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Acid–base blend membranes consisting of sulfonated poly(ether ether ketone) and 5-amino-benzotriazole tethered polysulfone for DMFC

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ABSTRACT

Low cost, acid–base blend membranes have been synthesized by blending sulfonated poly(ether ether ketone) (SPEEK) (an acid polymer) and various amounts of polysulfone tethered with 5-amino-benzotriazole (a basic polymer). The blend membranes have been characterized by ion-exchange capacity (IEC), liquid uptake, proton conductivity, methanol crossover, and fuel cell performance measurements. The blend membranes exhibit superior performance in direct methanol fuel cells (DMFC) compared to plain SPEEK and Nafion 115 membranes due to enhanced proton conductivity and much suppressed methanol crossover while preserving good swelling stability. The maximum power density of the blend membrane is two times higher than that of Nafion 115 membrane at 80 °C with 1 M methanol feed. Additionally, the effects of the size, pK_a , and the number of nitrogen atoms of the tethered heterocycle groups on the properties of the blend membranes have also been investigated by comparing the properties of the blend membranes consisting of SPEEK and different basic polymers.

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1. Introduction

Direct methanol fuel cells (DMFC) are attractive power sources for portable electronic devices as they do not need recharging with an electrical outlet [1,2]. The use of liquid methanol as a fuel also makes DMFC appealing as the difficulties encountered with the production, storage, and transportation of gaseous hydrogen fuel can be avoided [3]. However, the commercialization of the DMFC technology is hampered by the high methanol permeability through the currently used Nafion membranes as well as the sluggish methanol oxidation and oxygen reduction reactions.

Several aromatic polymers with attached sulfonic acid groups such as sulfonated poly(ether ether ketone) (SPEEK), sulfonated polysulfone (SPSf), and sulfonated polyimide (SPI) have been widely investigated as candidates to substitute for the Nafion membrane in DMFC due to their lower cost, high thermal stability, good mechanical properties, and excellent resistance to hydrolysis and oxidation [4–9]. More importantly, the more rigid aromatic polymer backbones in these polymers could lower methanol crossover due to the smaller ionic cluster size compared to that in Nafion membrane, which has a flexible polytetrafluoroethylene (PTFE) backbone. However, the lower acidity of the sulfonic acid groups in aromatic polymers ($pK_a \sim -1$) compared to that of Nafion ($pK_a \sim -6$) results in comparatively lower proton con-

ductivity [10]. In order to maximize the proton conductivity, a high degree of sulfonation (DS) is desired, which often causes an increase in membrane swelling and degradation in mechanical stability.

Covalent and ionic cross-linking is found to be an effective way to control the dimensional stability and suppress methanol crossover of aromatic polymer membranes with high DS without unduly sacrificing the proton conductivity [11]. Covalently cross-linked sulfonated aromatic polymers with high DS such as SPEEK and SPSf have been found to exhibit much better swelling stability and lower methanol permeability compared to the uncross-linked sulfonated polymers. However, covalently cross-linked polymers have a tendency to become brittle in the dry state, which is a critical problem for fuel cell application. The brittleness is possibly caused by the inflexibility of the covalent networks [12–15]. Because of this reason, more attention is being directed towards the development of ionomer networks containing ionically cross-linked blend systems such as SPPO (poly(2,6-dimethyl-1,4-phenylene oxide))/PBI (polybenzimidazole respectively), SPEEK/PBI, and SPSf/aminated PSf, which are more flexible [16–19]. Our group reported recently [20–23] that blend membranes based on acid–base interactions between the sulfonic acid groups of SPEEK and the *N*-heterocycle groups (benzimidazole (Blm), amino-benzimidazole (ABIm), nitro-benzimidazole (NBIm), and 1*H*-perimidine (Plmd)) tethered to PSf show improved DMFC performance compared to plain SPEEK membranes due to both suppressed methanol crossover and enhanced proton conductivity. This blend membrane concept is based on industrially available, inexpensive polymer precursors like PEEK

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Fig. 1. Synthesis scheme of polysulfone bearing 5-amino-benzotriazole side groups.

and PSf, which are compatible with each other due to their similar aromatic backbones.

To improve further the performance of the acid–base blend membrane systems, we present here the synthesis of a novel polymer, polysulfone bearing 5-amino-benzotriazole (PSf-BTraz), via a condensation reaction between carboxylated polysulfone (CPSf) and 5-amino-benzotriazole (BTraz). The blend membranes consisting of SPEEK and PSf-BTraz (with various PSf-BTraz contents) are prepared and investigated. The BTraz group is larger in size compared to BIm group, and the four nitrogen sites comprising BTraz could facilitate proton transfer more easily through a Grotthuss-type mechanism [24]. The ion-exchange capacity (IEC), proton conductivity, liquid uptake, electrochemical performance in DMFC, and methanol crossover of the SPEEK/PSf-BTraz blend membranes with various PSf-BTraz contents are compared with those of plain SPEEK and Nafion membranes.

Also, to further understand the effects of the size, pK_a , and the number of nitrogen atoms of the heterocycles tethered to PSf on the properties of the acid–base blend membranes, blend membranes consisting of SPEEK and different basic polymers with the same $[-SO_3H]/[heterocycle]$ ratio are prepared and characterized. The microstructure, proton conductivity, and electrochemical performance as well as the methanol crossover of those membranes are compared.

2. Experimental

2.1. Materials synthesis

The PSf-BTraz polymer was synthesized by a condensation reaction between CPSf and BTraz (Acros) as shown in Fig. 1. CPSf with a degree of carboxylation of 1.03, 1.58, and 1.90 were synthesized following the procedure reported elsewhere [25]. The PSf-BTraz samples prepared with these CPSf are hereafter designated as, respectively, PSf-BTraz-103, PSf-BTraz-158, and PSf-BTraz-190. Triphenyl phosphite (TPP) and *N,N*-dimethylacetamide (DMAC, Acros) were used, respectively, as dehydration agent and solvent

in the reaction. For the preparation of PSf-BTraz-158, 0.5 g of CPSf-158 and 0.207 g of BTraz were dissolved in 30 mL of DMAC in a 100 mL three-neck round-bottom flask, the solution was heated to 100 °C under nitrogen atmosphere, and 2.87 mL of TPP was then added. After holding the temperature for 12 h, the resulting solution was cooled down and poured into 400 mL of methanol, where a white power was precipitated. The precipitated product polymer was washed with methanol and de-ionized water and dried in a vacuum oven at 100 °C overnight. The other PSf-BTraz derivatives were made in a similar manner. The structures of the resulting polymers were characterized by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum BX FTIR instrument).

The SPEEK was synthesized by a sulfonation reaction using concentrated sulfuric acid as both a solvent and a sulfonating agent, and the detailed procedure has been reported elsewhere [23]. The degree of sulfonation was controlled by changing the reaction time. In this study, SPEEK with an IEC of 1.42 meq/g was used. The polysulfones tethered with different heterocycles (BIm, ABIm, NBIm, Plmd) were synthesized using CPSf-158 as a precursor and following the procedure reported before [20–23].

2.2. Membrane preparation

Plain SPEEK membrane and blend membranes consisting of SPEEK and PSf-BTraz were prepared by casting onto a glass plate from DMAC solutions containing the polymers (~10% w/w). The resulting membranes were dried at 90 °C overnight and at 130 °C for another 6 h, followed by washing thoroughly with boiled de-ionized water several times. All the membranes were controlled to have a thickness of $60 \pm 5 \mu\text{m}$ with an active area of 5 cm^2 for DMFC evaluation. Although blend membranes consisting of SPEEK and PSf-BTraz-103, PSf-BTraz-158, and PSf-BTraz-190 were prepared, mainly the data of the SPEEK/PSf-BTraz-158 membranes are presented here.

The blend membranes consisting of SPEEK and polysulfone tethered with various heterocycles were prepared by a similar procedure described above. The $[-SO_3H]/[heterocycle]$ ratio in the

Fig. 2. Schematic of the measurement setups employed for (a) dry membrane and (b) wet membrane impedance measurement.

different blend membranes were kept constant at 11.9 by controlling the weight ratio of the acidic and basic polymers when preparing the DMAc solution. The as-received Nafion 115 membrane (C.G. Processing) was pre-treated before use as reported elsewhere [26].

2.3. Ion-exchange capacity (IEC) and proton conductivity measurements

The IEC values of the membranes were determined by an acid–base titration using phenolphthalein as an indicator [26]. Proton conductivity values of the membranes were obtained from the impedance data collected with a computer interfaced HP 4192 ALF Impedance Analyzer in the frequency range of 5 Hz to 1 MHz with an applied voltage of 10 mV. The impedance data of the dry membranes were collected with a home-made two-electrode setup and stainless steel as blocking electrodes in the transverse direction (i.e. through-plane). The impedance data under humidified conditions were collected with an open window framed two-platinum-electrode cell in the lateral direction (i.e. in-plane) by soaking the membranes with de-ionized water. The temperature was controlled by holding the test setup in a temperature-controlled humidity oven. The schematic of the measurement setups is shown in Fig. 2.

2.4. Small angle X-ray scattering (SAXS) measurement

The SAXS experiments with the membranes were carried with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) using a gas-filled multiwire 2D detector. The experiments were typically carried out at room temperature for a duration of 90 min. The SAXS data of all the membranes were collected at dry state after pre-treating them by soaking in 2 M CsCl

Fig. 3. Comparison of the FTIR spectra of carboxylated polysulfone (CPSf) and polysulfone tethered with 5-amino-benzotriazole (PSf-BTraz).

solution for 24 h, washing with de-ionized water, and drying in an oven at 90 °C for 24 h.

2.5. Membrane-electrode assembly (MEA) preparation

The electrodes consisting of gas-diffusion and catalyst layers for DMFC evaluation were prepared as reported elsewhere [27]. Commercial 60 wt.% Pt–Ru (1:1) on Vulcan carbon (E-TEK) and commercial 60 wt.% Pt on Vulcan carbon (Johnson Matthey) were used, respectively, as the anode and cathode catalysts with a catalyst loading of 2.5 mg/cm² on both sides. The membrane-electrode assemblies (MEAs) were fabricated by uniaxially hot-pressing the anode and cathode onto the membrane at 120 °C for 3 min.

2.6. Fuel cell evaluation and methanol crossover measurement

The electrochemical performances of the MEAs in DMFC were evaluated with a 890e Fuel Cell Testing System (Scribner, Inc.) with a single cell hardware (5 cm² active area, Fuel Cell Technologies) and feeding a methanol solution into the anode at a flow rate of 2.5 mL/min and humidified oxygen into the cathode at a flow rate of 200 mL/min without back pressurization. Methanol crossover through the membranes was evaluated by a voltammetric method [28] 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 N₂ atmosphere.

3. Results and discussion

3.1. Synthesis of the PSf-BTraz polymers

The FTIR spectra of the PSf-BTraz polymers synthesized with the CPSf precursor with various degrees of carboxylation are shown in Fig. 3. The strong absorption band of the C=N stretching at 1580 cm⁻¹ and the broad absorption of the isolated N–H stretching around 3400 cm⁻¹ distinguish the PSf-BTraz from the CPSf precursor, indicating the attachment of BTraz groups onto PSf. The asymmetric C=O absorption band at 1740 cm⁻¹ indicates that the 5-amino-benzotriazole is tethered to the carboxyl group (Fig. 1).

Table 1
Comparison of the ion-exchange capacity (IEC) (calculated and measured), $[-SO_3H]/[BTraz]$ ratios, and proton conductivity (σ) of SPEEK/PSf-BTraz blend membranes with various contents of PSf-BTraz-158 with those of Nafion 115 and plain SPEEK membranes.

Membrane	IEC (meq/g)		$[-SO_3H]/[BTraz]$ ratio	σ (S/cm) ^a
	Calculated	Measured		
Plain SPEEK	1.42	1.42	–	0.039
SPEEK + 3 wt.% of PSf-BTraz	1.37	1.31	20.2	0.044
SPEEK + 5 wt.% of PSf-BTraz	1.35	1.27	11.9	0.054
SPEEK + 8 wt.% of PSf-BTraz	1.31	1.22	7.2	0.049
Nafion 115	0.90	0.89	–	0.091

^a 100% relative humidity condition at 25 °C.

3.2. Proton conductivity under anhydrous condition

Fig. 4 compares the temperature dependence of the proton conductivity under anhydrous condition of the Nafion 115, SPEEK, and its blend membranes with various PSf-BTraz contents. It should be recognized that although the membranes were dried before the conductivity measurements, there could be residual water still associated with the sulfonic acid groups [5]. We also noticed absorption of water by the membranes during the assembling of the dried membranes for the proton conductivity measurement as indicated by an increase in the weight of the membranes after we took them out from the measurement system. While the proton conductivity of Nafion 115 and SPEEK decrease with increasing temperature due to the decreasing amount of proton carriers (water), the proton conductivities of the SPEEK/PSf-BTraz blend membranes increase. The nitrogen sites on BTraz side groups play an important role in this phenomenon since nitrogen could act as proton donors and acceptors, facilitating proton transfer between the sulfonic acid groups by Grotthuss-type mechanism through acid–base interaction under anhydrous conditions. Based on the data in Table 1, the measured IEC values of the blend membranes are lower than those calculated from the concentration of the acidic and basic polymers. This result confirms the formation of hydrogen bonding between the sulfonic acid and heterocyclic groups in the blend membranes through acid–base interactions, so that protons could transfer in the hydrogen bonded network through Grotthuss mechanism. Also, the increase in proton conductivity with increasing BTraz content further confirms the assistance of the BTraz groups in proton transfer under anhydrous condition.

Table 1 gives the proton conductivity values measured at 100% relative humidity condition. The proton conductivity values of both Nafion and SPEEK-based membranes under anhydrous con-

dition (Fig. 4) are much lower than those measured under 100% relative humidity condition (Table 1). This is due to the much suppressed proton conduction through the vehicle mechanism under anhydrous condition, which is the predominant proton conduction mechanism in all the membranes. Also, the conductivity values at humidity condition were measured over lateral direction (in-plane) compared to those measured at anhydrous condition over transverse direction (through-plane). It has been reported that the in-plane proton conductivity is usually 2.5–5 times higher than the through-plane conductivity when measured at the same humidity condition [29,30]. The high interfacial resistance between the membrane and electrodes in the measurement cell due to the roughness of our home-made electrode could be another reason for the lower proton conductivity values.

3.3. Liquid uptake, IEC, and proton conductivity under humidity condition

Table 1 compares the liquid uptake, IEC, and proton conductivity of SPEEK, Nafion 115, and SPEEK/PSf-BTraz blend membranes. Since the acid–base interaction between the sulfonic acid and heterocycle groups reduces the number of dissociable H^+ ions from the sulfonic acid groups, all blend membranes show lower IEC values than plain SPEEK membrane. Moreover, as the basic polymer content increases, the IEC value decreases due to an increase in the degree of acid–base interaction. Also, the IEC values of the blend membranes are lower than the theoretical values calculated assuming that only SPEEK provides dissociable protons in the blend membrane, which further confirm the occurrence of acid–base interactions in the blend membranes.

The comparison of the proton conductivity under humidity condition in Table 1 also shows the effect of the acid–base interactions in the blend membrane. The blend membranes show an increase in conductivity with increasing PSf-BTraz content up to 5.0 wt.%, and all the blend membranes exhibit higher proton conductivity than plain SPEEK membrane. Since there is a greater number of sulfonic acid groups compared to the number of heterocycle groups in the blend membranes, the vehicle-type proton conduction mechanism is predominant, while the Grotthuss-type mechanism involving the nitrogen atoms on the heterocycles may provide an enhancement in the proton conduction by providing additional proton transfer “bridges”. Moreover, the insertion of the heterocycles into the ionic clusters formed by the sulfonic acid groups could broaden the proton transfer channels [22,23], resulting in an enhancement in the vehicle mechanism. The longer side chains of PSf-BTraz and the higher number of nitrogen sites (four) in the 5-amino-benzotriazole groups may facilitate easier proton hopping in the SPEEK/PSf-BTraz blend membranes compared to that in the SPEEK/PSf-BIm; in fact, the latter exhibits lower proton conductivity compared to the former with the same $[-SO_3H]/[heterocycle]$ ratio as shown in Table 3.

Compared to some blend membrane systems based on acid–base interactions that have been investigated in the literature

Fig. 4. Comparison of the proton conductivities of the Nafion 115, plain SPEEK, and SPEEK/PSf-BTraz (with various PSf-BTraz-158 contents) blend membranes under anhydrous condition at various temperatures.

Table 2

Comparison of the liquid uptake in water and methanol solution of SPEEK/PSf-BTraz blend membranes with various contents of PSf-BTraz-158 with those of Nafion 115 and plain SPEEK membranes.

Membranes	In water (wt.%)		In methanol solution (wt.%)			
			1 M		2 M	
	25 °C	65 °C	25 °C	65 °C	25 °C	65 °C
Plain SPEEK	26.2	32.7	31.1	37.8	43.8	51.5
SPEEK + 3 wt.% of PSf-BTraz	23.8	30.7	30.5	35.4	39.5	42.7
SPEEK + 5 wt.% of PSf-BTraz	21.4	27.2	25.7	32.3	30.8	35.8
SPEEK + 8 wt.% of PSf-BTraz	18.6	23.4	22.3	28.6	26.8	30.3
Nafion 115	30.8	39.2	36.4	41.2	42.1	48.7

[18,19,31,32], the SPEEK/PSf-BTraz blend membranes presented here show higher proton conductivity than plain SPEEK membrane despite a decrease in the IEC values due to acid–base interactions. We believe this is mainly due to the insertion of the heterocyclic groups of PSf-BTraz into the ionic clusters formed by the sulfonic acid groups of SPEEK as indicated by the SAXS data and the consequent widening of the ionic cluster size compared to that in plain SPEEK. The wider ionic clusters facilitate faster diffusion of the proton carriers through vehicle mechanism. While most of the previous studies pertain to blend membranes consisting of poly-benzimidazole (PBI) in which the heterocycles are in the backbone, the blend membranes presented here have the heterocycle groups tethered to the main chain as side groups. The pendant heterocycles as in PSf-BTraz could not only make it easier for the heterocycles to insert into the ionic cluster but also enhance the flexibility and mobility of the heterocycle groups within the wider ionic channels, which could help to facilitate proton conduction through Grotthuss mechanism as well [33,34].

Table 2 compares the liquid uptake of the various membranes in water and methanol solution at 25 and 65 °C. Although all the membranes exhibit an increase in liquid uptake with increasing temperature and methanol concentration, all the blend membranes show lower liquid uptake compared to plain SPEEK due to the acid–base interactions and lower hydrophilicity of the PSf-BTraz polymer. Moreover, at a given temperature or methanol concentration, the liquid uptake of the blend membrane decreases with increasing PSf-BTraz content, which further confirms the occurrence of acid–base interactions in the blend membranes.

3.4. Methanol crossover and fuel cell performance evaluation

Methanol crossover is a critical parameter for long-term DMFC operation and has a significant effect on the overall performance of DMFC. As BTraz is more hydrophobic than the sulfonic acid groups, the PSf-BTraz basic polymer shows much lower water swelling compared to SPEEK in both water and water/methanol solution. When comparing the methanol crossover current density of the SPEEK/PSf-BTraz blend membranes containing various amounts of PSf-BTraz (3.0–8.0 wt.%) in DMFC at 65 °C with 1 M methanol solution with those of plain SPEEK and Nafion 115 membranes as shown in Fig. 5, the thin blend membranes (~60 μm) show much lower methanol crossover than plain SPEEK (~60 μm) and Nafion 115 (125 μm) membranes, indicating the effectiveness of PSf-BTraz in blocking methanol permeation by the insertion of the more hydrophobic heterocycle groups into the hydrophilic region filled by sulfonic acid groups. Also, as reported for other acid–base blend membranes, the lower methanol crossover in the blend membranes is due to the lower swelling and lower IEC compared to the plain SPEEK membrane as a result of the ionic cross-linking through acid–base interaction in the blend membranes [31,32]. The lower methanol crossover in the blend membrane could not only help

Fig. 5. Comparison of the methanol crossover current density of SPEEK/PSf-BTraz (with various PSf-BTraz-158 contents) blend membranes with those of Nafion 115 and plain SPEEK in DMFC. Methanol concentration: 1 M, cell temperature: 65 °C.

to lower the Pt catalyst loading at the cathode but also lead to a better long-term stability and performance. Moreover, the lower methanol crossover of the blend membranes containing the BTraz groups compared to those containing the Blm groups (Table 3) may suggest that the size of the tethered *N*-heterocycle groups could play a role in tuning the methanol permeability property of this type of acid–base blend membranes.

Fig. 6 compares the polarization curves of the SPEEK/PSf-BTraz blend membranes containing various amounts of PSf-BTraz (3.0–8.0 wt.%) with those of plain SPEEK and Nafion 115 membranes at 65 °C in DMFC. The blend membranes show better performance in DMFC than plain SPEEK membrane due to higher proton conductivity (Table 1) and lower methanol crossover. More interestingly, although the plain SPEEK membrane shows similar performance to Nafion 115 membrane despite a lower methanol crossover due to lower proton conductivity, the blend membranes exhibit much better performance than Nafion 115, confirming the assistance of PSf-BTraz in enhancing the proton conduction and blocking methanol crossover. When comparing the open-circuit voltages (OCV) in our polarization curves with those reported by Wycisk et al. [31,32], the OCV values in our study are lower, which is mainly due to the lower catalyst loading on both the anode and

Fig. 6. Comparison of the polarization curves of SPEEK/PSf-BTraz (with various PSf-BTraz-158 contents) blend membranes with those of Nafion 115 and plain SPEEK in DMFC. Methanol concentration: 1 M, cell temperature: 65 °C.

Table 3
Comparison of open-circuit voltage (OCV), maximum power density, methanol crossover current density in DMFC, and proton conductivity (σ) of blend membranes consisting of various basic polymers with those of plain SPEEK, Nafion 115, Nafion 117 membranes. For DMFC operation and methanol crossover measurements, methanol concentration was 1 M and the cell temperature was 65 °C.

Membranes	OCV (V)	Maximum power density (mW/cm ²)	Methanol crossover current density (mA/cm ²)	σ (S/cm) ^a
Nafion 115	0.63	59	122	0.144
Nafion 117	0.71	49	86	0.143
SPEEK	0.69	64	115	0.069
SPEEK/PSf-ABIm	0.71	95	95	0.093
SPEEK/PSf-NBIm	0.73	84	87	0.087
SPEEK/PSf-BIm	0.72	73	91	0.079
SPEEK/PSf-Plmd	0.74	73	77	0.073
SPEEK/PSf-BTraz	0.72	101	87	0.096

^a 65 °C with 100% relative humidity.

cathode sides and un-optimized catalyst-layer structure in the electrodes [35,36].

It is worth mentioning that although using oxygen versus air at the cathode will have an influence on the absolute values of the power density in DMFC, by increasing the flow rate and back pressure of the air supply, DMFC performances similar to that obtained with oxygen as an oxidant could be achieved in a DMFC for the blend membrane [37,38]. Nevertheless, to investigate the effect of oxygen versus air on the performance of the acid–base blend membranes in DMFC, we have presented a comparison of similar blend membranes (SPEEK/PSf-Plmd blend membranes) with oxygen and air as oxidants [23]. The performance of the acid–base blend membrane with air feeding to cathode is lower compared to that with oxygen feeding due to the lower oxygen concentration in the cathode side. However, the power density at 0.4 V of the blend membrane with air feeding was still higher than that of Nafion 117 membrane with oxygen feeding [23].

Fig. 7 also compares the fuel cell performance and power density of the blend membranes (SPEEK + 5 wt.% PSf-BTraz-158 and SPEEK + 5 wt.% PSf-BTraz-103), plain SPEEK membrane, and Nafion 115 membranes at 80 °C. With the same basic polymer weight content, the blend membrane containing PSf-BTraz-158 shows higher fuel cell performance than that containing PSf-BTraz-103. The higher BTraz content in PSf-BTraz-158 compared to that in PSf-BTraz-103 could enhance proton conductivity and suppress methanol crossover further through a stronger acid–base interaction. With optimized basic polymer contents, the maximum power density offered by the SPEEK/PSf-BTraz-158 blend membrane (174 mW/cm²) is twice of that of the Nafion 115 membrane (84 mW/cm²) and 1.8 times of that of the SPEEK membrane (97 mW/cm²) at 80 °C with 1 M methanol solution.

Fig. 7. Comparison of the polarization curves and power density of SPEEK/5 wt.% PSf-BTraz-158 and SPEEK/5 wt.% PSf-BTraz-103 blend membranes with those of Nafion 115 and plain SPEEK in DMFC. Methanol concentration: 1 M, cell temperature: 80 °C.

3.5. Comparison of the blend membranes consisting of different basic polymers

As mentioned earlier, we previously reported tethering different *N*-heterocycles (BIm, ABIm, NBIm, and Plmd) to PSf and investigated the properties of blend membranes consisting of SPEEK and PSf tethered with the heterocycles [20–23]. To have a better understanding of the effects of the size, pK_a , and the number of nitrogen atoms of the heterocycles tethered to PSf on the properties of the blend membranes based on acid–base interactions, blend membranes consisting of the SPEEK and different basic polymers (shown in Fig. 8) with the same $[-SO_3H]/[heterocycle]$ ratio were prepared and characterized.

To assess the microstructural differences among Nafion, plain SPEEK, and different blend membranes, Fig. 9 compares the SAXS profiles of these membranes. In the sulfonated ionomers like SPEEK and Nafion, the anion packing is independent of the cation type [39,40]. Accordingly, by neutralization with Cs⁺ ions, the electron density contrast between the hydrocarbon PEEK polymer matrix and the ionic cluster could be enhanced. Also, the neutralized dry SPEEK membranes are known to show similar trends as that in water and methanol solutions [41]. As seen in Fig. 9, the plain SPEEK and all the blend membranes show ionomer peaks with higher q values compared to that of Nafion, suggesting a smaller Bragg distance and ionic cluster size than that in Nafion. This is due to the higher rigidity of the aromatic backbones in these polymers compared to that of the PTFE backbone in Nafion. The smaller free volume resulting from a smaller ionic cluster size in the SPEEK and blend membranes also leads to lower methanol/water permeability and suppressed methanol crossover in DMFC. Interestingly, all the blend membranes show larger ionic cluster size than plain SPEEK due to the insertion of the heterocycle side groups into the ionic cluster formed by the sulfonic acid groups of SPEEK.

Another interesting result is that the Bragg distance of the blend membranes increases slowly with increasing size of the heterocycle side groups in the basic polymers. For example, a shift in the SAXS peak to a lower q value could be clearly seen on going from the SPEEK/PSf-BIm to SPEEK/PSf-Plmd blend membrane. Since the concentration of the heterocycles in the blend membranes are almost the same in these two samples, the shift could only be due to the difference in the size of the different heterocycles in the blend membranes. With similar basic polymer concentrations, these two samples have similar IEC, and the pK_a values are also similar for BIm and Plmd [42]. It is clear that the larger size of Plmd blocks methanol permeation more effectively than the smaller BIm.

Table 3 and Fig. 10 compare the proton conductivity, electrochemical performance, and methanol crossover in DMFC of the Nafion, plain SPEEK, and various SPEEK blend membranes. All the blend membranes show higher fuel cell performance than plain SPEEK as seen in Fig. 10, which is consistent with the higher proton conductivity values (measured at 65 °C) in Table 3. More importantly, although the plain SPEEK membrane shows performance

Fig. 8. Structures of the various basic polymers used to obtain the blend membranes with SPEEK. X = benzimidazole (BIm), nitro-benzimidazole (NBIm), 2-amino-benzimidazole (ABIm), 1H-perimidine (PImd), and 5-amino-benzotriazole (BTraz).

similar to that of Nafion 115 membrane despite a lower methanol crossover due to lower proton conductivity, all the blend membranes exhibit higher performance than Nafion 115, confirming the assistance of the heterocycles in enhancing the proton conduction mainly through the widening of the ionic cluster size. Since the longer side chain and the more number of nitrogen sites (four) in amino-benzotriazole may make the proton hopping much easier in the blend membranes consisting of SPEEK and PSf-BTraz compared to that in membranes consisting of other *N*-heterocycles, the SPEEK/PSf-BTraz membrane shows the highest proton conductivity among the blend membranes investigated.

Fig. 9. Comparison of the SAXS profiles of cesium-neutralized (a) Nafion, (b) plain SPEEK, (c) SPEEK/PSf-BIm, (d) SPEEK/PSf-NBIm, (e) SPEEK/PSf-ABIm, (f) SPEEK/PSf-PImd, and (g) SPEEK/PSf-BTraz.

Additionally, as we reported before [22], the pK_a values of the heterocycles could also influence the proton conductivity of this type of blend membranes. For example, the SPEEK/PSf-NBIm blend membrane shows higher proton conductivity compared to that of SPEEK/PSf-BIm as the pK_a value of NBIm is lower than that of BIm due to the electron-withdrawing effect of the nitro functional group attached to BIm. As BTraz is known to have lower pK_a value (higher acidity) than BIm and NBIm by experimental and computational methods [24,42–44], the higher proton conductivity of the SPEEK/PSf-BTraz blend membranes compared to those of blend membranes containing BIm or NBIm could also be due to the lower pK_a value.

The higher fuel cell performance could also be due to the lower methanol crossover in the blend membranes compared to that in Nafion 115 and plain SPEEK as seen in Table 3. Among the blend membranes studied, the SPEEK/PSf-PImd blend membrane shows the lowest methanol crossover due to the largest size of the 1H-perimidine side groups in the basic polymers. This conclusion is also supported by the observed higher open-circuit voltage (OCV) of

Fig. 10. Comparison of the polarization curves of Nafion 115, Nafion 117, plain SPEEK, and blend membranes consisting of SPEEK and various basic polymers in DMFC. Methanol concentration: 1 M, cell temperature: 65 °C.

DMFC at the steady-state. For example, the SPEEK/PSf-PImd blend membrane shows OCV values 0.05 and 0.11 V higher than those of, respectively, plain SPEEK and Nafion 115 membranes. The lower methanol crossover suppresses the cathode catalyst poisoning and lowers the mixed potential at the cathode, resulting in an increase in the OCV at steady-state. More interestingly, even though the blend membranes show larger ionic cluster size than plain SPEEK, they exhibit lower methanol crossover, indicating the effectiveness of the basic polymers in blocking methanol permeation by the insertion of the heterocycle side groups into the hydrophilic region that are formed by the sulfonic acid groups of the SPEEK polymer. Since the blend membranes show increased proton conductivity and suppressed methanol crossover than plain SPEEK, they all show higher maximum power density in DMFC compared to plain SPEEK and Nafion 115 membranes.

4. Conclusions

Polysulfone tethered with 5-amino-benzotriazole (PSf-BTraz) has been synthesized and characterized. The IEC, liquid uptake, proton conductivity, DMFC performance, and methanol crossover in DMFC of the SPEEK/PSf-BTraz blend membranes consisting of various PSf-BTraz contents have been compared with those of plain SPEEK and Nafion 115 membranes. The SPEEK/PSf-BTraz blend membranes exhibit higher proton conductivity, lower liquid uptake in water and methanol solution, lower methanol crossover, and better performance in DMFC compared to plain SPEEK membrane. The superior fuel cell performance of the blend membranes compared to the plain SPEEK and Nafion membranes is due to the enhanced proton conductivity and suppressed methanol crossover facilitated by the acid–base interaction, while maintaining good swelling property. The maximum power density of the blend membrane (with optimized PSf-BTraz contents) is 2 and 1.8 times higher than that of, respectively, Nafion 115 and plain SPEEK membranes at 80 °C with 1 M methanol feed.

By comparing the properties of the blend membranes consisting of SPEEK and different basic polymers, the size, pK_a value, and the number of nitrogen atoms of the tethered *N*-heterocycle groups were found to play critical roles in tuning the proton conductivity and methanol permeability properties of this type of acid–base blend membranes. Among the various blend membranes studied, the SPEEK/PSf-PImd blend membrane shows the lowest methanol crossover due to the largest size of the 1*H*-perimidine group. The SPEEK/PSf-BTraz blend membrane shows the highest proton conductivity and electrochemical performance due to the easiest proton transfer through the 5-amino-benzotriazole groups and the lowest pK_a value (highest acidity) of the BTraz group compared to those of the other *N*-heterocycles investigated here. The blend membrane strategy presented here is an effective way to increase the proton conductivity and lower the methanol crossover simultaneously of the aromatic polymer membranes for DMFC applications.

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References

- [1] A. Heinzel, V.M. Barragan, A review of the state-of-the-art of the methanol crossover in direct methanol fuel cells, *J. Power Sources* 84 (1999) 70–74.
- [2] S. Wasmus, A. Kuver, Methanol oxidation and direct methanol fuel cells: a selective review, *J. Electroanal. Chem.* 461 (1999) 14–31.
- [3] S. Srinivasan, R. Mosdale, P. Stevens, C. Yang, Fuel cells: reaching the era of clean and efficient power generation in the twenty-first century, *Annu. Rev. Energy Environ.* 24 (1999) 281–328.
- [4] B. Yang, A. Manthiram, Sulfonated poly(ether ether ketone) membranes for direct methanol fuel cells, *Electrochem. Solid-State Lett.* 6 (2003) A229–A231.
- [5] P.X. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, K.P. Wang, S. Kaliaguine, Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes, *J. Membr. Sci.* 229 (2004) 95–106.
- [6] Y.-Z. Fu, A. Manthiram, Synthesis and characterization of sulfonated polysulfone membranes for direct methanol fuel cells, *J. Power Sources* 157 (2006) 222–225.
- [7] Z.X. Hu, T. Ogou, M. Yoshino, O. Yamada, H. Kita, H.-I. Okamoto, Direct methanol fuel cell performance of sulfonated polyimide membranes, *J. Power Sources* 194 (2009) 674–682.
- [8] J.M. Song, K. Miyatake, H. Uchida, M. Watanabe, Investigation of direct methanol fuel cell performance of sulfonated polyimide membrane, *Electrochim. Acta* 51 (2006) 4497–4504.
- [9] C.H. Lee, C.H. Park, Y.M. Lee, Sulfonated polyimide membranes grafted with sulfoalkylated side chains for proton exchange membrane fuel cell (PEMFC) applications, *J. Membr. Sci.* 313 (2008) 199–206.
- [10] K.D. Kreuer, On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells, *J. Membr. Sci.* 185 (2001) 29–39.
- [11] J.A. Kerres, Development of ionomer membranes for fuel cells, *J. Membr. Sci.* 185 (2001) 3–27.
- [12] R. Nolte, K. Ledjeff, M. Bauer, R. Mülhaupt, Partially sulfonated poly(arylene ether sulfone)—a versatile proton conducting membrane material for modern energy conversion technologies, *J. Membr. Sci.* 83 (1993) 211–220.
- [13] J.A. Kerres, W. Zhang, W. Cui, New sulfonated engineering polymers via the met-alation route. II. Sulfonated/sulfonated poly(ether sulfone) and its crosslinking, *J. Polym. Sci. A* 36 (1998) 1441–1448.
- [14] M.L. Vona, E. Sgreccia, S. Licocchia, G. Alberti, L. Tortet, P. Knauth, Analysis of temperature-promoted and solvent-assisted cross-linking in sulfonated poly(ether ether ketone) (SPEEK) proton-conducting membranes, *J. Phys. Chem. B* 113 (2009) 7505–7512.
- [15] H. Jeong, K.-S. Lee, J.-S. Lee, Cross-linking density effect of fluorinated aromatic polyethers on transport properties, *Macromolecules* 42 (2009) 1652–1658.
- [16] M. Walker, K.-M. Baumgärtner, M. Kaiser, J. Kerres, A. Ullrich, E. Rächle, Proton-conducting polymers with reduced methanol permeation, *J. Appl. Polym. Sci.* 74 (1999) 67–73.
- [17] B. Kosmala, J. Schauer, Ion-exchange membranes prepared by blending sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) with polybenzimidazole, *J. Appl. Polym. Sci.* 85 (2002) 1118–1127.
- [18] L. Jörissen, V. Gogel, J. Kerres, J. Garche, New membranes for direct methanol fuel cells, *J. Power Sources* 105 (2002) 267–273.
- [19] J.A. Kerres, Blended and cross-linked ionomer membranes for application in membrane fuel cells, *Fuel Cells* 5 (2005) 230–248.
- [20] Y.-Z. Fu, A. Manthiram, M.D. Guiver, Blend membranes based on sulfonated poly(ether ether ketone) and polysulfone bearing benzimidazole side groups for direct methanol fuel cells, *Electrochem. Solid-State Lett.* 10 (2007) B70–B73.
- [21] Y.-Z. Fu, A. Manthiram, M.D. Guiver, Acid–base blend membranes based on 2-amino-benzimidazole and sulfonated poly(ether ether ketone) for direct methanol fuel cells, *Electrochem. Commun.* 9 (2007) 905–910.
- [22] W. Li, Y.-Z. Fu, A. Manthiram, M.D. Guiver, Blend membranes consisting of sulfonated poly(ether ether ketone) and polysulfone bearing 4-nitro-benzimidazole for direct methanol fuel cells, *J. Electrochem. Soc.* 156 (2009) 258–263.
- [23] W. Li, A. Manthiram, M.D. Guiver, Blend membranes consisting of sulfonated poly(ether ether ketone) and 1*H*-perimidine tethered polysulfone for direct methanol fuel cells, *Electrochem. Solid-State Lett.* 12 (2009) B180–B184.
- [24] Z. Zhou, S.W. Li, Y.L. Zhang, M.L. Liu, W. Li, Promotion of proton conduction in polymer electrolyte membranes by 1*H*-1,2,3-triazole, *J. Am. Chem. Soc.* 127 (2005) 10824–10825.
- [25] M.D. Guiver, S. Croteau, J.D. Hazlett, O. Kutow, Synthesis and characterization of carboxylated polysulfones, *Brit. Polym. J.* 23 (1990) 29–39.
- [26] W. Li, A. Bellay, Y.-Z. Fu, A. Manthiram, *N,N'*-bis-(1*H*-benzimidazol-2-yl)isophthalamide as an additive in sulfonated polymer membranes for direct methanol fuel cells, *J. Power Sources* 180 (2008) 719–723.
- [27] W.A. Li, Manthiram sulfonated poly(arylene ether sulfone) as a methanol-barrier layer in multilayer membranes for direct methanol fuel cells, *J. Power Sources* 195 (2009) 962–968.
- [28] X. Ren, T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, Methanol transport through Nafion membranes. Electro-osmotic drag effects on potential step measurements, *J. Electrochem. Soc.* 147 (2000) 466–474.
- [29] S.H. Ma, Z. Siroma, H. Tanaka, Anisotropic conductivity over in-plane and thickness directions in Nafion-117, *J. Electrochem. Sci.* 153 (2006) A2274–A2281.
- [30] T. Soboleva, Z. Xie, Z. Shi, E. Tsang, T. Navessin, S. Holdcroft, Investigation of the through-plane impedance technique for evaluation of anisotropy of proton conducting polymer membranes, *J. Electroanal. Chem.* 622 (2008) 145–152.
- [31] R. Wycisk, J.K. Lee, P.N. Pintau, Sulfonated polyphosphazene-polybenzimidazole membranes for direct methanol fuel cells, *J. Electrochem. Soc.* 152 (2005) A892–A898.
- [32] R.J. Wycisk, J. Chisholm, J. Lee, J. Lin, P.N. Pintau, Direct methanol fuel cell membranes from Nafion-polybenzimidazole blends, *J. Power Sources* 163 (2006) 9–17.
- [33] H.D. Lin, C.J. Zhao, Z.M. Cui, W.J. Ma, T.Z. Fu, H. Na, W. Xing, Novel sulfonated poly(arylene ether ketone) copolymers bearing carboxylic or benzimidazole pendant groups for proton exchange membranes, *J. Power Sources* 193 (2009) 507.

- [34] Y. Alvarez-Gallego, B. Ruffmann, V. Silva, H. Silva, A.E. Lozano, J.G. De La Campa, S.P. Nunes, J. de Abajo, Sulfonated polynaphthalimides with benzimidazole pendant groups, *Polymer* 49 (2008) 3875–3883.
- [35] T.V. Reshetonkon, H.-T. Kim, U. Krewer, H.-J. Kweon, The effect of the anode loading and method of MEA fabrication on DMFC performance, *Fuel Cells* 3 (2007) 238–245.
- [36] T.V. Reshetonkon, H.-T. Kim, H. Lee, M. Jang, H.-J. Kweon, Performance of a direct methanol fuel cell (DMFC) at low temperature: cathode optimization, *J. Power Sources* 160 (2006) 925–932.
- [37] A.S. Arico, P. Creti, P.L. Antonucci, J. Cho, H. Kim, V. Antonucci, Optimization of operating parameters of a direct methanol fuel cell and physico-chemical investigation of catalyst–electrolyte interface, *Electrochim. Acta* 43 (1998) 3719–3729.
- [38] S.H. Seo, C.S. Lee, Effect of operating parameters on the direct methanol fuel cell using air or oxygen as an oxidant gas, *Energy Fuels* 22 (2008) 1212–1219.
- [39] K.A. Mauritz, Review and critical analyses of theories of aggregation in ionomers, *J. Macromol. Sci. Rev. Macromol. Chem. Phys. C* 28 (1998) 65–98.
- [40] J.A. Lefelar, R.A. Weiss, Concentration and counterion dependence of cluster formation in sulfonated polystyrene, *Macromolecules* 17 (1984) 1145–1148.
- [41] B. Yang, A. Manthiram, Comparison of the small angle X-ray scattering study of sulfonated poly(ether ether ketone) and Nafion membranes for direct methanol fuel cells, *J. Power Sources* 153 (2006) 29–35.
- [42] W. Li, B.C. Norris, P. Snodgrass, K. Prasad, A.S. Stocket, V. Pryamitsyn, V. Ganesan, C.W. Bielawski, A. Manthiram, Evaluating the role of additive pKa on the proton conductivities of blended sulfonated poly(ether ether keton) membranes, *J. Phys. Chem. B* (2009) 10063–10067.
- [43] T.N. Brown, N. Mor-Diez, Computational determination of aqueous pKa values of protonated benzimidazole, *J. Phys. Chem. B* 110 (2006) 20546–20554.
- [44] F.G. Bordwell, Equilibrium acidities in dimethyl-sulfoxide solution, *Acc. Chem. Res.* 21 (1988) 456–463.