C–N)
1040		ν(–SO$_3$H)
1065		ν(C–C–C)
1106	1106	ν(CH–NH$_2$)
1175		ν(CH–NH–C)

ν, stretching; ρ, rocking; ω, wagging.

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 (2 M) for 1 day and then washed out 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
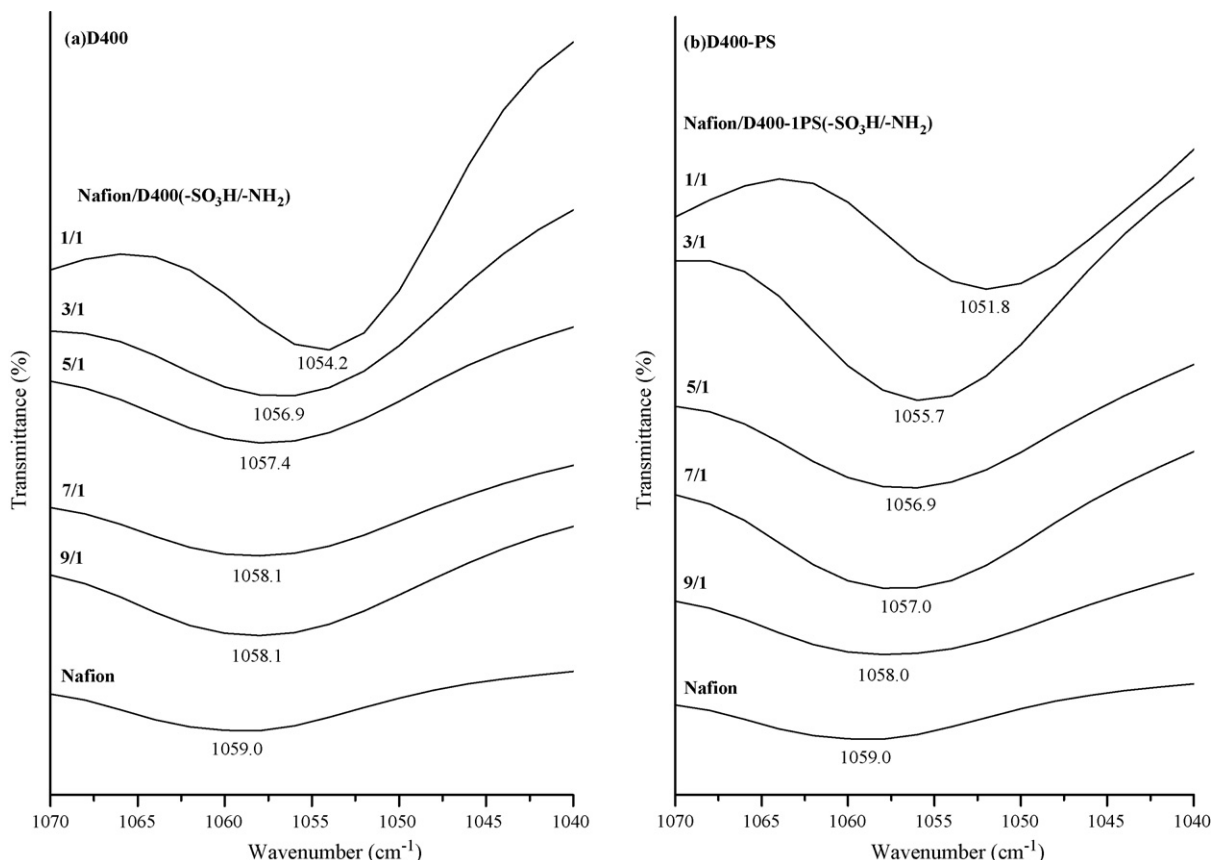

Fig. 2. FT-IR spectra of the 1070–1040 cm^{-1} region of (a) Nafion®/D400 and (b) Nafion®/D400-PS blend membranes.

self designed single cell [16,17]. The single-cell was tested with 2 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.

3. Results and discussion

3.1. FT-IR analysis of the structure of D400-PS

Scheme 1 presents the synthesis of the D400-bearing sulfonic acid side group by a ring-opening reaction between the primary amine of D400 and 1,3-propane sultone. Fig. 1a displays the infrared spectrum of D400 cast onto the surface of the KBr pellet. In this spectrum, the infrared bands appear at 824, 860, 924, 1015 and 1106 cm^{-1}. After D400 was modified, the new absorption wavenumbers of the D400-PS are 607, 671, 730, 790, 1040, 1065 and 1175 cm^{-1}, as shown in Fig. 1b. Table 1 compares the infrared absorptions of D400 and D400-PS [17,18]. A comparison of the IR frequencies of both materials reveals that the new IR bands correspond to C–S (607, 671 cm^{-1}), C–C–C (1065 cm^{-1}) and CH–N–C (1175 cm^{-1}). Moreover, the segmental similarity between the absorption frequencies in both cases shows that the D400-PS was prepared successfully.

3.2. FT-IR spectroscopy of blend membranes

Fig. 2a presents the symmetric –SO$_3$H stretching bands of the blend Nafion®/D400 membranes at approximately 1060 cm^{-1}. The –SO$_3$H stretching band (1059 cm^{-1}) of the pristine Nafion® membrane shifts when a change in polarization of the S–O dipole is caused by its ionic environment. Tannenbaum et al. [19] have 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 the polarization of the S–O dipole due to the increase in the separation between SO$_3^-$ and H$^+$. Fig. 2b depicts the same result for Nafion®/D400-PS blend membranes. The –SO$_3$H band shifts from 1059 cm^{-1} for Nafion® to 1052 cm^{-1} for Nafion® in the presence of the D400-PS and the shift is higher than that of Nafion®/D400 blend membranes. Scheme 2 represents the interaction between –SO$_3$H (Nafion®) and –NH$_2$ (D400 or D400-PS) in the cluster of Nafion® blend membranes. As can be seen in Scheme 2, the mean SO$_3^-$–SO$_3^-$ group spacing of Nafion® ranges from 6.5 to 9.1 Å [20], and D400 materials have a chain length of approximately 15 Å [21]. Therefore, a weak acid-base interaction may occur in the Nafion®/D400 blend membranes. Additionally, the amine group of D400-PS in Nafion® exhibits a stronger acid-base interaction than that of D400 in Nafion®, which finding is consistent with the FT-IR results. As proposed by Tan and Bélanger that a stronger electrostatic polarization is associated with a higher peak shift [22].
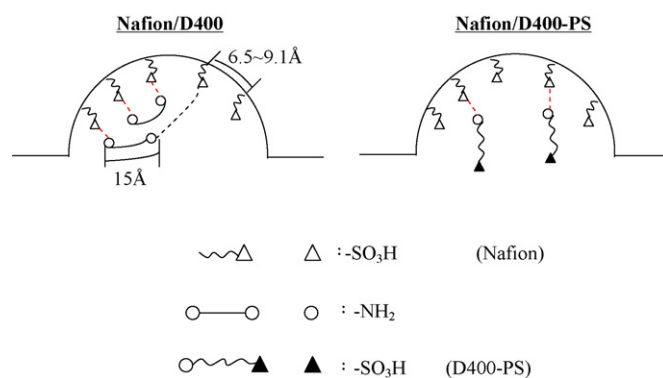
Scheme 2. The interaction between –SO$_3$H (Nafion®) and –NH$_2$ (D400 or D400-PS) in the cluster network of Nafion® blend membranes.

3.3. 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 tempera-
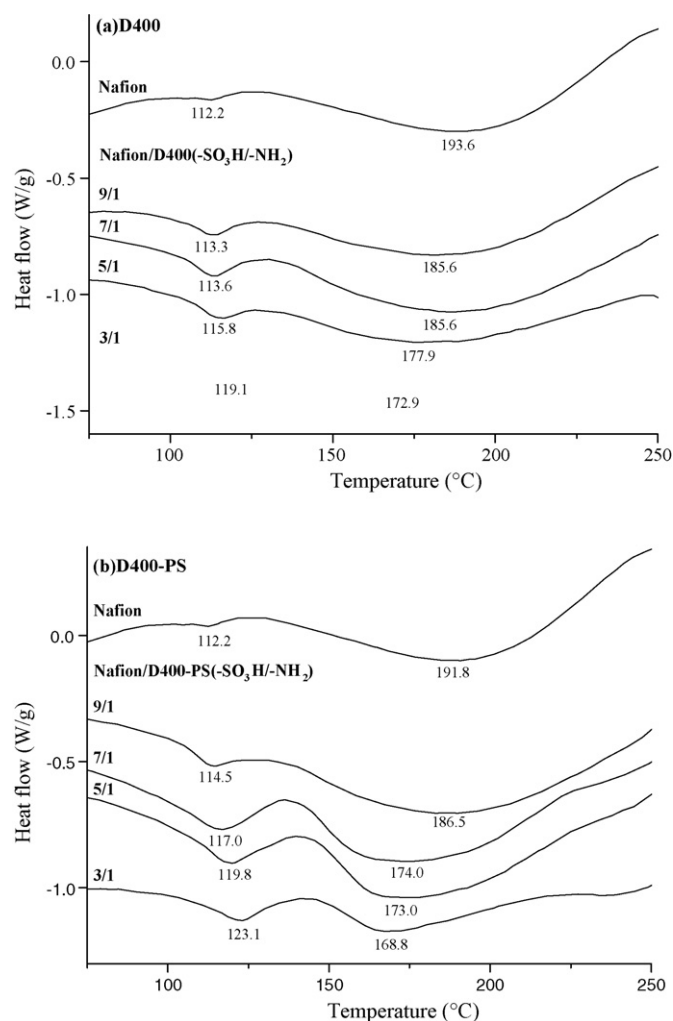

Fig. 3. DSC thermograms of (a) Nafion®/D400 and (b) Nafion®/D400-PS blend membranes.

ture. That can be accompanied by polymer contraction due to the loss of water with an increase in entropy [23]. The second peak is a weak and broad endothermic peak is present at around 200 °C, which is assigned to the melting peak of the nonpolar crystallite backbone [24]. Fig. 3 compares the DSC curves of pristine Nafion® and the Nafion®/D400 and Nafion®/D400-PS blended membranes. Incorporating D400 or D400-PS into the Nafion® matrix decreased the melting temperature of the nonpolar crystallite as shown in Fig. 3. These tendencies are consistent with those observed by Park et al. [11] for Nafion® membranes that have been modified with

polypyrrole and by Tan and Bélanger [22] for Nafion® membranes that have been modified with polyaniline. The presence of D400 or D400-PS forces the Nafion® polymer chains to reorganize themselves and forms a more cross-linked structure within the clusters, which would increase the cluster transition temperature. Moreover, the stronger interaction between the ammonium groups of D400-PS and the sulfonate groups of Nafion® may cause the cluster transition temperature to shift to higher than that of the Nafion®/D400 blend membranes, which result is also consistent with the FT-IR data [17].
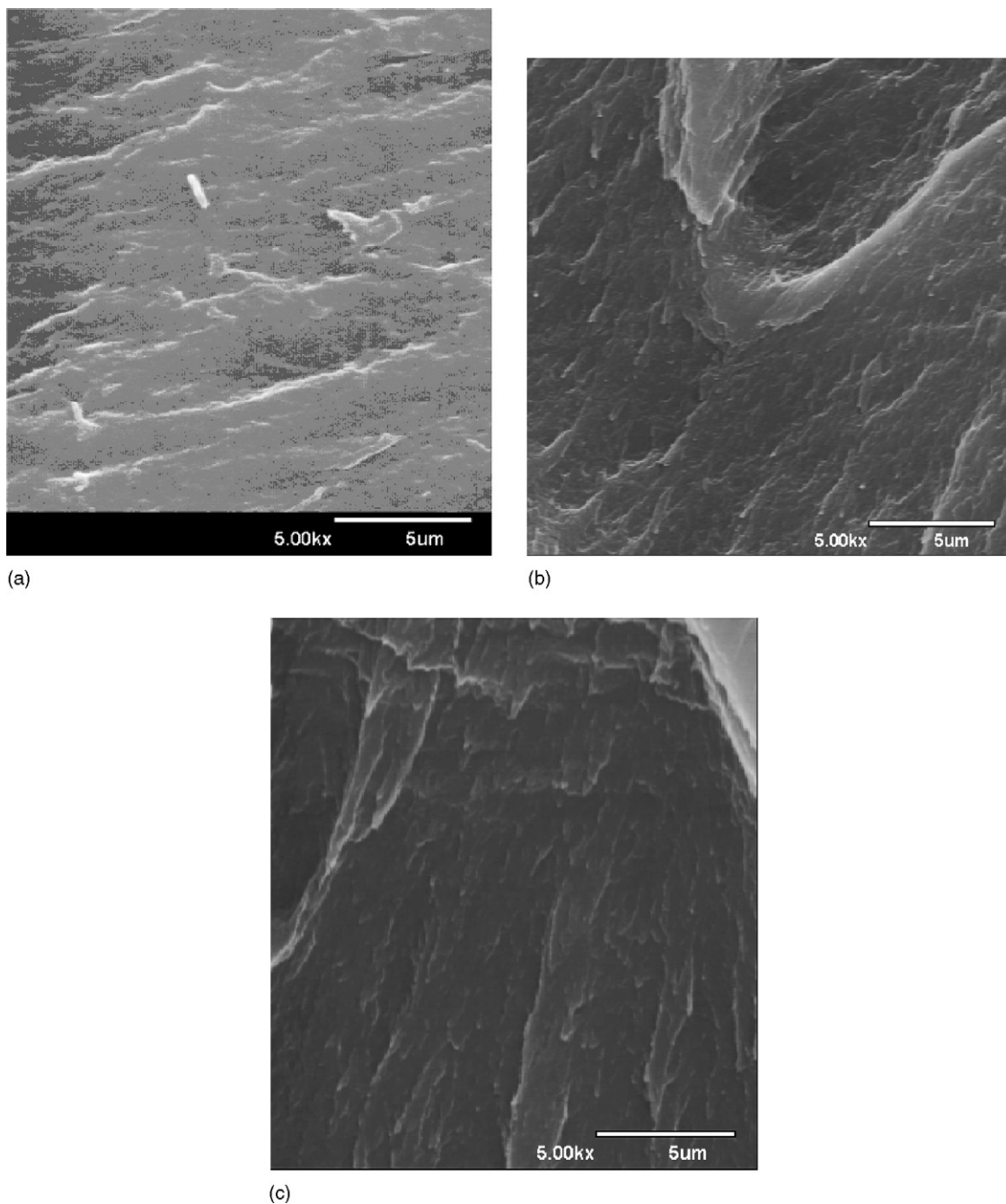

(a)

(b)

(c)

Fig. 4. SEM images of the surface of (a) pristine Nafion®, (b) Nafion®/D400 (5/1) and (c) Nafion®/D400-PS (5/1) blend membranes (bar scale represents 5 μm).
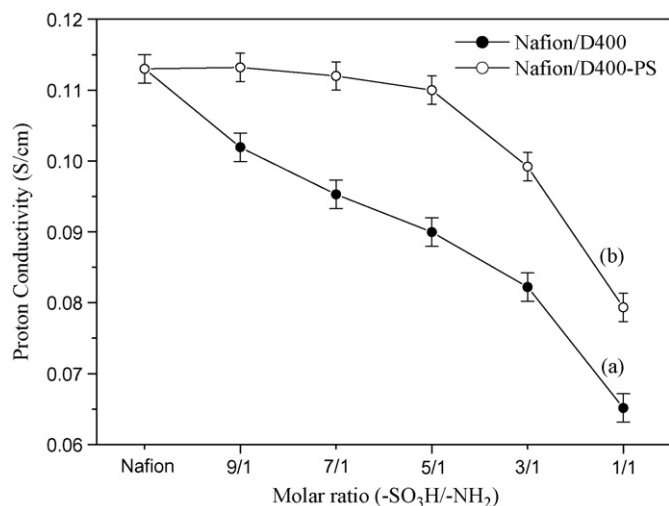
Fig. 5. The proton conductivity of (a) Nafion®/D400 and (b) Nafion®/D400-PS blend membranes.

Fig. 6. The methanol permeability of (a) Nafion®/D400 and (b) Nafion®/D400-PS blend membranes.

3.4. SEM micrographs

Scanning electron microscopy is a very convenient tool for investigating morphology of the electrode, and it can also be used for studying the surface structure of the membranes. The SEM images in Fig. 4(a–c) show the morphology of the cross section of the pristine Nafion®, the blend membranes Nafion®/D400 (5/1) and Nafion®/D400-PS (5/1), respectively. No pores were detected in all membranes which possess dense structures. The presence of dense structures can be explained in terms of the interaction between the sulfonic acid groups of Nafion® and the amine units of D400 (or D400-PS). Due to the strong acid-base interaction, no phase separation occurred during solvent evaporation, hence homogeneous and transparent films formed.

3.5. Proton conductivity

Fig. 5 compares the proton conductivities of various compositions of Nafion®/D400 and Nafion®/D400-PS blend membranes. In the proton conductivity experiment, each sample was measured more than five times. Every result was averaged in the error range ±5%. Increasing the D400 content tends to reduce the proton conductivity of the membranes. Numerous researches have studied the modification of Nafion® to reduce the methanol crossover in the direct methanol fuel cell have noted this loss of conductivity [10,11,14]. The linear relationship between D400 contents and proton conductivity suggests that the POP chains of D400 partially block the ionic cluster network by reducing the number of ion-exchange sites. The D400 contains an organic sulfonic acid group, which is responsible for the proton conductivity. The proton conductivity of the Nafion®/D400-PS blend membranes was slightly reduced, as shown in Fig. 5. The maintenance of proton conductivity were caused by (i) the hydrophilic regions, the sulfonic acid groups, of D400-PS and (ii) the promotion of the hopping mechanism by the D400-PS with a long organic chain, as described in our prior study [17].
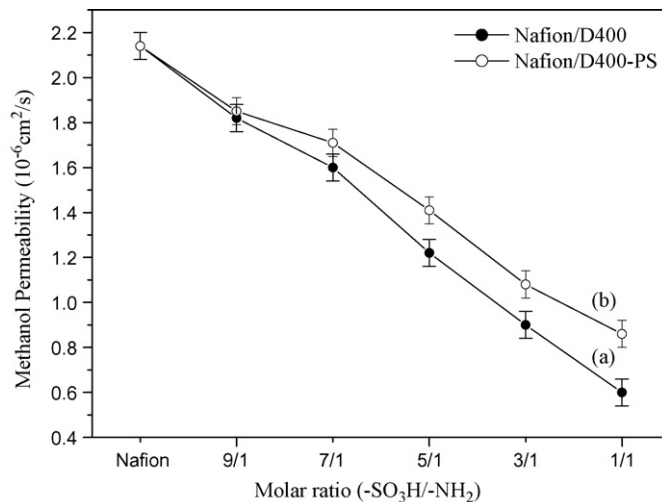
3.6. Methanol permeability

As shown in Fig. 6, the methanol permeability decreased with the increasing of D400 or D400-PS, 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 (D400 or D400-PS) and the sulfonate groups (Nafion®), as demonstrated by the FT-IR results described above. Additionally, Fig. 6 indicates that the methanol permeability of Nafion®/D400-PS blend membranes slightly exceeds that of Nafion®/D400 blend membranes, because the methanol is easily transported together with solvated protons $(H_3O^+, H_5O_2^+)$, since the hydrophilicity of the sulfonate groups of D400-PS is higher than that of D400.

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 D400-PS 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 composite 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.

3.7. Fuel cell performance

The performance of blend membranes in a DMFC single cell was tested. Fig. 8 plots the cell potential as a function of current density for the DMFC membrane-electrode assembly (MEA) with blend membranes of D400-PS and pristine Nafion®. The blend membrane with Nafion®/D400-PS molar ratio of 5/1 (–SO₃H/–NH₂) outperformed pristine Nafion®. The suppression of the methanol crossover exhibits higher OCV at lower current densities, as presented in Fig. 8. The current densities that were measured with the Nafion®/D400-PS blend membranes in the ratios, 1/0, 5/1 and 3/1 (–SO₃H/–NH₂), were 51 and 72 and
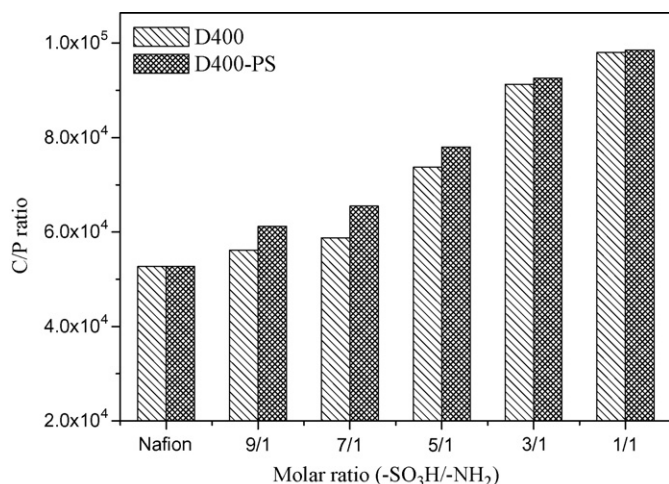
Fig. 7. Ratio of the ionic conductivity to the methanol permeability for Nafion® composite membranes filled with various contents of D400 and D400-PS.

53 mA cm^{-2}, respectively, at a potential of 0.2 V. In addition, the current density of the Nafion®/D400 5/1 (–SO$_3$H/–NH$_2$) blend membranes were measured at 59 mA cm^{-2} at a potential of 0.2 V. Furthermore, the blend membranes that contain D400-PS showed better performance at high current densities than that of pristine Nafion® up to a blend membrane compositional ratio of 3/1 (–SO$_3$H/–NH$_2$). However, the membranes with the composition of Nafion®/D400 (5/1) and Nafion®/D400 (3/1) (–SO$_3$H/–NH$_2$) do not directly improve the cell performance, may be due to the decreased proton conductivity as shown in Fig. 5. Hence, the performance of the DMFC was improved by introducing the organics of D400-PS. The proposed Nafion®/D400-PS system provides promising results for two following reasons: (i) D400-PS possess hydrophilic regions, i.e. sulfonic acid group, leads to maintain the proton conductivity at molar ratio up to 5/1 (as shown in Fig. 5), and (ii) ion–dipole interaction restricts both the mobility of the ionic clusters and the agglomeration of D400-PS.
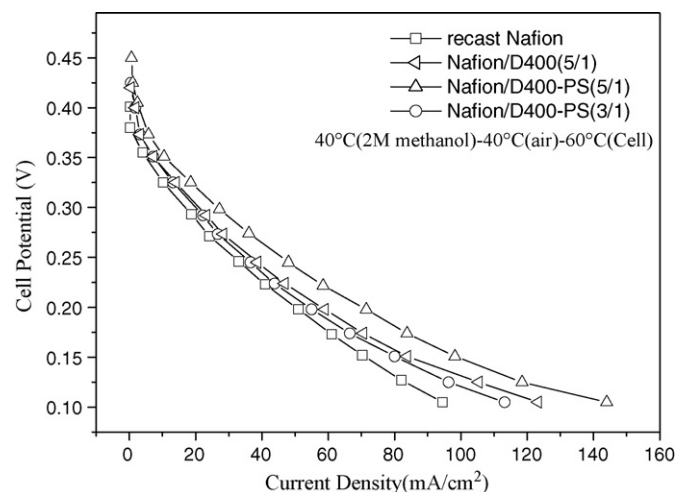

Fig. 8. Polarization curves for the MEA made with pristine Nafion® membrane and composite membranes operated at 313 K.

4. Conclusions

Poly(propylene oxide) D400-PS has been synthesized by grafting sulfonic acid onto poly(propylene oxide)-backboned diamines of D400 to improve the performance of Nafion® membranes use in direct methanol fuel cells. The proton conductivity of Nafion®/D400-PS blend membrane was maintained by adding D400-PS which possesses the hydrophilic regions, the sulfonic acid groups and a long organic chain. The methanol permeability of the blend membrane decreased dramatically with increasing content of D400-PS in the blend membrane for two reasonable factors: (i) the restricted mobility of the ionic clusters, even through swelling, as revealed by the DSC data; (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 Nafion®/D400-PS 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 Nafion®/D400-PS blend membranes in the ratios, 1/0, 5/1 and 3/1 (–SO$_3$H/–NH$_2$), were 51 and 72 and 53 mA cm^{-2}, respectively, at a potential of 0.2 V. The combination of these effects significantly improved the performance of Nafion®/D400-PS blend membranes in DMFCs.

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