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## Blend Membranes Consisting of Sulfonated Poly(ether ether ketone) and Polysulfone Bearing 4-Nitrobenzimidazole for Direct Methanol Fuel Cells

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Low-cost blend membranes consisting of sulfonated poly(ether ether ketone) (SPEEK) (an acidic polymer) and polysulfone-4-nitrobenzimidazole (PSf-NBIm) (a basic polymer) have been prepared with various PSf-NBIm contents (0–5.0 wt %) and characterized by ion-exchange capacity, proton conductivity, and water uptake measurements. The blend membranes with PSf-NBIm contents of 2.5 and 5.0 wt % show higher proton conductivity and lower water uptake in water and methanol/water solutions at a given temperature than plain SPEEK. The blend membranes also exhibit better electrochemical performance and lower methanol crossover in a direct methanol fuel cell than plain SPEEK and Nafion 115 membranes due to an enhancement in proton conductivity through acid-base interactions and an insertion of the benzimidazole side groups into the ionic clusters of SPEEK, as indicated by small-angle X-ray scattering. The maximum power density of the blend membrane with a PSf-NBIm content of 2.5 wt % is 1.5 times higher than that of the Nafion 115 in 1 M methanol solution at 80°C.

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Direct methanol fuel cells (DMFCs) are intensively being pursued as a potential power source for portable electronic devices because they can provide continuous and uninterrupted power. The Nafion membrane from DuPont, which is a hydrated perfluorosulfonic acid polymer, is currently used as the electrolyte in DMFC because of its high proton conductivity, low methanol swelling, and high thermal stability. However, the high methanol permeability through the membrane remains a barrier for their commercialization. The methanol that permeates from the anode to the cathode through the membrane not only poisons the cathode catalyst but also wastes the fuel, resulting in performance loss.<sup>1</sup>

Several strategies have been pursued to lower methanol permeability in Nafion membranes. A few examples are incorporation of organic Si or inorganic silica additives into Nafion membrane,<sup>2,3</sup> partial substitution of the sulfonic acid groups by Cs<sup>+</sup> ions,<sup>4</sup> impregnation of Pd or PtRu into Nafion membrane,<sup>5,6</sup> applying a plasma<sup>7</sup> or electron beam<sup>8</sup> to modify the surface structure of Nafion, creation of a thin methanol impermeable barrier at the membrane surface, and addition of polymers such as polyfurfuryl alcohol,<sup>9</sup> poly(vinyl alcohol),<sup>10</sup> and poly(3,4-ethylenedioxythiophene)<sup>11</sup> to form a composite membrane. Although these approaches reduce methanol crossover, they generally tend to decrease proton conductivity and sometimes lead to a loss in the mechanical strength.

In view of this, there has been considerable interest to develop membrane materials that can suppress methanol crossover while offering acceptable proton conductivity. Many efforts have been made in recent years to develop fluorine-free polyelectrolyte membrane materials, such as sulfonated derivatives of poly(ether ether ketone) (SPEEK),<sup>12,13</sup> polyphosphazene,<sup>14</sup> polysulfone (PSf),<sup>15,16</sup> and polyimide,<sup>17-19</sup> as well as phosphoric acid doped poly(benzimidazole) (PBI).<sup>20-22</sup> These materials generally exhibit lower methanol crossover and are less expensive than Nafion.<sup>13,16</sup> With an optimized degree of sulfonation, some of them show performance in fuel cell comparable to that of Nafion. However, the high degrees of sulfonation necessary to maximize the proton conductivity often lead to an increase in membrane swelling and degradation in mechanical stability.

Covalent and ionic cross-linking in the membrane has been investigated as an effective approach to reduce the swelling of membranes. However, cross-linked polymers usually become brittle on

drying out. Also, acid-base blends containing ionic cross-links, such as Nafion/PBI, SPEEK/PBI, and SPPO/PBI [PBI and SPPO refer, respectively, to poly(benzimidazole) and sulfonated poly(2,6-dimethyl-1,4-phenylene oxide)], have been found to exhibit lower methanol crossover in DMFCs.<sup>23-26</sup> Unfortunately, they usually lead to a sacrifice in fuel cell performance, and microphase separation is easy to occur in such blends due to the incompatibility between the acidic and basic (polybenzimidazole) polymer structures.<sup>27,28</sup>

Recently, we reported that polysulfone bearing benzimidazole (PSf-BIm) or amino-benzimidazole (PSf-ABIm) side groups could promote proton conduction in SPEEK under anhydrous conditions through acid-base interaction between the sulfonic acid groups of the SPEEK and the nitrogen atoms of the benzimidazole groups tethered to similar aromatic backbones.<sup>29,30</sup> This blend membrane concept is based on industrially available, inexpensive polymer precursors that are compatible with each other due to similar aromatic backbones. In addition to SPEEK being known to exhibit lower methanol crossover compared to Nafion, the benzimidazole side groups tethered to the PSf backbone could also help to suppress methanol crossover further by inserting into the hydrophilic channels.

However, the  $pK_a$  values of the acidic and basic polymers in the blend play a significant role on the proton transfer between the acid and benzimidazole groups. With this perspective, we present here the tethering of 4-nitrobenzimidazole that has a lower  $pK_a$  value than benzimidazole due to the substitution of electron-withdrawing nitro groups in the benzimidazole groups and an investigation of the blend membranes consisting of the basic polymer polysulfone-4-nitrobenzimidazole (PSf-NBIm) and the acidic polymer SPEEK. The ion exchange capacity, proton conductivity, water uptake, and structural and microstructural characterizations of these blend membranes are presented. In addition, the electrochemical performances in DMFCs as a function of the PSf-NBIm content are compared to that of Nafion 115 membrane.

### Experimental

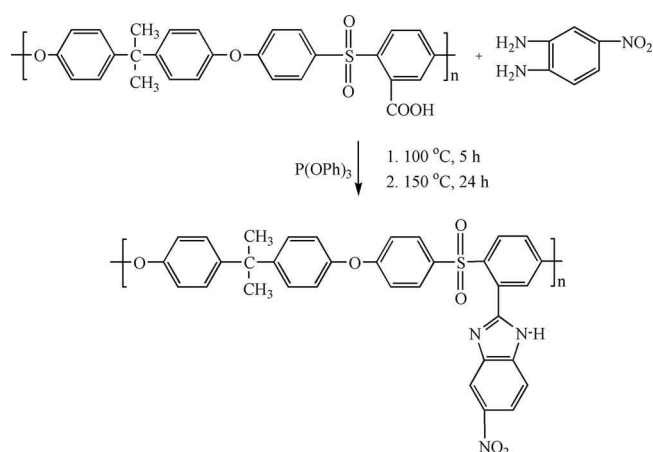
**Materials synthesis.**— 4-nitro-1,2-phenylenediamine (99%) was purchased from Alfa Aesar. Triphenyl phosphite (TPP) (99%) and *N,N*-dimethylacetamide (99 + %) (DMAc) were purchased from Acros. Sulfuric acid was purchased from Fisher Scientific. Poly(ether ether ketone) (PEEK450 PF) was obtained from Victrex. All chemicals were used as received.

The synthesis of PSf-NBIm was carried out by a condensation reaction between carboxylated polysulfone (CPSf) and 4-nitro-1,2-

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**Figure 1.** Synthesis scheme of polysulfone bearing 4-nitrobenzimidazole side group.

phenylenediamine as shown in Fig. 1. The details of the synthesis of CPSf with different degrees of carboxylation per repeat unit are available elsewhere.<sup>31</sup> The CPSf with a degree of carboxylation of 1.03, 1.58, and 1.90 were used, and the PSf–NBIm polymers prepared with it is thereafter designated, respectively, as PSf–NBIm-103, PSf–NBIm-158, and PSf–NBIm-190. Figure 1 shows the reaction between the carboxylated polysulfone and 4-nitro-1,2-phenylenediamine in the presence of a dehydrating agent TPP to give polysulfone bearing 4-nitrobenzimidazole. For example, PSf–NBIm-158 was prepared by dissolving 0.5 g of CPSf with a degree of carboxylation of 1.58 (designated as CPSf-158) and 0.236 g of 4-nitro-1,2-phenylenediamine in 30 mL of DMAc in a three-neck flask, followed by the addition of 2.9 mL of TPP into the flask. The solution was stirred at 100°C for 5 h and then at 150°C for 24 h under nitrogen atmosphere and poured into 1 L of methanol to precipitate the polymer. The precipitate was then filtered and washed with methanol and deionized water several times before drying the product in a vacuum oven at 100°C overnight.

The SPEEK polymer was obtained by sulfonating the PEEK polymer with concentrated sulfuric acid.<sup>13</sup> SPEEK with an ion-exchange capacity (IEC) of 1.36 and a degree of sulfonation of 44% was used in this study.

**Membrane preparation.**— Plain SPEEK membrane and blend membranes consisting of SPEEK and PSf–NBIm were prepared by casting from DMAc solutions. The resulting membranes were dried at 90°C overnight, followed by holding in a vacuum oven at 130°C for 6 h. The membranes were washed thoroughly in boiled DI water several times to remove the residual solvent. The thickness of the membrane was controlled by changing the weight percent of SPEEK and PSf–NBIm in the solution, and all the membranes in this study had a thickness of  $60 \pm 5 \mu\text{m}$  with an active area of  $5 \text{ cm}^2$  for DMFC evaluation.

The Nafion 115 membranes obtained from DuPont were pretreated with a 5% solution of hydrogen peroxide, DI water, and 0.5 M sulfuric acid at  $\sim 90^\circ\text{C}$ , with a thorough washing with DI water between each step. The pretreated membranes were then stored in DI water at room temperature before use.

**FTIR and proton conductivity measurement.**— The structure of the synthesized PSf–NBIm polymers was characterized by Fourier transform IR (FTIR) spectroscopy with a Nicolet FTIR instrument in the range of  $4000\text{--}400 \text{ cm}^{-1}$ . Proton conductivity values of the membranes were obtained from the impedance data, which were collected with a computer interfaced HP 4192 ALF Impedance Analyzer in the frequency range of 5 Hz to 13 MHz with an applied voltage of 10 mV. However, only the data up to 10 kHz were used to calculate the proton conductivity in order to avoid errors from

inductive impedance at high frequencies. The proton conductivity values of dry membranes were obtained from the impedance data collected with a laboratory-made two-electrode setup and stainless steel as blocking electrodes in the transverse direction (i.e., through-plane). Before the test, the membranes were dried overnight at 100°C to remove any free water present in the membrane. Also, the membranes were maintained at each desired temperature without humidification for 30 min before collecting the data. The proton conductivity values under humidified conditions were obtained from the impedance data collected with an open window-framed two platinum electrode cell in the lateral direction (i.e., in plane) by maintaining the membrane in a humidity chamber oven with water vapor at 100% relative humidity (RH), and the details of the setup are available elsewhere.<sup>32</sup>

**IEC measurement.**— The IEC values were determined by suspending 0.1–0.2 g of SPEEK or SPEEK/PSf–NBIm blend membranes in 2.0 M NaCl solution (30 mL) for 24 h to liberate the  $\text{H}^+$  ion and then titrating with standardized 0.05 N NaOH solution (Fisher Scientific) using phenolphthalein as an indicator.

**SAXS measurement.**— The small angle X-ray scattering (SAXS) experiments with the membranes were carried with 1.54 Å Cu K $\alpha$  radiation and a multiwire gas-filled two-dimensional detector (Molecular Metrology, Inc.). The experiments were typically carried out at room temperature for a duration of 90 min. Before the SAXS experiment, the membranes were pretreated by soaking in 2 M CsCl solution for 24 h, followed by washing with DI water and drying in an oven at 90°C for 24 h.

**MEA fabrication.**— The electrodes consisting of gas-diffusion and catalyst layers were prepared as reported elsewhere.<sup>13</sup> Commercial 40 wt % Pt–Ru (1:1) on Vulcan carbon (E-TEK) and commercial 20 wt % Pt on Vulcan carbon (Alfa Aesar) were used, respectively, as the anode and cathode catalysts. The anode and cathode loadings were, respectively, 0.6 and 1.0  $\text{mg}/\text{cm}^2$ . A Nafion loading of 0.35  $\text{mg}/\text{cm}^2$  in both the anode and cathode were accomplished by impregnating the electrodes with a 5 wt % Nafion solution and drying at 90°C under vacuum for 30 min. The membrane electrode assembly (MEAs) were fabricated by uniaxially hot pressing the anode and cathode onto the membrane at 140 and 110°C for 3 min. The electrochemical performances of the MEAs in DMFC were evaluated using a fuel cell hardware (Electrochem Inc.) with serpentine flow-field pattern ( $5 \text{ cm}^2$  active area) and feeding a preheated methanol solution into the anode at a flow rate of 2.5 mL/min by a peristaltic pump without back pressurization and humidified oxygen into the cathode at a flow rate of 200 mL/min with a back pressure of 20 psi.

**Methanol crossover evaluation.**— Methanol crossover through the membranes was evaluated by a voltammetric method<sup>33</sup> by feeding the methanol solution at a flow rate of 2.5 mL/min into the anode side of the MEA while the cathode side was kept under an inert humidified  $\text{N}_2$  atmosphere. By applying a positive potential at the cathode side, the flux rate of the permeating methanol was determined by measuring the steady-state limiting current density resulting from the electro-oxidation of methanol at the cathode side.

## Results and Discussion

**Polymer synthesis.**— Figure 2 shows the FTIR spectra of carboxylated polysulfone and PSf–NBIm with different degrees of carboxylation. The main absorption bands of PSf–NBIm indicating the presence of 4-nitrobenzimidazole are closely similar to those of PBI or poly(2,5-benzimidazole). The bands at  $\sim 3400 \text{ cm}^{-1}$  are attributed to the isolated N–H stretching. The strong absorption at  $1740 \text{ cm}^{-1}$  due to the C=O asymmetric stretching in CPSf almost disappeared in PSf–NBIm, indicating nearly the full conversion of the carboxylic acid groups into 4-nitrobenzimidazole groups. More importantly, the C=N stretching at  $1650 \text{ cm}^{-1}$  clearly distinguishes the PSf–NBIm from CPSf. Thus, the spectral data confirm the for-

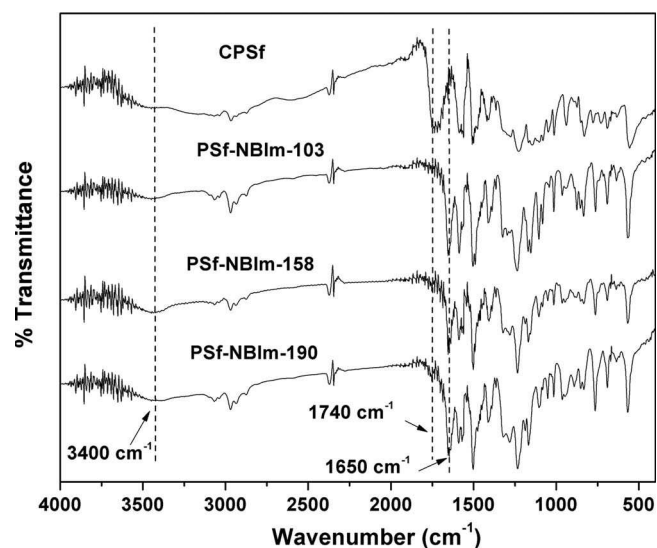


Figure 2. FTIR spectra of carboxylated polysulfone and polysulfone bearing 4-nitrobenzimidazole side group.

mation of the 4-nitrobenzimidazole side groups on polysulfone. Although blend membranes containing SPEEK and PSf-NBIm synthesized from precursors having different degrees of carboxylation were prepared, only the data of the blend membrane containing PSf-NBIm-158 that was prepared with the carboxylic acid precursor having a degree of carboxylation of 1.58 are presented below, and the blend membrane is referred to hereafter as SPEEK/PSf-NBIm for convenience.

**Proton conductivity and IEC.**—In order to study the effectiveness of the 4-nitrobenzimidazole side group as a proton transfer medium, blend membranes containing SPEEK and various PSf-NBIm contents were prepared. Figure 3 compares the proton conductivities of the SPEEK/PSf-NBIm blend membranes with various PSf-NBIm contents and the plain SPEEK membrane under anhydrous conditions. It can be seen that the proton conductivity of the plain SPEEK membrane decreases with increasing temperature above 100°C due to the decreasing amount of water, which is the proton transfer medium (vehicle). However, the proton conductivity of the SPEEK/PSf-NBIm blend membranes increases with increas-

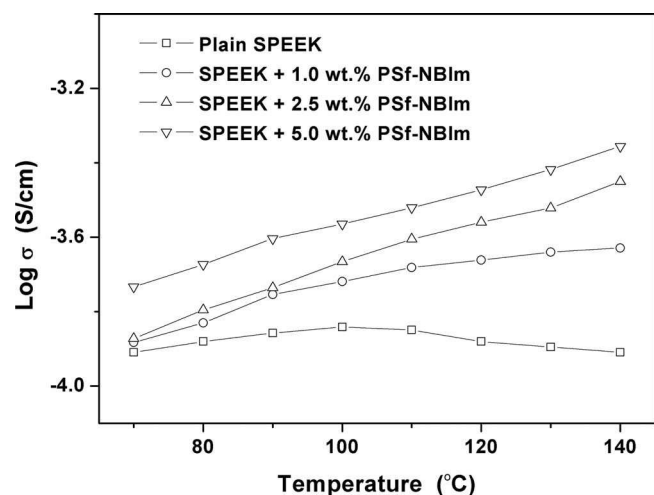


Figure 3. Variations with temperature of the proton conductivities of the plain SPEEK and SPEEK/PSf-NBIm (with various PSf-NBIm contents) blend membranes under anhydrous conditions.

Table I. Ion-exchange capacity (IEC) and proton conductivity ( $\sigma$ ) of plain SPEEK and SPEEK/PSf-NBIm blend membranes with various  $[-SO_3H]/[NBIm]$  mole ratios.

Membrane	$[-SO_3H]/[NBIm]$ Mole ratio	IEC (meq/g)	$\sigma$ at 100% RH and 65°C (S/cm)
Plain SPEEK		1.36	$6.9 \times 10^{-2}$
SPEEK + 1.0 wt % PSf-NBIm	56.3	1.31	$6.4 \times 10^{-2}$
SPEEK + 2.5 wt % PSf-NBIm	22.1	1.26	$9.2 \times 10^{-2}$
SPEEK + 5.0 wt % PSf-NBIm	10.8	1.19	$8.1 \times 10^{-2}$

ing temperature due to the presence of the nitrobenzimidazole groups tethered onto polysulfone. The nitrogen atoms on the benzimidazole ring can act as proton donors and acceptors and thereby help proton transfer under anhydrous conditions between the sulfonic acid groups of SPEEK by a hopping mechanism. This assertion is further supported by an increase in proton conductivity with increasing PSf-NBIm content in the blend membrane.

Table I gives the ion-exchange capacity values and the proton conductivity values measured under 100% RH at 65°C for various contents of PSf-NBIm (or  $[-SO_3H]/[NBIm]$  ratios) in the SPEEK/PSf-NBIm blend membranes. It can be seen that the IEC values of the blend membranes are lower than that of the plain SPEEK, indicating the occurrence of acid-base interactions in the blend membranes and the consequent reduction in the amount of  $H^+$  ions dissociating from the sulfonic acid groups. Moreover, the IEC value decreases as the PSf-NBIm content increases due to an increase in the degree of acid-base interaction. At a given temperature, while the blend membrane with 1.0 wt % PSf-NBIm show proton conductivity similar to that of plain SPEEK, the blend membranes with 2.5 and 5.0 wt % PSf-NBIm show higher conductivity than the plain SPEEK membrane. The increase in proton conductivity is due to the assistance of proton transfer by the nitrobenzimidazole groups in PSf-NBIm through the acid-base interactions as illustrated in Fig. 4. The sulfonic acid groups of SPEEK can protonate the nitrogen atoms in nitrobenzimidazole, facilitating a hopping of the proton bound to the other nitrogen of the nitrobenzimidazole unit to another sulfonate anion group. However, the proton conductivity is maximum at an intermediate PSf-NBIm content of 2.5 wt %, and decreases thereafter on going to 5 wt % PSf-NBIm, suggesting that the proton conductivity is maximized at an optimum PSf-NBIm content.

Under humidified conditions, the vehicle-type mechanism for proton transfer is predominant due to the availability of a greater number of sulfonic acid groups compared to the nitrobenzimidazole

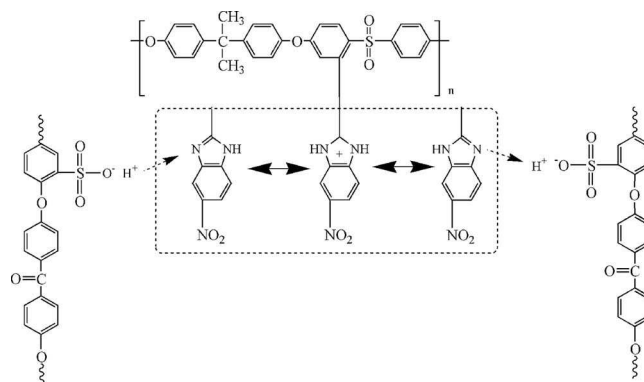
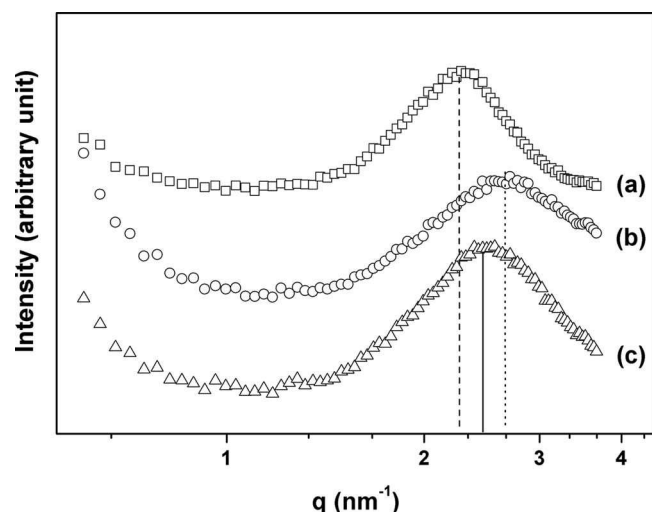


Figure 4. Illustration of the proton transfer mechanism involving acid-base interactions in the SPEEK/PSf-NBIm blend membrane.





**Figure 5.** Comparison of the SAXS profiles of cesium-neutralized (a) Nafion, (b) plain SPEEK, and (c) SPEEK/PSf-NBIm (2.5 wt % PSf-NBIm) blend membranes.

groups in the blend membranes, while the Grotthuss-type mechanism involving the nitrogen atoms on the nitrobenzimidazoles could provide an enhancement in proton conduction. Moreover, the insertion of the nitrobenzimidazole side groups into the ionic channels of the sulfonic acid groups could expand the width of ionic channels, enhancing the proton transfer by the vehicle-type mechanism (see below). However, if the nitrobenzimidazole content becomes too high as in the case of 5.0 wt % PSf-NBIm with a  $[-SO_3H]/[NBIm]$  ratio of 10.8, then the presence of the hydrophobic nitrobenzimidazole groups within the ionic clusters could perturb the proton conduction by the vehicle-type mechanism, resulting in an overall reduction in proton conductivity.

**Ionic cluster size.**—To study the microstructural differences among Nafion, plain SPEEK, and SPEEK/PSf-NBIm blend membranes, small angle X-ray scattering was performed with dry membranes after neutralizing with  $Cs^+$ . In the sulfonated ionomers, such as SPEEK and Nafion, the anion packing is determined by the counterion but is independent of the cation type.<sup>34,35</sup> By neutralization with  $Cs^+$  ions, the electron density contrast between the hydrocarbon PEEK polymer matrix and the ionic cluster should be enhanced. Also, the neutralized dry SPEEK membranes with a degree of sulfonation <50 % are known to show similar trends as that in water and methanol solutions.<sup>36</sup> Figure 5 compares the SAXS profiles of the Nafion 115, plain SPEEK, and SPEEK/PSf-NBIm membranes after neutralization with  $Cs^+$  ions. It can be seen that both the plain SPEEK and SPEEK/PSf-NBIm membranes show the ionomer peak with a higher  $q$ -value compared to Nafion 115, indicating that the plain and blend SPEEK membranes exhibit a smaller Bragg distance (center-to-center distance of clusters) and ionic cluster size compared to Nafion 115 due to the high rigidity of the PEEK backbone to which the  $-SO_3H$  groups are attached. The smaller free volume resulting from a smaller ionic cluster size leads to lower methanol/water permeability and suppressed methanol crossover in DMFC (discussed later). Moreover, even though the degree of sulfonation of the plain and blend SPEEK membranes are the same, the SPEEK/PSf-NBIm blend membrane shows slightly larger Bragg distance compared to plain SPEEK, indicating the expansion of the ionic cluster size due to the insertion of the nitrobenzimidazole side groups into the cluster formed by the sulfonic acid groups in SPEEK.

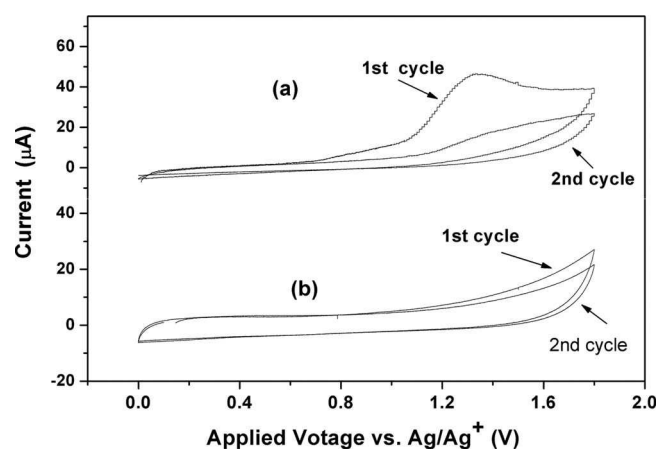
**Liquid uptake.**—Membrane swelling is a critical issue for MEA stability in fuel cells, and it generally trends with liquid uptake. Table II compares the percent liquid uptake at different temperatures

**Table II.** Comparison of the liquid uptake in water and 1 M methanol solution for plain SPEEK and SPEEK/PSf-NBIm-158 blend membranes.

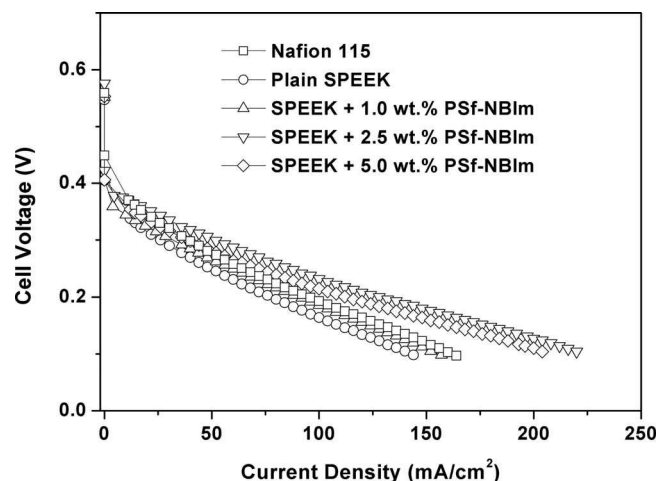
Membrane	Liquid uptake			
	Water (wt %)		1 M methanol solution (wt %)	
	25°C	65°C	25°C	65°C
Plain SPEEK	34.3	45.3	47.5	59.3
SPEEK + 1.0 wt % PSf-NBIm	32.8	43.2	44.1	57.3
SPEEK + 2.5 wt % PSf-NBIm	30.1	41.6	41.7	54.2
SPEEK + 5.0 wt % PSf-NBIm	27.1	39.1	38.9	47.8

in water and in 1 M methanol solution for various PSf-NBIm contents of the SPEEK/PSf-NBIm blend membranes. The liquid uptake increases as the temperature or the concentration of methanol increases at a given PSf-NBIm content and decreases with increasing PSf-NBIm content at a given temperature or methanol concentration. The lower liquid uptake of the SPEEK/PSf-NBIm blend membrane is believed to be due to the increase in both the hydrophobicity of PSf-NBIm and the acid-base interaction between and sulfonic acid and nitrobenzimidazole groups in the blend membrane. The lower liquid uptake could also help to lower the methanol crossover in DMFC as the crossover is known to have a similar trend as the liquid uptake in the SPEEK membrane.<sup>13</sup>

**Electrochemical stability.**—Although the SPEEK/PSf-NBIm blend membrane shows higher proton conductivity and lower water uptake compared to the plain SPEEK, there is a possibility that the nitrobenzimidazole with a nitro-group could poison the Pt catalyst like imidazole in fuel cells. To investigate the poisoning effect, cyclic voltammetry was performed with imidazole and 4-nitrobenzimidazole in  $N(n-C_4H_9)_4PF_6-CH_3CN$  solution in the presence of Pt catalyst, and Fig. 6 compares the voltammograms. Although a large irreversible oxidation peak is seen in the voltammogram of imidazole as reported in the literature,<sup>37</sup> no obvious oxidation peaks are found in the case of 4-nitrobenzimidazole in the



**Figure 6.** Cyclic voltammograms (first two cycles) of Pt/C catalysts in (a) imidazole and (b) 4-nitrobenzimidazole solution at 25°C. The experiments were carried out with an acetonitrile ( $CH_3CN$ ) solution consisting of  $5 \times 10^{-3}$  mol/dm<sup>3</sup> imidazole or 4-nitrobenzimidazole and 0.1 mol/dm<sup>3</sup> tetra-n-butylammonium hexafluorophosphate  $[N(n-C_4H_9)_4PF_6]$  at room temperature with a potential sweep rate of 50 mV/s using a glassy carbon electrode, a platinum auxiliary electrode, and an Ag/AgCl reference electrode.

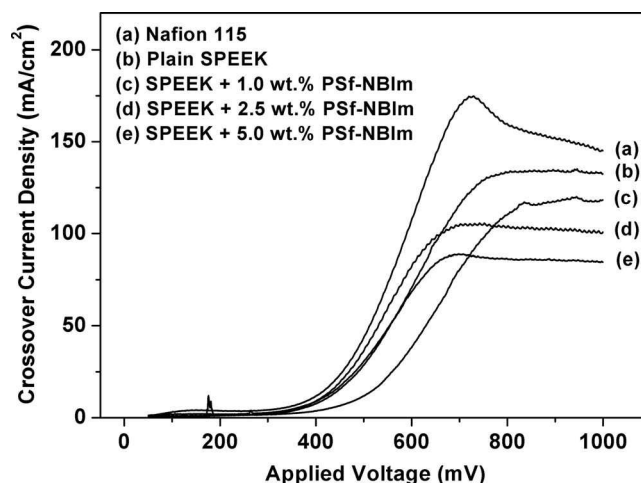


**Figure 7.** Comparison of the polarization curves recorded with Nafion-115, plain SPEEK, and SPEEK/PSf-NBIm (with various PSf-NBIm contents) blend membranes in DMFC. Methanol concentration: 1 M, cell temperature: 65°C.

potential range of 0 to + 1.8 V, indicating that 4-nitrobenzimidazole exhibits better electrochemical stability than imidazole under fuel cell operating conditions. This is further confirmed by the electrochemical performance measurements in fuel cell as presented below.

**Fuel cell performance and methanol crossover.**— Figure 7 compares the polarization curves of the SPEEK/PSf-NBIm blend membranes containing various PSf-NBIm contents (1.0–5.0 wt %) with those of plain SPEEK and Nafion 115 membranes at 65°C. The SPEEK/PSf-NBIm blend membranes show higher fuel cell performance than plain SPEEK membrane, which is consistent with the higher proton conductivity values seen in Table I. More importantly, although the plain SPEEK membrane shows lower performance than Nafion 115 membrane due to the lower proton conductivity, the SPEEK/PSf-NBIm blend membranes with PSf-NBIm contents of 2.5 and 5.0 wt % exhibit higher performance than Nafion 115, confirming the assistance of PSf-NBIm in enhancing the proton conduction. The higher performance is also due to the lower methanol crossover in the blend membrane compared to that in Nafion 115 membrane (see below). Interestingly, the performance of the SPEEK/PSf-NBIm blend membrane containing the nitrobenzimidazole groups is higher than that of the SPEEK/PSf-BIm blend membrane containing the benzimidazole groups with similar  $[-SO_3H]/[BIm]$  ratio in the blend membranes, which is due to a higher proton conductivity measured with the former. We believe this is because the nitrobenzimidazole groups with a lower  $pK_a$  value than the benzimidazole groups facilitate faster proton conduction in the acidic environment.

Methanol crossover is a critical parameter for long-term DMFC operation. Figure 8 compares the methanol crossover current density of the SPEEK/PSf-NBIm blend membranes containing various PSf-NBIm contents to those of plain SPEEK and Nafion 115 membranes. The plain SPEEK membrane shows lower methanol crossover than Nafion 115 although it is much thinner ( $\sim 60 \mu m$ ) than Nafion 115 ( $125 \mu m$ ) due to the narrower hydrophilic regions and smaller ionic cluster size in SPEEK. Interestingly, even though the SPEEK/PSf-NBIm blend membrane shows slightly larger cluster size compared to the plain SPEEK as seen in Fig. 5, it shows much lower methanol crossover than plain SPEEK, indicating the effectiveness of PSf-NBIm in blocking methanol crossover by the insertion of the side groups into the hydrophilic region. The lower methanol crossover in the blend membrane could also help to lower the Pt catalyst loading at the cathode.

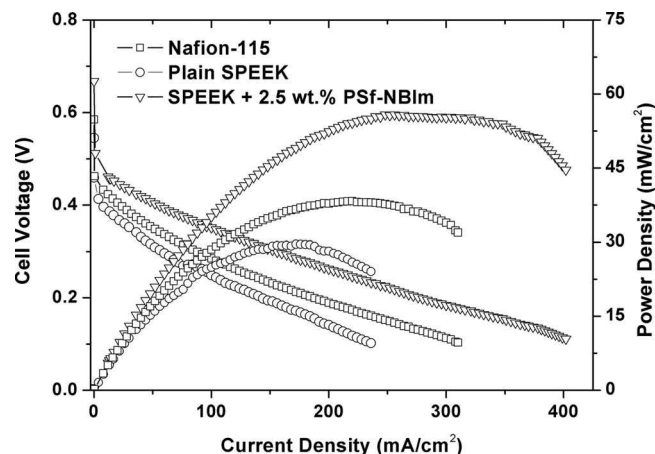


**Figure 8.** Comparison of the methanol crossover current densities for the Nafion-115, plain SPEEK, and SPEEK/PSf-NBIm (with various PSf-NBIm contents) blend membranes in DMFC. Methanol concentration: 1 M, cell temperature: 65°C.

Figure 9 compares the polarization curves and power density of the plain SPEEK, SPEEK/PSf-NBIm (2.5 wt %), and Nafion 115 membrane at 80°C with 1 M methanol solution. The power density value of the blend membrane is higher than those of both plain SPEEK and Nafion 115 membrane. The maximum power density of the blend membrane ( $56 \text{ mW/cm}^2$ ) is 1.5 times higher than that of the Nafion 115 ( $37 \text{ mW/cm}^2$ ).

### Conclusions

Polysulfone bearing 4-nitrobenzimidazole pendant group has been synthesized by a condensation reaction between carboxylated polysulfone and 4-nitro-1,2-phenylenediamine. Blend membranes containing sulfonated poly(ether ether ketone) (an acidic polymer) and various contents (0–5.0 wt %) of PSf-NBIm (a basic polymer) have been characterized by ion exchange capacity, proton conductivity, water uptake, ionic cluster size, and fuel cell performance measurements. Although the blend membranes show larger ionic cluster size compared to plain SPEEK due to the insertion of the nitrobenzimidazole side groups of PSf-NBIm into the ionic cluster formed by the sulfonic acid group of SPEEK, they exhibit lower liquid uptake in water and methanol/water solutions and reduced



**Figure 9.** Comparison of the polarization curves and power densities recorded with Nafion-115, plain SPEEK, and SPEEK/PSf-NBIm (2.5 wt % PSf-NBIm) blend membranes in DMFC. Methanol concentration: 1 M, cell temperature: 80°C.

methanol crossover due to the hydrophobicity and methanol blocking effect of the PSf-NBIm groups. The blend membranes with an optimum PSf-NBIm content of 2.5 and 5.0 wt % exhibit better performance in DMFC than plain SPEEK and Nafion 115 membranes due to an enhancement in proton conduction by acid-base interaction and a reduction in methanol crossover. Moreover, the slightly better performance of the blend membranes containing the nitrobenzimidazole groups compared to those containing the benzimidazole groups suggests that the  $pK_a$  value of the tethered N-heterocycle groups may play a critical role in tuning the properties and performance of these types of acid-base blend membranes.

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