# Sulfonated Poly(ether imide) and Poly(ether sulfone) Blends for Direct Methanol Fuel Cells. II. Membrane Preparation and Performance

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Received 8 January 2007; accepted 25 October 2007 DOI 10.1002/app.27575 Published online 29 January 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** This study describes the preparation and characterization of new ionomer blend membranes containing sulfonated poly(ether imide) (SPEI) and poly(ether sulfone) (PES). Thermogravimetric analysis indicated that the obtained blend membranes were more thermally stable than the parent SPEI. As the PES content increased, the extent of membrane swelling by water decreased, and the oxidative stability was significantly increased by the specific interactions between PES and the sulfonic acid groups. Under both dry and wet conditions, the tensile strength of all the blend membranes was larger than that of the pure SPEI membrane and Nafion 112 because of the reinforcing effect of PES. Scanning electron microscopy

#### **INTRODUCTION**

Fuel cells have been identified as a very feasible energy source with minimal noxious emissions and have been the subject of academic and industrial interest for over a decade.<sup>1</sup> Among the various fuel cells, direct methanol fuel cells (DMFCs) are the most suitable for vehicles (cars, trucks, and buses) or portable devices (cell phones and laptops) because they have a high charge density, low operating temperature, and simple fuel-cell setup (with easy storage of methanol and no need for a reformer).<sup>2-4</sup> The electrolyte is the most important component in any fuel-cell system. One of the main components in DMFCs is the electrolyte membrane. Dupont Nafion or other perfluorinated sulfonic acid membranes are widely acknowledged to be electrolyte membranes because of their high proton conductivity and chemical stability. However, the perfluorinated polymers that are used in DMFCs are expensive and have relatively poor resistance to methanol transport.<sup>5–9</sup>

and atomic force microscopy indicated that the blend membranes became more compact as the PES content increased, and this reduced the methanol diffusion. The blend membranes with PES contents below 50% showed adequate proton conductivity. The lower permeability of the blend membranes compared with the Nafion 112 membrane resulted in higher methanol resistance. This considerable reduction in methanol crossover revealed the feasibility of the blend membranes as promising electrolytes for direct methanol fuel cells. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1783–1791, 2008

Key words: blends; membranes; poly(ether sulfones)

Contemporary electrolyte membrane research involves the development of new polymer electrolytes that are based on hydrocarbon polymers.<sup>10</sup> The main approach, which is presently of considerable industrial interest and has been adopted by numerous researchers, involves the attachment of sulfonic acid groups onto various aromatic polymers with high thermal, chemical, and oxidative stability, good mechanical properties, and low cost. Examples include sulfonated poly(arylene ether sulfone),<sup>8,11-13</sup> sulfonated poly(ether ether ketone),<sup>2,3,14–17</sup> and sulfonated polyimides.<sup>18–23</sup> However, when their ionexchange capacity (IEC) values are comparable, the stronger acidity of the perfluorosulfonic acid compared with the sulfonated hydrocarbon polymers results in the higher proton conductivities.<sup>24</sup> Therefore, a sulfonated hydrocarbon polymer with a higher IEC value has been prepared to achieve appropriate proton conductivity. Yet, the increase in the concentration of sulfonated groups in the membranes produces poor mechanical properties when they are highly swollen by water.

Polymer blends, in which a sulfonated polymer with high proton conductivity is combined with a nonconductive engineering thermoplastic, are employed because they retain their mechanical integ-

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Journal of Applied Polymer Science, Vol. 108, 1783–1791 (2008) © 2008 Wiley Periodicals, Inc.

rity, and they have become popular for use in newly designed and improved proton exchange membranes (PEM) materials.<sup>25,26</sup> The improvement in mechanical stability is attributable to the entanglement of these polymers and to possible mixing by specific interactions, such as ion–dipole, dipole–dipole, and proton-transfer interactions.<sup>27–31</sup> Such interactions have also been found to reduce methanol crossover significantly in DMFCs.<sup>30</sup> Intermolecular interactions may also weaken the sulfonated ion pair, reducing the amount of water that is required to promote proton transport.<sup>25</sup>

The aim of this study is to examine possible excellent membranes for use in DMFCs. A series of new blend membranes with various ratios of the poly(ether sulfone) (PES) content to sulfonated poly(ether imide) (SPEI) weight have been prepared. The morphologies and properties, including the thermal and oxidative stability, mechanical properties, proton conductivities, and methanol permeability, have been varied by the variation of the composition of the blend.

#### **EXPERIMENTAL**

#### Materials

SPEI with IECs of 0.56, 0.78, and 0.97 mequiv/g was prepared with chlorosulfonic acid as the sulfonating agent and chloroform as the solvent. PES (Ultrason E6020P; weight-average molecular weight = 58,000 Da) was kindly provided by BASF Corp. (CA) and was dried in a vacuum oven at 130°C for 10 h before it was used. Methanol and ethanol were chromatographicgrade, and other chemicals were analytical-reagentgrade and were used without further purification.

#### Preparation of the blend membranes

Blends of calculated amounts of SPEI and PES were dissolved in *N*-methyl-2-pyrrolidone (NMP) and oscillated homogeneously with an ultrasonic wave oscillator. Membranes with controlled thickness (dry membrane thickness = 50–80  $\mu$ m) were prepared by the casting of the blend solutions onto clean glass plates and drying at 40°C for 8 h, at 60°C for 10 h, and then in a vacuum oven at 100°C for 24 h. The membranes were carefully removed from the glass substrates with a sharp razor blade after they had been cooled to room temperature. Hereafter, the blend membranes are labeled SPEI *x*/PES (*a*/*b*), where *x* is the sulfonation level expressed as an IEC value and *a*/*b* is the ratio of weights of SPEI and PES.

## Thermogravimetric analysis (TGA)

Thermogravimetric results were obtained with a thermogravimetry analyzer (SDT-Q600, TA Instru-

ments, New Castle, DE) at a heating rate of  $10^{\circ}C/$  min in an N<sub>2</sub> atmosphere.

# Morphology

The surface morphology of the blend membranes was observed with a Nanoscope IIIa atomic force microscope (Nanoprobes, Digital Instruments, New York) in the tapping mode. Silicon probes with 125- $\mu$ m cantilevers were used at their fundamental resonance frequencies, which varied from 270 to 350 Hz. The measurements were made under ambient conditions with a vibration isolation floating table. The films were prepared from a 1 wt % polymer solution that was filtered in advance through a Teflon filter with a 0.1- $\mu$ m pore size.

The cross-sectional morphology of the membranes was examined with an X-650 scanning electron microscope from Hitachi (Tokyo, Japan). The membranes were fractured by brief immersion in liquid nitrogen. Fresh cross-sectional cryogenic fractures of the membranes were vacuum-sputtered with a thin layer of Pt/Pd before analysis.

#### Water uptake

The blend membranes were dried in a vacuum oven at 80°C for 24 h, weighed ( $W_{dry}$ ), and immersed in deionized water at room temperature for 24 h. Then, the wet membranes were blotted to remove surface water droplets and quickly weighed ( $W_{wet}$ ). The water uptake of the membranes was calculated as follows:

Water uptake (%) = 
$$\frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$
 (1)

# **Oxidative stability**

A small membrane sample with a thickness of 60  $\mu$ m was soaked in Fenton's reagent (3% H<sub>2</sub>O<sub>2</sub> with 2 ppm FeSO<sub>4</sub>) at 80°C. The stability was evaluated by the recording of the time when the membrane began to dissolve. The dissolving time was defined as the time when the sharp edge of a membrane had disappeared into the solution.

#### **Tensile properties**

The tensile strength was measured with a Shimadzu Autograph AG-10kNA tension tester (Kyoto, Japan) at room temperature. Dry samples were dried in a vacuum oven at 80°C for 24 h before the measurements were made. Wet samples were immersed in deionized water for 1 day at room temperature. Tensile conditions were based on Chinese Standard GB-1040-92 (type V), and samples were measured with a programmed elongation rate of 2 mm/min. Five specimens of each membrane were tested, and the final results are presented as averages of each set of five measurements.

#### Conductivity

Proton conductivities of blend membranes were measured with the alternating-current impedance method. In a chamber, the tested membranes were put into the clamp, connected by two platinum electrodes to a Solatron 1260 complex impedance analyzer (CA) with a frequency range of 0.1 Hz to 10 MHz and an alternating-current voltage amplitude of 10 mV. Before the proton conductivity was measured, all membranes were hydrated by immersion in deionized water for 24 h at room temperature. A sample of the prehydrated membrane ( $3 \times 3 \text{ cm}^2$ ) was clamped between the two electrodes. The proton conductivity ( $\sigma$ ) was calculated as follows:

$$\sigma = l/Rdw \tag{2}$$

where *l* is the distance between the electrodes; *d* and *w* are the thickness and width of the films, respectively; and *R* is the resistance value measured.<sup>32</sup>

#### Methanol permeability

The methanol permeability of the membrane was measured with a two-compartment cell, as presented in Figure 1, at room temperature.<sup>23</sup>

Initially, compartment B of the cell (volume = 20 mL) was filled with a 0.2 vol % ethanol solution in deionized water, whereas compartment A (volume = 20 mL) was filled with 8 vol % methanol, 0.2 vol % ethanol, and deionized water. The membrane, sandwiched by an O-ring of Teflon with a diffusion area of 3.14 cm<sup>2</sup>, was clamped between the two compartments. Before testing, the membrane samples were equilibrated in deionized water for 24 h. The diffusion cell was stirred slowly during the experiment. Solution samples (ca. 2 µL) were extracted in compartment B at intervals and were detected by gas chromatography (GC-5890 series II, Hewlett-Packard, San Diego, CA) with an HP-20M (Carbowax 20M phase) chromatographic column together with a flame ionization detector. The methanol permeability was calculated with the following equation:<sup>33</sup>

$$C_B = \frac{D \times K \times C_A \times A}{V_B \times L} \times t \tag{3}$$

where  $C_B$  is the methanol concentration in compartment B and  $C_A$  is the methanol concentration in compartment A. A, L and  $V_B$  denote the diffusion



Figure 1 Experimental setup of the measurement of methanol permeability.

area of the membrane, and the thickness and the solution volume of compartment B, respectively. D, K, and t are the methanol diffusivity, solubility, and permeation time, respectively. The methanol permeability is defined as the product of the diffusivity and solubility (DK).

#### **RESULTS AND DISCUSSION**

# Thermal stability

The thermal stability of the blend membranes has been studied with TGA. Table I presents the initial temperatures of the degradation steps in a nitrogen atmosphere, and Figure 2 depicts representative thermograms. The membranes exhibit similar thermal stabilities, and all the blend films exhibit a three-step degradation pattern. The first weight loss was observed at approximately 100°C and was caused by the loss of moisture that had been absorbed by hygroscopic sulfonic groups in the poly (ether imide)s. The second step of degradation corresponded to the split of aromatic sulfonic acid groups. The third step indicated the decomposition of the polymer main chains. Table I reveals that the blend membranes are more thermally stable than the pure SPEI membranes, so a hypothesis has been established that -SO<sub>3</sub>H groups interact strongly with the PES polymer. Meanwhile, the higher stability of the PES backbone (whose temperature of initial decomposition is ca. 500°C<sup>34</sup>) versus that of the poly(ether imide) main chain (whose temperature of initial decomposition is ca. 470°C) might be the reason for the increase in thermal stability in the second step.

#### Morphology of blend membranes

The properties of membranes are closely related to their microstructures, especially the spatial distribution of the ionic site. The aggregation of ionic polymers has been studied extensively with small-angle X-ray scattering, atomic force microscopy (AFM), transmission electron microscopy, and other approaches.<sup>35–37</sup> The analysis of Eisenberg<sup>38</sup> demon-

Journal of Applied Polymer Science DOI 10.1002/app

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SPEI $x/PES$	Onset tem	perature (°C)	Water	Oxidative	strength	ı (MPa)	Proton	Methanol
(a/b) membrane	Two-step	Three-step	uptake (%)	stability (min)	Dry	Wet	conductivity (S/cm)	permeability $(cm^2/s)$
SPEI 0.56/PES (10/90)	284	478	$4.26 \pm 0.22$	210	$45.94 \pm 1.38$	$43.04 \pm 1.29$	$(5.0 \pm 0.25)  imes 10^{-5}$	$(7.9 \pm 0.39) \times 10^{-10}$
SPEI 0.56/PES (50/50)	267	459	$12.42 \pm 0.12$	100	$38.75 \pm 1.16$	$31.09 \pm 0.93$	$(3.3 \pm 0.16) \times 10^{-3}$	$(3.28 \pm 0.16) \times 10^{-8}$
SPEI 0.56/PES (75/25)	242	440	$14.50 \pm 0.08$	58	$32.55 \pm 0.97$	$25.04 \pm 0.75$	$(5.7 \pm 0.29) \times 10^{-3}$	$(6.62 \pm 0.31) \times 10^{-8}$
SPEI 0.78/PES (10/90)	274	470	$4.90 \pm 0.20$	195	$42.90 \pm 1.09$	$39.81 \pm 1.02$	$(8.0 \pm 0.40)  imes 10^{-5}$	$(1.08 \pm 0.05) \times 10^{-9}$
SPEI 0.78/PES (35/65)	259	458	$10.29 \pm 0.10$	128	$40.03 \pm 0.80$	$35.69 \pm 1.07$	$(9.3 \pm 0.46) \times 10^{-4}$	$(8.0 \pm 0.40) \times 10^{-9}$
SPEI 0.78/PES (50/50)	254	452	$13.96 \pm 0.06$	94	$36.42 \pm 1.09$	$30.47 \pm 0.91$	$(5.5 \pm 0.27)  imes 10^{-3}$	$(5.3 \pm 0.26) \times 10^{-8}$
SPEI 0.78/PES (75/25)	238	436	$16.63 \pm 0.07$	55	$30.41 \pm 0.91$	$21.19 \pm 0.64$	$(7.8 \pm 0.39) \times 10^{-3}$	$(8.6 \pm 0.43) \times 10^{-8}$
SPEI 0.78/PES (100/0)	237	434	$21.38 \pm 0.05$	7	$25.40 \pm 0.76$	$12.63 \pm 0.38$	$(9.7 \pm 0.48) \times 10^{-3}$	$(1.42 \pm 0.07) \times 10^{-7}$
SPEI 0.97/PES (50/50)	244	447	$13.84 \pm 0.11$	80	$33.81 \pm 1.01$	$24.08 \pm 0.72$	$(6.1 \pm 0.30) \times 10^{-3}$	$(7.08 \pm 0.35) \times 10^{-8}$
SPEI 0.97/PES (75/25)	235	433	$18.05 \pm 0.13$	46	$28.64 \pm 0.86$	$20.17 \pm 0.60$	$(8.3 \pm 0.41) \times 10^{-3}$	$(1.13 \pm 0.05) \times 10^{-7}$
Nafion 112			$16.30 \pm 0.14$	I	$26.13 \pm 0.78$	$20.90 \pm 0.63$	$(8.7 \pm 0.43) \times 10^{-2}$	$(1.05 \pm 0.04) \times 10^{-6}$



100 SPEI 0.97/PES (50/50) 90 80 SPEL0.97 Weight(%) 70 60 50 40 ò 100 200 300 400 500 600 700 200 Temperature(°C)

Figure 2 TGA thermograms of the pure SPEI and SPEI/ PES blend membranes.

strated that the sulfonated groups may aggregate in clusters, providing cationic transport pathways or ionic transport channels. The proton conductivity of membranes depends on the distribution and connectivity of the conductive pathways through the cluster network.<sup>2</sup> The morphology of SPEI/PES blend membranes was analyzed by both AFM and scanning electron microscopy (SEM). AFM tapping-mode images of SPEI/PES blend membranes were obtained under ambient conditions. As shown clearly in Figure 3(d), the light domains surrounded by dark domains are regarded as hydrophilic segments, which represent the hydrophilic sulfonated groups. The dark regions were assigned to the hydrophobic polymer matrix. The images of the SPEI/PES blend membranes show strong compatibility, as shown in Figure 3(a-c). Furthermore, the microstructures of blend membranes become more compact as the density of PES increases. Similar phenomena were observed in the cross-sectional cryogenic fractures of membranes. In the SEM images, the pure SPEI membrane exhibits clear microphase separation and an interpenetrating network due to the clustering of ionic groups, as shown in Figures 4 and 5. Additionally, the dimensions of microphase separation become smaller as more PES is added to the blends. This phenomenon is hardly visible in the SPEI 0.78/PES (10/90) membrane, even under high magnification in Figure 5(a); this suggests a homogeneous morphology. The following two factors explain these results. Strong hydrogen-bonding interactions exist between sulfonic acid groups and PES backbones. However, because SPEI and PES do not seem to be a miscible pair, the excellent solvent quality of NMP for SPEI and PES seems to be partially responsible for the compatible morphologies in the solution of cast blends. The connectivity and the size of hydrophilic regions strongly affect the trans-



**Figure 3** AFM tapping-phase images of the SPEI 0.78/PES blend membranes: (a) 10/90, (b) 50/50, (c) 75/25, and (d) 100/0. The scan size was  $10 \times 10 \ \mu\text{m}^2$ . [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

port properties of the membranes.<sup>2</sup> The images reveal that the sizes of the hydrophilic and hydrophobic domains decrease as the PES content increases. This increase in size changes the properties of the membranes, such as the proton conductivity and methanol diffusion.

# Water uptake

The ability to take up water is one of the important properties of sulfonated polymers that enable them to be used in fuel cells. The proton conductivity of the polymer generally increases with water uptake: the uptake of more water improves the formation of the hydrophilic domain that conducts protons.<sup>39</sup> The water uptake of the polymer can be increased by an increase in the ionic group content in the polymer chain, but most often, the uptake of more water increases the swelling of a membrane, leading to the loss of the mechanical stability of membranes and high methanol permeability. Therefore, water uptake and polymer swelling must be optimized for successful operation in fuel cells.

Table I relates the water uptake to the weight fraction and IEC values for SPEI x/PES (a/b) blend membranes at room temperature. The absorption of water increases with the sulfonic acid group content for a given weight fraction of the blend membrane



Figure 4 SEM micrographs of the SPEI 0.78/PES blend membranes at a low magnification: (a) 10/90, (b) 50/50, (c) 75/25, and (d) 100/0.

because the sulfonic acid group has strong hydrophilicity. Meanwhile, the water uptake decreases as PES is added to SPEI, and this accounts for the hydrophobicity of PES and the formation of hydrogen bonding between PES and sulfonic acid groups. However, the amount of hydrogen bonding generated between PES and sulfonic acid groups increases with the PES content, and this reduces the excessive swelling of the polymer under wet conditions and thereby improves the mechanical properties of the blend membranes. This result can be confirmed by the tensile property experiments, as discussed later.

# **Oxidative stability**

Table I presents the oxidative stability of the blend membranes, which was evaluated with Fenton's reagent at 80°C. A pure SPEI membrane (with an IEC value of 0.78) without blended PES polymer was also tested. The SPEI homogeneous membrane was

Journal of Applied Polymer Science DOI 10.1002/app

very unstable against oxidation and dissolved into Fenton's reagent only after 7 min. However, when 25% PES was present in the SPEI 0.78/PES blend membrane, the membrane was stable for up to 55 min. The SPEI 0.78/PES (10/90) membrane began to dissolve after 3 h. This result indicates that SPEI/ PES blend membranes have better oxidative stability than pure SPEI membranes because of the robust and hydrophobic nature of the PES polymer.

## **Tensile properties**

The mechanical strength of the membrane affects the manufacturing conditions of the membrane electrode assembly and the durability of the DMFC because the temperature, pressure, and humidification vary frequently during DMFC operation.

The mechanical strength of the membranes was evaluated by a tensile test under dry and wet conditions. Table I lists the mechanical properties of the



Figure 5 SEM micrographs of the SPEI 0.78/PES blend membranes at a high magnification: (a) 10/90, (b) 50/50, (c) 75/25, and (d) 100/0.

blend membranes. The Nafion 112 membrane was also tested under the same conditions. The Nafion 112 membrane shows a maximum tensile strength of 21.20 MPa, which is quite similar to that given in the Nafion product information, as presented by Xing.<sup>3</sup> Table I reveals that the number of sulfonate groups in the polymers significantly affects the mechanical properties of the polymers. The tensile strength of the blend membranes prepared from PES and SPEI with the same IEC value decreased as the SPEI content increased. This relationship is evidenced by the plot of the tensile strength as a function of the weight ratio of SPEI 0.78 in blends in Figure 6. This result, which is explained by the introduction of strongly polar -SO<sub>3</sub>H in the polymer chain, is responsible for the ordering in the aggregative state.

The changes in wet membranes should be accounted for more specifically. The modulus and tensile strength both decrease somewhat. The water molecules that are absorbed in the membranes function as plasticizers, reducing the ion-ion interaction of the interpolymer chain by the hydration of sulfonate groups. However, the amplitude of the decrease is not identical for all of the membranes. The blend membranes retain their mechanical strength because of the matrix effect of the PES polymer and specific interactions in the blends. Nevertheless, the tensile strength of the pure SPEI membrane [SPEI 0.78/PES (100/0)] decreases substantially. The tensile strength decreases from 25.40 MPa for the pure membrane in the dry state to only 12.63 MPa under the wet condition because the homogeneous membrane swells excessively in the hydrous state.

# **Proton conductivity**

The proton conductivity of membranes was measured in the longitudinal direction by alternatingcurrent impedance spectroscopy. The proton conductivity, a crucial property for fuel-cell membranes,



Figure 6 Tensile strength of the SPEI 0.78/PES (a/b) membranes in the dry and wet states.

depends directly on the water uptake and the IEC of the sulfonated polymer.<sup>5</sup> As stated previously, the water uptake decreases as the PES content increases. This decrease is expected to reduce the conductivity of the blend membranes because pure PES is not conductive. Figure 8 (shown later) plots the results concerning the conductivity of blend membranes at room temperature. The conductivity decreases as more PES is incorporated into SPEI. This fact is explained as follows: the formation of hydrogen bonds with the sulfonated groups reduces the number of free SO<sub>3</sub>H groups, increasing the protonic resistance and reducing conductivity. A similar trend has been identified for sulfonated poly(ether ether ketone)/PES blends.<sup>25</sup> Figure 8 also reveals that, as the content of PES increases up to 50%, the conductivity decreases slightly. For example, as the content of PES increases from 0 to 50%, the conductivity decreases from 9.7 to 5.5 mS/cm; that is, the decrease in amplitude is only 0.084 mS/cm percentage point of PES. However, when the PES content increases from 50 to 65%, the evident decrease in the amplitude is 0.285 mS/cm per percentage point of PES. For the blend membrane with 90% PES, the proton conductivity is only 8.0  $\times$  10<sup>-5</sup> S/ cm. This different decrease in conductivity may be caused by the formation of the PES continuous phase in the blends when the PES content exceeds 50%. This result indicates that the blend membranes exhibit an adequate proton transmission property when the PES content is below 50%.

#### Methanol permeability

Methanol permeability is crucial in DMFC. The permeability of methanol, which is determined by the change in concentration  $C_B$  with time, is determined





Figure 8 Proton conductivity and methanol permeability of the SPEI 0.78/PES blends. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]



Figure 7 Concentration change of methanol with time for Nafion 112 and the blend membrane. The methanol permeability was calculated from the slope.

from a linear slope, as plotted in Figure 7. The methanol permeability for the Nafion 112 membrane was  $1.05 \times 10^{-6}$  cm<sup>2</sup>/s, which is close to the value obtained by Jiang.<sup>40</sup> Table I presents all values of methanol permeability. The proton conductivity and methanol permeability of SPEI/PES blend membranes were measured as functions of the PES content and were compared with those of the Nafion 112 membrane. As presented in Figure 8, the conductivity decreases as the PES content increases. The methanol permeability also exhibits analogous behavior. The mechanism by which methanol permeates through ionomer membranes such as Nafion and whether methanol moves along the same pathway as protons are matters of ongoing debate.<sup>23</sup> As stated elsewhere,<sup>11</sup> the proton conductivity and methanol permeability are believed to proceed mostly along the same path because both properties exhibit the same trend.

A reasonable explanation of the trend in the methanol permeability of blend membranes is that most of the methanol passes through a channel in which an ion cluster forms. As discussed in relation to the morphology of blend membranes and revealed by AFM, the membranes become more compact and their hydrophilic domain sizes become smaller than the SPEI membranes without PES as hydrogen bonds are formed in the blend membranes. This phenomenon reduces proton conductivity and methanol permeability as the PES content increases.

Table I presents the proton conductivities of the blend membranes with 25 and 50% PES, which are 7.8 and 5.5 mS/cm, respectively. Although the proton conductivities are approximately 1 order of magnitude less than that of Nafion 112, the methanol permeability of the two membranes is only 5% (5.30 ×  $10^{-8}$  cm<sup>2</sup>/s) of that of the Nafion 112 membrane. This very large decrease in methanol crossover demonstrates the feasibility of the blend membrane as an electrolyte for DMFC.

#### CONCLUSIONS

SPEI/PES blend membranes with various IEC values and weight ratios were prepared. The effect of the weight ratio of PES to SPEI on the properties of the blend membranes was evaluated with respect to the thermal and oxidative stability, water uptake, morphology, tensile strength, proton conductivity, and methanol permeability. The blend membranes had higher thermal stability than the pure SPEI membranes. Also, the oxidative stability increased with the PES content because of the increase in the strength of the hydrogen-bond interactions, which resisted the excessive swelling of the blend membranes under wet conditions and thereby increased their mechanical stability. The morphological study indicated that the blend membranes were more compact and their hydrophilic domain sizes were smaller than those of the pure SPEI membrane. Therefore, the proton conductivity and the methanol permeability decreased as the PES content increased. The pure SPEI membrane exhibited clear microphase separation and an interpenetrating network because of the clustering of ionic groups. Furthermore, the extent of the microphase separation decreased as more PES was added to the blends. This study suggests that the thermal stability, water uptake, mechanical properties, proton conductivity, and methanol permeability of blend membranes with PES contents between 25 and 50% make such membranes potentially suitable as electrolytes in DMFC applications.

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