

Preparation of organic/inorganic composite membranes using two types of polymer matrix via a sol–gel process

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Abstract

Organic/inorganic composite membranes were prepared using two different polymers. BPO₄ particles were introduced into polymers via an in situ sol–gel process. Pre-/post-sulfonated polymers were used to prepare composite membranes as matrix. Pre-sulfonated poly(aryl ether ketone) (SPAEEK-6F) copolymer was synthesized via nucleophilic aromatic substitution. Degree of sulfonation was adjusted by the percentage of sulfonated monomer. Post-sulfonated poly(ether ether ketone) (SPEEK) was prepared using concentrated sulfuric acid as sulfonation agent. The membranes were characterized in terms of the ion-exchange capacity (IEC), proton conductivity, water uptake, AFM, SEM and their thermal properties. The SPAEK-6F plain membranes showed higher proton conductivity than that of the SPEEK plain membranes at similar water uptake or IEC due to their structural difference. SEM images of the composite membranes showed that the BPO₄ particles were homogeneously dispersed in the polymer matrices and BPO₄ particle size was greatly influenced by polymer matrix. The SPAEK-6F/BPO₄ composite membranes had much smaller BPO₄ particle size than the SPEEK/BPO₄ composite membranes due to well dispersion of BPO₄ sol-like particulates in SPAEK-6F polymer solutions forming more hydrophobic/hydrophilic nanophase than SPEEK polymer solutions. The latter containing a few micrometer-scale BPO₄ particles showed higher proton conductivity than the former containing hundreds nanometer-scale BPO₄ particles at similar water uptake due to the increase in freezable water and effect of particle size.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been developed as alternative power sources for stationary, automobile and portable power [1,2]. Proton exchange membrane (PEM) is an essential component of the PEMFC systems, which is functioned as proton conductor from anode to cathode. The commercial perfluorosulfonic polymers such as NafionTM from DuPont have been largely used due to their excellent mechanical property, chemical stability and high proton conductivity ($\sim 0.1 \text{ S cm}^{-1}$ at room temperature) in a fully hydrated state. However, high costs of the material and loss in performance at

either high temperature ($>80^\circ\text{C}$) or low humidity have limited its large-scale industrial applications [3]. Sulfonated aromatic hydrocarbons such as poly(ether ether ketone) (SPEEK) [4–8] were actively investigated as alternative membranes due to their good chemical, mechanical properties, thermal stability and low cost. In order to obtain the sulfonated materials as proton exchange membranes, chemical modification of the polymers was carried out by treatment of sulfonation agents. However, post-sulfonation of polymers is difficult to adjust the degree of sulfonation due to its heterogeneous sulfonation with respect to the reaction conditions such as temperature, mechanical stirring, concentration and so on. Nowadays, sulfonated aromatic hydrocarbons were directly synthesized using sulfonated monomer. This direct synthesis (in other words, pre-sulfonation) enables easily to control the degree of sulfonation and to avoid the problems such as cross-linking and side reaction which are likely

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to occur during post-sulfonation [5,9,10]. Moreover, sulfonated copolymers are able to have two sulfonic acid groups per a repeating unit via the pre-sulfonation and result in higher proton conductivities at the same ion-exchange capacity (IEC) and/or water uptake [11].

Incorporation of the inorganic particles into polymer matrices can improve the electrochemical properties of the PEM because the inorganics mostly functioned as fast solid proton conductors and water absorbers. Among several types of inorganic particles, boron phosphate (BPO_4) has been used for composite membranes due to its high proton conduction property [12–14]. The size and structure of particles in a general sol–gel process depend on several experimental variables such as concentration of precursor, reaction time, reaction temperature, nature of solvent, pH and so on [15]. In our previous works [16,17], the BPO_4 particles were successfully prepared by the modified sol–gel route. We found that the BPO_4 particle size was dependent on the concentration of precursors to form BPO_4 particle [16]. In addition, at the same amount of BPO_4 , the particle size was dependent on the ionic form of solution-casting polymers [17]. In conclusion, the proton conductivity of the composite membranes was higher than that of the plain membranes with an increase in BPO_4 particle size. In this work, we carry out the synthesis of pre-/post-sulfonated polymers and the preparation of the composite membranes using these two polymers. The effect of polymer matrix on BPO_4 particle size and then on the proton conductivity of composite membranes will be investigated.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (PEEK) from Victrex was dried overnight at 110 °C under vacuum. Tripropylborate (98%), 4,4'-difluorobenzophenone (DFBP), hexafluorobisphenol A (6F-BPA), anhydrous potassium carbonate (99%), fuming sulfuric acid (containing 30% SO_3), *N,N*-dimethylacetamide (DMAc) and toluene were purchased from Sigma–Aldrich Corp. Sulfuric acid (95%), phosphoric acid (85%) and sodium chloride (98.5%) obtained from Junsei Chemicals, Japan, were used as received.

2.2. Preparation of SPEEK polymer

For sulfonation of PEEK, 25 g of PEEK was slowly added into 500 mL of H_2SO_4 in a three-neck round bottom flask under mechanical stirring. The flask was heated in an oil bath to 50 °C under nitrogen atmosphere. PEEK was gradually dissolved in H_2SO_4 and the reaction was kept for 6–8 h. Afterwards, the solution was cooled down to room temperature, and the sulfonated polymer was precipitated into a large excess of demineralised (DM) water in an ice-water bath. The polymer was washed with DM water several times until the pH of the rinsed water was neutral and was further stirred overnight with fresh DM water to remove any residual acid. The resulting SPEEK was dried at 60 °C for 12 h and then 110 °C for overnight under vacuum [17].

2.3. Synthesis of sulfonated monomer

Na^+ -form of 5,5'-carbonylbis(2-fluorobenzene-sulfonate) (SDFBP) was synthesized by sulfonation of 4,4'-difluorobenzophenone with the concentrated fuming sulfuric acid at 140 °C for 6 h, followed by neutralization, according to the procedure described elsewhere [18].

2.4. Synthesis of SPAEK-6F

The sulfonated random copolymers were synthesized via nucleophilic aromatic substitution [19]. DFBP, SDFBP, 6F-BPA and an excess of anhydrous potassium carbonate were added into a 250 mL three-neck round bottom flask equipped with a magnetic stirrer, a Dean-Stark trap and a nitrogen inlet. Monomers were mixed in DMAc/toluene and refluxed at 130 °C for 4 h to remove water by azeotropic distillation. Then the reaction temperature was gradually increased to 160 °C and maintained for 36 h. The mixture was cooled to 100 °C, precipitated into a large excess of ethanol with vigorous stirring and washed with water to remove residual inorganic salt. Then, in order to convert the Na^+ -form into H^+ -form, precipitated SPAEK-6Fs were soaked in 1.0 M H_2SO_4 for 12 h, rinsed with water several times to remove residual acid and then dried in a vacuum oven at 120 °C for 24 h.

2.5. Membrane preparation

The plain membranes were prepared by casting 10 wt.% polymer solutions in DMAc, which were filtered by a 0.45 μm membrane filter onto flat Pyrex Petri dishes. Cast solutions were dried at 70 °C for 4 h, the temperature was raised to 110 °C and maintained for 12 h and further 12 h under vacuum. For the organic/inorganic composite membranes, tripropylborate and H_3PO_4 were used to make BPO_4 particles as precursors [16]. All the composite membranes prepared in this study contained 20 wt.% BPO_4 . Quantitative tripropylborate and H_3PO_4 were added into the 10 wt.% polymer solutions and stirred with a magnetic stirrer for 10 min. Then the mixtures were heated to 120 °C in an oil bath for 20 min under magnetic stirring. The resulting solutions were cast onto flat Petri dishes. Cast solutions were dried at the same condition for the plain membranes. The thickness of all membranes was in the range of 70–100 μm .

2.6. Membrane characterization

2.6.1. AFM image

Atomic force microscopy (AFM) imaging was performed on a Nanoscope III multimode scanning probe microscope (Veeco, United States) in a tapping mode etched silicon probe (TESP). Wet samples, which were kept in DM water for 24 h, were used for the measurement.

2.6.2. SEM

Before the measurement, the samples were dried at 100 °C for 24 h under vacuum. SEM images were taken on each cross-section of the membranes using a scanning electron

microscope (SEM) S-4700 from HITACHI. The membranes were cryogenically fractured in liquid nitrogen and were then vacuum-sputtered with Pt/Pd.

2.6.3. Thermal analysis

TGA analysis was carried out on a TGA 2050 instrument (TA Instruments) under nitrogen atmosphere. Before the measurement, the samples were dried in the vacuum oven at 80 °C for 24 h to remove the water present in the membranes. Then, to remove the trace of the water absorbed during the sampling, the samples in the TGA chamber were heated to 110 °C, kept for 10 min, cooled down to 80 °C and then reheated till 500 °C at a rate of 10 °C min⁻¹ to get the data which have no effect of an increasing rate of temperature on TGA analysis.

2.6.4. Water uptake

Water uptake of the plain and composite membranes was determined from the difference in membrane weight before and after hydration. The membrane samples were dried at 100 °C vacuum oven for 24 h and weighed (W_{dry}). Then the samples were immersed in DM water for 24 h at room temperature. Surface water of the samples was wiped out and the samples were immediately weighed (W_{wet}). Water uptake was calculated using a following equation:

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

2.6.5. Proton conductivity

Before the measurement of proton conductivity, the membranes were soaked in DM water for 24 h. The size of the membrane samples was 2 cm long and 1 cm wide. Proton conductivity of the membranes was measured by an impedance spectroscopy using a Solartron 1260 gain phase analyzer, interfaced to a Solartron 1480 multistat. The measurement was carried out in a potentiostatic mode in the frequency range of 0.1 Hz to 10 MHz with 5 mV of oscillating voltage. The laboratory-made four-probe conductivity cell was used and its configuration was found elsewhere (see Fig. 1). The conductivity cell was placed in the head-space of a temperature-controlled sealed vessel which was maintained at 100% relative humidity [21]. Proton conductivity of the samples was calculated from impedance data using a following equation:

$$\sigma = \frac{L}{RWd} \quad (2)$$

where σ is the proton conductivity, L the length between two potential sensing platinum wires and d the membrane thickness, R the membrane resistance derived from the impedance value at zero phase angle and W is the width of the potential sensing platinum wire.

2.6.6. Ionic exchange capacity

The measurement of ion-exchange capacity (IEC, meq of SO₃H g⁻¹ of dry membrane) was measured by a titration method. The membranes were rinsed with DM water after H₂SO₄ treatment. The H⁺-form membranes were immersed in

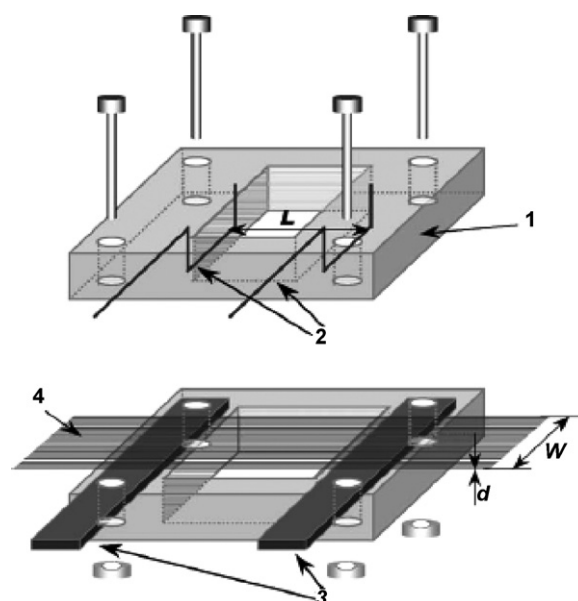


Fig. 1. Four-point-probe conductivity cell for measuring ionic conductivities in membranes: (1) Teflon block, (2) Pt wires for potential readout, (3) Pt foils for constant current supply, and (4) membrane specimen [20].

a 1.0 M NaCl solution for 1 day. The H⁺ ions released by the ion-exchange reaction with Na⁺ ions were titrated with a 0.01 M NaOH solution, in which phenolphthalein was used as an indicator. The ion-exchange capacity (IEC) of the membranes was calculated from the titration data using a following equation:

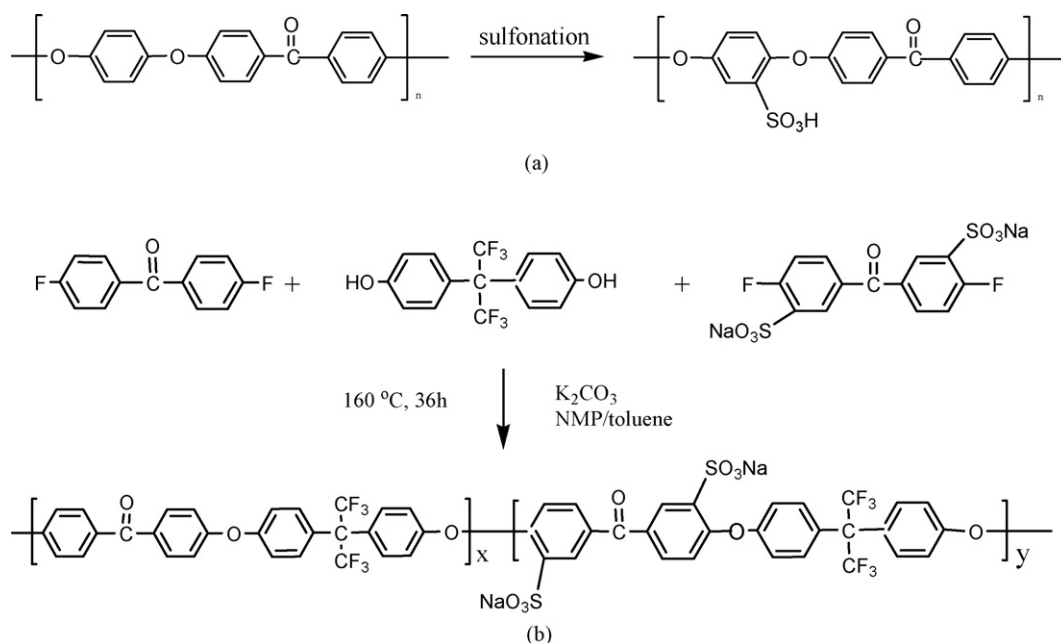
$$\text{IEC} = \frac{\text{volume of consumed NaOH (mL)} \times \text{molarity of NaOH}}{\text{weight of a dried membrane}} \quad (3)$$

3. Results and discussion

3.1. Effect of sulfonation methods

As shown in Scheme 1, two types of the sulfonated polymers (SPEEK and SPAEK-6F) were prepared by different sulfonation methods. The water uptake, the degree of sulfonation, IEC and proton conductivity of the membranes are summarized in Table 1. IEC of the SPAEK-6F membranes showed similar theoretical IEC values. As mentioned earlier, pre-sulfonation enables to control the degree of sulfonation. In this study, the degree of sulfonation was successfully controlled. Water uptake of membranes proportionally increases with increasing the degree of sulfonation, in other words, IEC. Two membranes with similar water uptake, i.e., SPEEK 6 h and SPAEK-6F-40, show much different proton conductivity in Table 1. The SPAEK-6F-40 has higher proton conductivity than the SPEEK 6 h.

Fig. 2 shows proton conductivity of the membranes as a function of IEC. Proton conductivity is also proportional to IEC. As expected, the SPAEK-6F plain membranes show higher proton conductivity than the SPEEK plain membranes at similar IEC. For example, the SPEEK 6 h exhibits 0.0164 S cm⁻¹ at 1.55 IEC value, and the SPAEK-6F-50 shows 0.057 S cm⁻¹ at



Scheme 1. (a) Preparation of post-sulfonated copolymer and (b) synthesis of pre-sulfonated copolymer.

Table 1
Water uptake, degree of sulfonation, ion-exchange capacity, proton conductivity of membranes

Membranes	Water uptake ^a (%)	Degree of sulfonation ^b (%)	IEC (meq g ⁻¹)		Proton conductivity ^a (S cm ⁻¹)
			Theoretical	Measured	
SPEEK 6 h	25	55	–	1.55	0.0164 ± 0.0007
SPEEK 8 h	35	60	–	1.67	0.0368 ± 0.0008
SPAEEK-6F-30 ^c	16	53	1.04	0.95	0.0090 ± 0.0002
SPAEEK-6F-40 ^c	23	72	1.34	1.25	0.0227 ± 0.0014
SPAEEK-6F-50 ^c	37	88	1.62	1.50	0.0571 ± 0.0033

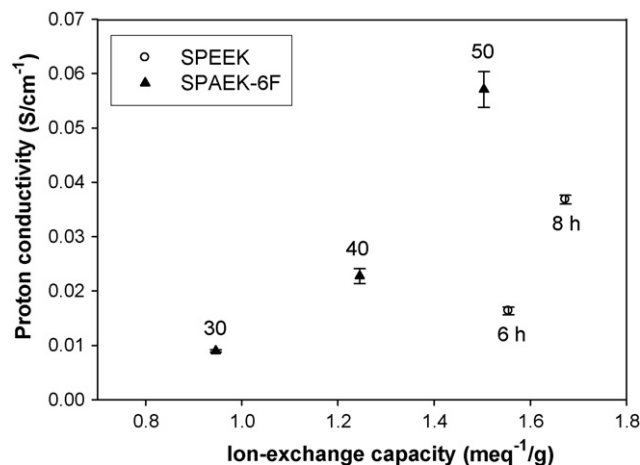
^a Measured at 30 °C.^b Degree of sulfonation (DS) was calculated from a following equation: $DS = M_{w,p} \times IEC / [1 - M_{w,f} \times IEC] \times 100$, where $M_{w,p}$ is the molecular weight of the non-functional polymer repeat unit and $M_{w,f}$ the molecular weight of functional group with counter ion ($-SO_3Na$) [16].^c The percentage of sulfonated monomer SDFBP = monomer SDFBP / [monomer DFBP + monomer SDFBP] × 100 as shown in Scheme 1.

Fig. 2. Proton conductivity of membranes with ion-exchange capacity.

1.50 IEC value. Even at lower IEC, the SPAEK-6F plain membranes have higher proton conductivities than the SPEEK plain membranes (SPEEK 6 h vs. SPAEK-6F-40 and SPEEK 8 h vs. SPAEK-6F-50).

The higher proton conductivity of the SPAEK-6Fs at the similar water uptake or IEC than the SPEEKs arises from their chemical structural difference. It can be inferred that pre-sulfonated polymers form a better proton conducting pathway such as NafionTM-like ionic clustering than post-sulfonated polymers. It allows pre-sulfonated copolymers easily to form the broad water-filled channels because they have two sulfonic acid groups per a polymer repeating unit in contrast to post-sulfonated polymers which have one sulfonic acid group per a repeating unit as discussed in Section 1.

To visually investigate the aforementioned chemical structural difference, the AFM measurement was carried out. The AFM images showed definite hydrophobic/hydrophilic separation with increasing the degree of sulfonation of both polymers and all the SPAEK-6F samples showed most well-separated AFM image. To compare the channel formation effect of dif-

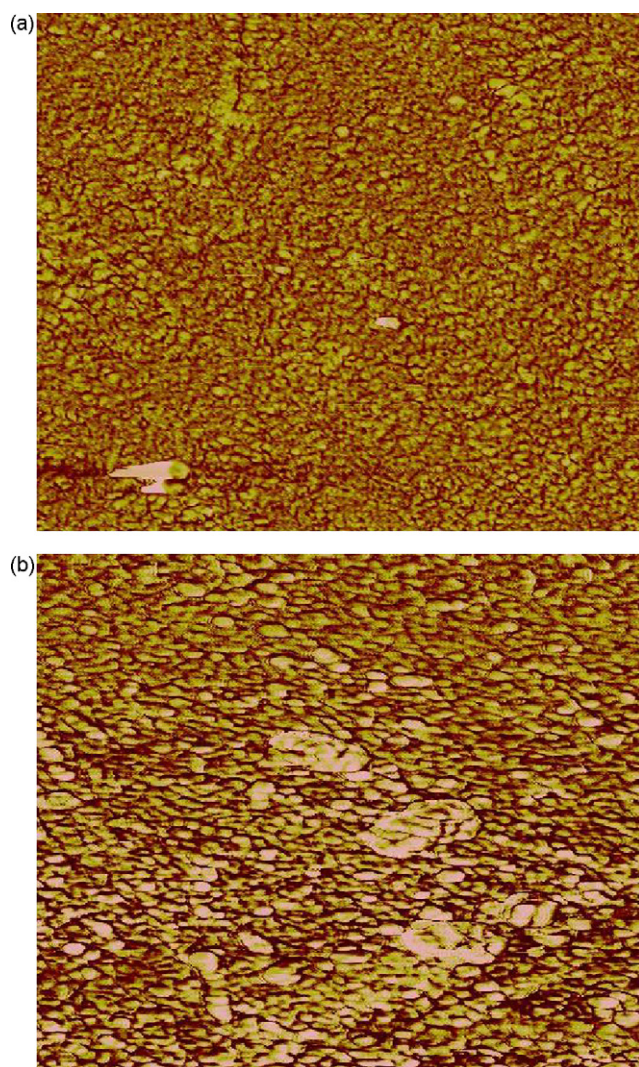


Fig. 3. AFM phase image of plain membranes: (a) SPEEK 6 h and (b) SPAEK-6F-50.

ferent hydrophobic/hydrophilic properties of both polymers, AFM images of the SPEEK 6 h and SPAEK-6F-50 which have similar IEC values are shown in Fig. 3. The darker parts represent the hydrophilic sulfonic acid groups containing water [9]. The SPAEK-6F-50 shows more well-separated hydrophobic/hydrophilic domains and forms larger channels of ionic rich phase compared with the SPEEK 6 h. The visual structure difference well supports the formation of the broader water-filled channels in the SPAEK-6Fs than the SPEEKs and finally explains the higher proton conductivity of the SPAEK-6Fs at similar IEC or water uptake as discussed earlier.

Fig. 4 shows the TGA curves of the membranes in acid form. The first weight loss of the SPAEK-6Fs begins around 250 °C. This may be caused by the thermal degradation of sulfonic acid groups. Thermal degradation of backbones of the SPAEK-6F was occurred around 450 °C. The 5% weight loss of the SPAEK-6Fs and SPEEKs is above 300 °C. It indicates that the SPAEK-6Fs were well synthesized to have thermal stability as much as the SPEEKs prepared using a commercially available thermoplastic, i.e., PEEK. It is noted that the percentage of

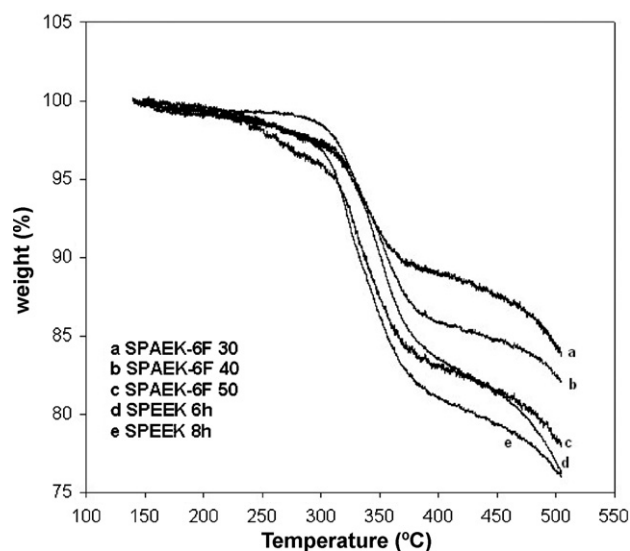


Fig. 4. Thermogravimetric weight loss curves for pre-/post-sulfonated membranes.

weight at 400 °C is different with the type of membrane in order of SPAEK-6F-30 > SPAEK-6F-40 > SPEEK 6 h \approx SPAEK-6F-50 > SPEEK 8 h. The difference in weight arises from the different IECs of the membranes because the first weight loss attributes to the thermal degradation of sulfonic acid groups. The IEC of the membranes is in order of SPAEK-6F-30 < SPAEK-6F-40 < SPEEK 6 h \approx SPAEK-6F-50 < SPEEK 8 h.

3.2. Effect of polymer matrix for composite membranes

The composite membranes using two types of polymer were prepared via an in situ sol–gel process. The effect of polymer matrix was studied on the size of BPO₄ and membrane properties. Normalized water uptake and proton conductivity are summarized in Table 2. In general, water uptake proportionally increases as IEC increases up to percolation threshold at which polymer abruptly begins to swell excess water and phase inversion between water and polymer occurs. The higher water uptake below the percolation threshold results in an increase in proton conductivity. The normalized water uptake for the SPAEK-6F composite membranes in Table 2 shows much higher water uptake than the SPAEK-6F plain membranes, compared with

Table 2
Normalized water uptake and proton conductivity of the pre-/post-sulfonated composite membranes based on the pre-/post-sulfonated plain membranes

Composite membrane	Normalized water uptake ^a	Normalized proton conductivity	
		30 °C	70 °C
SPEEK 6 h/BPO ₄	2.52	1.989	1.022
SPEEK 8 h/BPO ₄	1.75	1.367	1.083
SPAEEK-6F-30 ^b /BPO ₄	3.06	0.632	0.722
SPAEEK-6F-40 ^b /BPO ₄	2.52	0.600	0.632

^a Measured at 30 °C.

^b The percentage of sulfonated monomer SDFBP = monomer SDFBP/[monomer DFBP + monomer SDFBP] \times 100 as shown in Scheme 1.

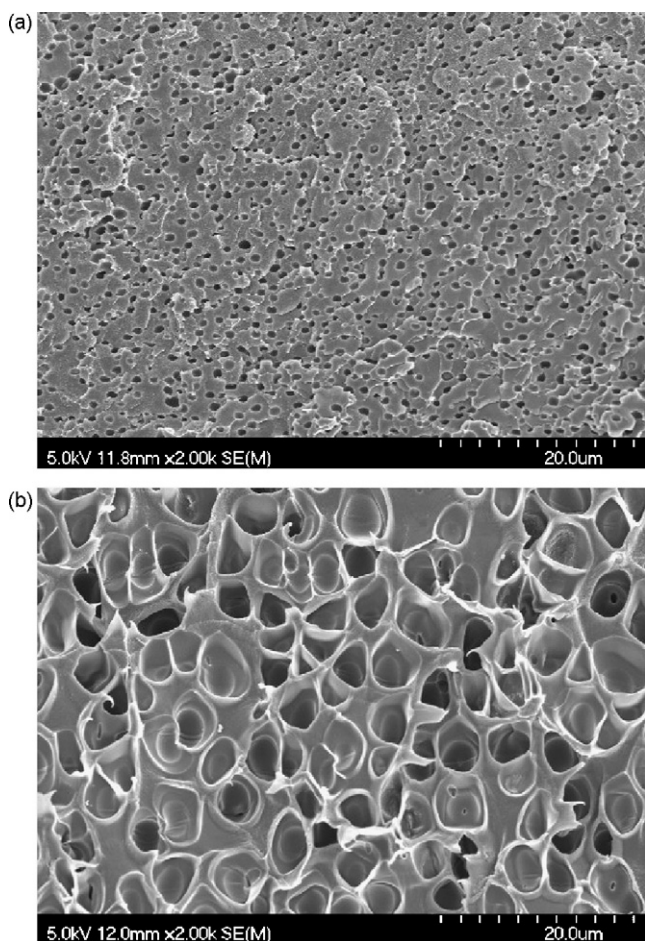


Fig. 5. SEM images of cross-section of composite membranes: (a) SPAEK-6F-40 and (b) SPEEK 6 h.

the SPEEK plain/composite membranes. However, the proton conductivity of the SPAEK-6F composite membranes decreased rather than the SPAEK-6F plain membranes as opposed to the aforementioned explanation on the relationship between water uptake and proton conductivity. On the other hands, a slight increase in water uptake for the SPEEK composite membranes caused to increase the proton conductivity. As a result, the SPEEK composite membranes had higher proton conductivity than the SPAEK-6F composite membranes despite better proton conductivity of the SPAEK-6F plain membranes.

To investigate the aforementioned reason, morphology of the BPO₄ particles in the composite membranes by SEM measurement and sorption characteristics by DSC ice-melting diagrams was investigated.

Fig. 5 shows cross-sectional SEM images for the SPAEK-6F/BPO₄ and SPEEK composite membranes. The BPO₄ particles were homogeneously introduced into both polymer matrices. It is noted in Fig. 5 that the BPO₄ particle size is greatly influenced with respect to polymer matrix. The SPAEK-6F composite membranes possessed 100 nm to 1 μm inorganic particles in contrast to 3–4 μm of BPO₄ particles in the SPEEK composite membranes. This result may arise from well segregation of hydrophilic/hydrophobic part in the SPAEK-6F polymer. The SPAEK-6Fs form well-separated nanophase (see Fig. 3) com-

prising of hydrophilic hydrated domains containing sulfonic acid groups (see the right hand side of SPAEK-6F's chemical structure in Scheme 1b) and hydrophobic domains containing 6F groups (see the left hand side of SPAEK-6F's chemical structure in Scheme 1b). It is expected that 6F-groups (C–F bonds) in the hydrophobic domains provide more hydrophobic property and two sulfonic acid groups per a repeating unit in the hydrophilic domains more hydrophilic property. On the other hands, SPEEK has hydrophobic domains (i.e., unsulfonated PEEK) dominantly consisting of C–H bonds and hydrophilic domains (i.e., sulfonated PEEK) with a sulfonic acid group per a repeating unit. The difference in chemical structure between SPAEK-6F and SPEEK gives a rise to more well-separated hydrophilic/hydrophobic nanophase in the SPAEK-6F membranes. As a result, during the in situ sol–gel reaction taking place in the SPEEK or SPAEK-6F polymer solution, the BPO₄ sol-type particulates are well dispersed in the SPAEK-6F rather than in the SPEEK polymer solution. This resulted in smaller size of BPO₄ particles in the SPAEK-6F membranes, finally causing to a decrease in proton conductivity, which is consistent with our previous work [17].

The reason on higher proton conductivity of the SPEEK composite membranes with bigger BPO₄ particles can be addressed using water sorption property of the SPEEK and SPAEK-6F composite membranes. Sorption of water in membranes plays an essential role in proton conductivity. Water affects the microstructure formation of cluster, channel size and the mechanical properties [22]. Proton conductivity to a large extent mostly depends on the amount and behavior of water absorbed in membranes [23–26]. The three states of water in a membrane have been previously defined as follows [27]: (1) freezable bound water is weakly bound to clusters and embedded particles in the polymer; (2) free water corresponds to water existed in free volume of a membrane and crystallizes at a higher temperature than freezable bound water; (3) non-freezable water, strongly bound to cluster and embedded particles in the polymer and shows no thermal transition by DSC ice-melting diagrams. Since the endothermic peaks in DSC ice-melting diagrams are attributed to the freezable water (i.e., freezable bound water and free water), the amount of the freezable water in the composite membranes can be estimated from DSC profile. The melting enthalpy is obtained by integration and normalization in unit of J g⁻¹ of the swollen membranes [28]. The latent heat of water, i.e., 333.3811 J g⁻¹, was used for the calculation. Based on the calculation, the portion of freezable and non-freezable water in water uptake is illustrated in Fig. 6. Carbone et al. [8] has reported that SPEEK prepared by DMAc (as same as in this study) had a low crystallinity with an amorphous structure and all the water contained in the membranes was shown to be strongly linked to sulfonic groups and of a non-freezable type. In this study, no recognizable peaks were found in DSC ice-melting diagrams for all the plain membranes and thus all the water in the SPEEK and SPAEK-6F plain membranes was regarded as non-freezable water as shown in Fig. 6a. On the other hands, all the composite membranes due to BPO₄ particles embedded had freezable water and simultaneously increased the amount of non-freezable water. Especially the SPEEK com-

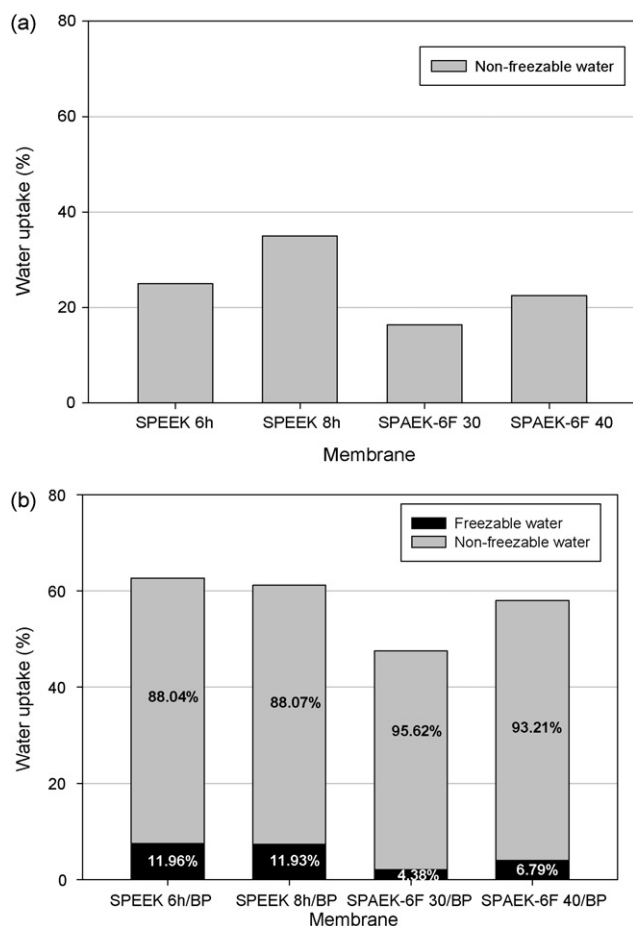


Fig. 6. Portion of freezable water and non-freezable water in water uptake of (a) plain membranes and (b) composite membranes.

posite membranes had much higher portion of freezable water than the SPAEK-6F composite membranes. It is believed that BPO₄ particles in the SPEEK composite membranes attribute to an increase in the amount of both non-freezable and freezable water and an increase in the amount of freezable water results in increasing proton conductivity. The decreased surface area of particles in the SPEEK composite membrane as increasing particle size (see Fig. 5) may forecast the smaller amount of freezable water weakly bound to the surface of BPO₄ particles than the SPAEK-6F composite membranes if the freezable water in all the composite membranes is attributed by the surface of BPO₄ particles. However, the amount of freezable water in the SPEEK composite membranes with the larger size of BPO₄ particles is larger than the SPAEK-6F composite membranes. Thus, it is inferred that the fact that the composite membranes containing bigger BPO₄ particles can hold more freezable water is due to more weakly bound freezable water (i.e., freezable water) in the larger inner volume of BPO₄ particles.

As discussed earlier, interestingly, the SPEEK 6 h plain membranes showed lower proton conductivity than the SPAEK-6F-40 plain membranes at similar water uptake (see Table 1), while for the composite membranes vice versa still at similar water uptake (see Table 2) despite the contribution arising from the

freezable water in BPO₄ particles and an increase in water uptake. This reason can be addressed by the effect of nano-scale inorganics well dispersed in the SPAEK-6F membranes. Some researchers have reported a decrease in proton conductivity of the composite membranes with inorganics well dispersed in polymer matrix [29,30]. It is well-known that proton conduction in proton conducting membranes is governed by two mechanisms—one is a “proton hopping” (Grotthus) mechanism, and the other is migration of hydrated protons (vehicular) [H⁺(H₂O)_n species] [30,31]. Miyake et al. [29] reported that in the composite membranes excess water molecules are likely to be involved in hydrating the incorporated inorganics. Thus, water available for either the hopping mechanism or solvating protons for migration may be lower. This could lead to the interruption of both conduction mechanisms and thus decrease the conductivity.

4. Conclusions

Organic/inorganic composite membranes were prepared using two types of matrix polymer prepared by different sulfonation methods (i.e., pre- and post-sulfonation). The SPAEK-6F plain membranes showed higher proton conductivity than the SPEEK plain membranes at similar water uptake or IEC because of structural difference between both polymers. Composite membranes with BPO₄ were prepared via an in situ sol–gel process. The BPO₄ particle size in the SPEEK composite membranes was approximately 3–4 times bigger than the SPAEK-6F composite membranes. It indicates that BPO₄ particle size is greatly influenced by polymer matrix. The dependency arose from well dispersion of BPO₄ sol-like particulates in SPAEK-6F polymer solutions forming more hydrophobic/hydrophilic nanophase than SPEEK polymer solutions. The SPEEK composite membranes containing a few micrometer-scale BPO₄ particles showed higher proton conductivity than the SPAEK-6F composite membranes containing hundreds nanometer-scale BPO₄ particles at similar water uptake due to an increase in freezable water and effect of particle size.

For the preparation of composite membranes containing BPO₄ via an in situ sol–gel process, the particles size of BPO₄ is dependent on the hydrophobic/hydrophilic separation property of sulfonated polymers used as matrix and then the amount of freezable water weakly bound to BPO₄, finally influencing proton conductivity of composite membranes. For the relationship between the hydrophobic/hydrophilic separation of sulfonated polymers and proton conductivity, it is the plain membranes forming more separated hydrophobic/hydrophilic nanophase that show enhanced proton conductivity such as NafionTM-like membranes, while for composite membranes containing BPO₄ prepared by an in situ sol–gel process vice versa due to its decreased particle size. Despite the dilemma, to develop polymer electrolytes more adaptable to fuel cells, copolymers using pre-sulfonated monomers have to be kept being developed due to their advantages on membrane properties. Further composite membranes using copolymers with particle size to give a rise to enhanced proton conductivity will be investigated via an in situ sol–gel process.

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