Synthesis and Characterization of Homogeneously Sulfonated Poly(ether ether ketone) Membranes: Effect of Casting Solvent

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ABSTRACT: Poly(ether ether ketone) (PEEK) was homogeneously sulfonated to have various degrees of sulfonation from 48 to 83%. The sulfonated PEEK (sPEEK) membranes were prepared by a solvent casting method using a few solvents such as *N*,*N*-dimethyl formamide, *N*,*N*-dimethyl acetamide, and 1-methyl-2-pyrrolidinone. The effect of casting solvent on the membrane morphology and properties was investigated. The sulfonation degree and ion exchange capacity were determined by a back titration method, and the morphology of membrane by SEM. It has been demonstrated that the surface morphology and properties of sPEEK membranes, such as water uptake, methanol permeability, ion conductivity, and mechanical strength, were considerably affected by the type of solvent, where the DMAC-sPEEK system showed the best performance in the polymer electrolyte membrane application for DMFC. This solvent effect on the membrane morphology and properties was caused by interaction strength (hydrogen bonding) between polymer and solvent. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1763–1770, 2008

Key words: membrane; PEEK; proton conductivity; methanol permeability; direct methanol fuel cell

INTRODUCTION

At present, one of the most promising power supplies for portable electric devices is a direct methanol fuel cell (DMFC).[1–3] The proton exchange membrane (PEM) commonly used in DMFC is a perfuorosulfonic acid-type electrolyte membrane, Nafion® as a typical example. It is stable against lots of solvents, even strong bases, strong oxidizing and reducing acids such as H_2O_2, Cl_2, H_2, and O_2 at temperatures up to 125°C.[4] Wide water channels were provided by aggregation of the hydrophilic domains in hydrophobic matrix in the presence of water. It was caused by high hydrophilic–hydrophobic phase separation associated with hydrophilic sulfonic acid groups and hydrophobic tetrafluoro backbones.[5] In consequence, methanol and water are easily transported across membranes through those channels.[6,7] The methanol transport from anode to cathode causes the oxidation reaction to take place not only in anode but cathode, resulting in low efficiencies, mixed potential, and loss of fuel. Another drawback of Nafion membrane is in its expensive purchasing cost.

For those reasons, there have been a number of approaches in the development of nonfluorinated polymeric PEMs in which the proton transport property is generally provided by sulfonic acid groups. Poly(ether ether ketone) (PEEK)[8–11] is one of them. According to the results from other researches,[10–14] the postsulfonated PEEK showed high mechanical property, low methanol permeability, and acceptable ion conductivity, and thus is considered to be a promising alternative membrane for Nafion. Furthermore, the sulfonated PEEK (sPEEK) allows casting from organic solution, offering more convenient and less expensive membrane fabrication process than perfluorosulfonic acid membranes.[15] sPEEK membranes were usually prepared using one of a few solvents such as *N*,*N*-dimethyl formamide (DMF), *N*,*N*-dimethyl acetamide (DMAC), and 1-methyl-2-pyrrolidinone (NMP). However, each kind of solvent affects membrane properties differently. In the publication of Robertson et al.[16] and Kaliaguine et al.,[17] the strong interaction between DMF or DMAC and the sulfonic acid groups of sPEEK prepared by a heterogeneous sulfonation method decreased both the number and mobility of protons, resulting in dramatic reduction of conductivity.[16]

sPEEK has been mostly synthesized by heterogeneous sulfonation method, where the sulfuric acid is

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used as a dissolution agent as well as a sulfonation agent, and thus it cannot produce truly random copolymers.[18] The truly random copolymers can be produced by the homogeneous method, where an appropriate solvent is used to dissolve PEEK completely, and then the homogeneous solution is sulfonated by H_2SO_4 solution.[19] Because of difference in distribution of sulfonic groups on the polymer chain, the random products from homogeneous method are expected to offer more advantageous properties to apply for fuel cell system. In the present article, the PEEK was sulfonated in a homogeneous manner to prepare sPEEK (homo-sPEEK) membrane. For profound understanding of the influence of solvents on properties and morphologies of homo-sPEEK membrane, a variety of bulk and transport properties were investigated, including water uptake, methanol permeability, ion conductivity, mechanical property, etc.

EXPERIMENTAL

Materials

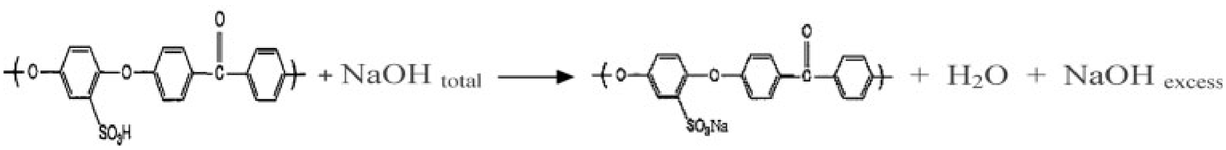
The PEEK samples (Vitrex® 450PF) of molecular weight 100,000 g/mol were purchased from ICI Company (Rotherham, UK). The average particle size was around 100 μm, melting point 340°C, relative density 1.32 g/cm^3, and glass transition temperature 143°C, respectively. Sulfuric acid (analyzed A.C.S Reagent) was supplied from Mallinckrodt Baker (Phillipsburg, NJ). Methylsulfonic acid (MSA) was from Acros Organics (New Jersey, USA). *N*,*N*-dimethyl acetamide (DMAC) from Fluka Chemie AG (CH-9470 Buchs, Switzerland), *N*,*N*-dimethyl formamide (DMF) from Deajung Chemicals and Metals Company (Gyonggi-do, Korea) and 1-methyl-2-pyrrolidinone (NMP) from Sigma-Aldrich Chemical Company (Germany), respectively.

Sulfonation of polymers

Before sulfonation, PEEK particles were dried in a vacuum oven (<30 mmHg) at 100°C for 24 h. Twenty grams of PEEK samples was dissolved gradually in 100 mL MSA under vigorous stirring for 24 h. The solution was sulfonated by diluting with 800 mL of 97% sulfuric acid in a three-neck flask under nitrogen atmosphere at room temperature. The sPEEK was recovered by precipitation in a large excess of ice-water for a prescribed time. The products were filtered and washed repeatedly with distilled water, and then dried at room temperature for 24 h. The final products were ground into smaller particles to be kept in vacuum at 60–100°C for 1 day.

Degree of sulfonation and ion exchange capacity

The degree of sulfonation (DS) was determined by a back titration method.[20] sPEEK particles, 0.1 g, were placed in 20 mL of 0.05*N* NaOH aqueous solution and kept for 3 days for neutralization reaction as eq. (1). The solution was titrated with 0.05*M* HCl aqueous solution using a pH meter (Orion, 420$^+$, USA) as eq. (2).



(1)

$$NaOH_{excess} + HCl \rightarrow NaCl + H_2O \quad (2)$$

The number of sulfonated repeat units in sPEEK molecules, x, was calculated from eq. (3):

$$x = V_{NaOH}M_{NaOH} - V_{HCl}M_{HCl} \quad (3)$$

where V_i and M_i indicate the volume and morality of component i containing aqueous solution, respectively.

The number of nonsulfonated units in sPEEK molecules, y, was then calculated from eq. (4).

$$y = (W - M_s x)/M_{non} \quad (4)$$

where W indicates the weight of sPEEK sample, M_s and M_{non} the molecular weights of sulfonated and nonsulfonated repeat units, respectively. The sulfonation degree, DS, and ion exchange capacity (IEC) values were then calculated from eqs. (5) and (6), respectively.

$$DS = x/(x + y) \quad (5)$$

$$IEC = 1000x/W \quad (6)$$

Membrane preparation

The dry sPEEK particles with different DSs of 48%, 60%, 68%, and 83% were dissolved in each of DMF, DMAC, and NMP to have 3–5 wt % concentration, respectively. Each solution was magnetically stirred at different temperatures depending on the sulfonation degree of sPEEK. sPEEKs with DS over 80% were dissolved easily at room temperature, but those with 60–70% DS around 60°C and those with DS below 50% about 100°C. Each polymer solution was cast on a flat-roll glass plate, and then dried in a vacuum oven at 25–140°C for a few days. The sPEEK membrane was peeled off from the glass plates with distilled water. It was rinsed in distilled water several times and kept in distilled water before characterization. The thickness of the membrane was from 80 to 100 μm.

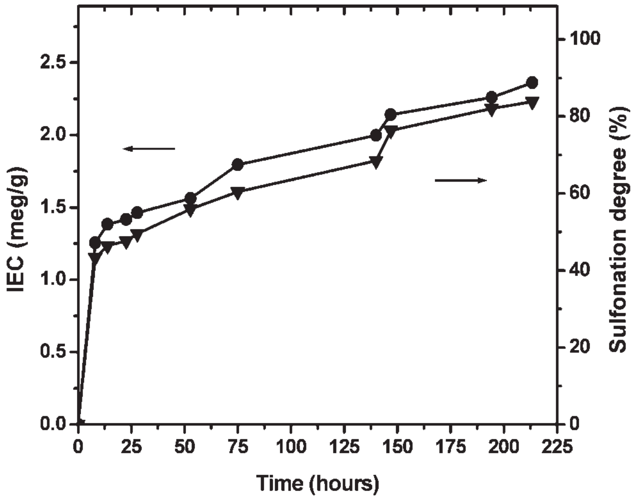


Figure 1 Variation of sulfonation degrees and IEC values during the sulfonation of PEEK.

Characterization of sPEEK membranes

Surface morphology

The scanning electron microscope (SEM Hitachi S-3000H, Tokyo, Japan) was used to investigate the morphology of the membrane surfaces. The sPEEK membranes with 68% DS were annealed at different treatment temperatures of 140, 160, and 200°C in 2 days. Samples were placed on a holder, and then platinum-coated for 120 s before SEM pictures were taken.

Water uptake

All membranes were kept in desiccators at room temperature for a week. After dry membranes were weighted, the membranes were placed in distilled water at room temperature for 48 h. The wet membranes were periodically weighed after prompt removal of water from their surface by soft tissues. The water uptake of membrane was calculated by

$$\%\ \text{water uptake} = \frac{(W_{\text{wet}} - W_{\text{dry}}) \times 100}{W_{\text{dry}}} \tag{7}$$

where W_{wet} and W_{dry} indicate the weight of wet and dry membranes, respectively.

Methanol permeability

A glass diffusion cell was used to measured methanol permeability. The 2*M* methanol aqueous solution, 50 mL, was placed on one side of the cell and the distilled water, 50 mL, on the other side. To ensure uniform concentration, a magnetic stirrer was placed in each compartment. The methanol concentration in the water compartment was continuously monitored by detector (RI750F, Young Lin Instrument Co, Anyang, Korea) at room temperature. Each membrane was tested three times to take average value for determination of methanol permeability.

Proton conductivity

Before measuring ion conductivity, the fully hydrated membranes were kept in 1*M* H_2SO_4 aqueous solution for 2 days. The electrochemical instrumentation (Pastat 2263, Princeton Applied Research, Oak Ridge, USA) was used to detect the resistance over a frequency range of 1–10^5 Hz at the voltage of 50 mV. The measurements were conducted in transversal direction across the membrane.[21] The conductivity σ of the samples in the transverse direction was calculated from the impedance data, using a relationship $\sigma = t/RA$, where t (cm) and A (cm^2) are the thickness and face area of the sample, respectively. The resistance R (Ω) was derived from the low intersect of the high frequency semicircle on a complex impedance plane with the Re(Z) axis. The ion conductivity was determined from the average value of three measurement results.

Mechanical properties

The tensile strength and Young's moduli of fully hydrated membranes were measured using a universal tensile machine (UTM-model 5565, Lloyd, Fareham, UK). Samples with 20 mm in width and 50 mm in length were tested with a 250 N load cell pulled at 50 (mm/min) within 21-cm gauge length. Because the environmental humidity influences the water content and thus the mechanical properties of hydrated samples, each measurement was conducted as quickly as possible in around 1 min. Each sample was tested three times, and the average values were taken for determination of tensile strength and Young's modulus. Tensile strength was obtained at the stress of maximum load; Young's modulus, E in

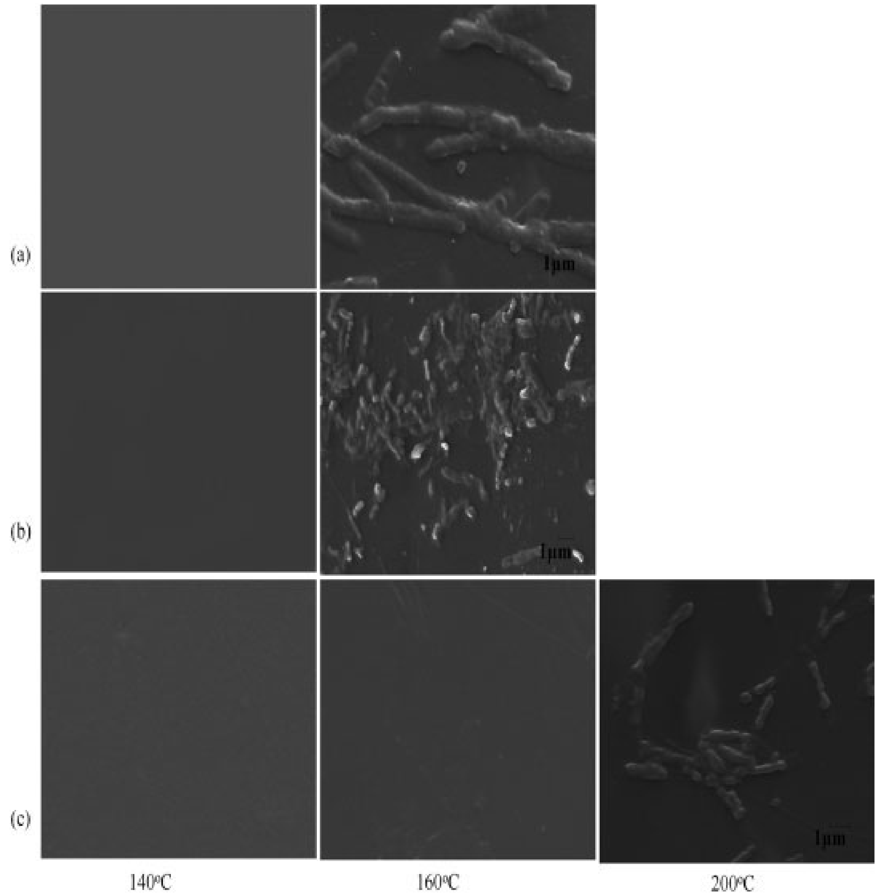


Figure 2 SEM microphotographs of homo-sPEEK membranes prepared using (a) DMF at 140 and 160°C, (b) DMAC at 140 and 160°C, (c) NMP at 140, 160, and 200°C, respectively.

eq. (8) was determined from the initial slope of curve relating tensile stress σ and elongation, ε.

$$\sigma = E\varepsilon \tag{8}$$

RESULTS AND DISCUSSION

DS and IEC

Some papers[10–14] showed that heterogeneous sulfonation is easy to obtain high DS; around 100 h is required for 80% DS. According to Bailly et al.,[19] the sulfonation kinetics in the homogeneous sulfonation method depended on the volumetric ratio (r) of H_2SO_4 to MSA (solvent); nearly 120 h for 16% DS when $r = 2$, while just 72 h for 40% DS when $r = 6$. The sulfonation level of the sample prepared by homogeneous method is reported to be given by the fourth power of sulfuric acid concentration.[19] MSA affected the rate of reaction in at least two ways: (1) dilution of the sulfonating species and their precursors, (2) solvation and reaction with part of the SO_3, further decreasing the concentration of active spe-

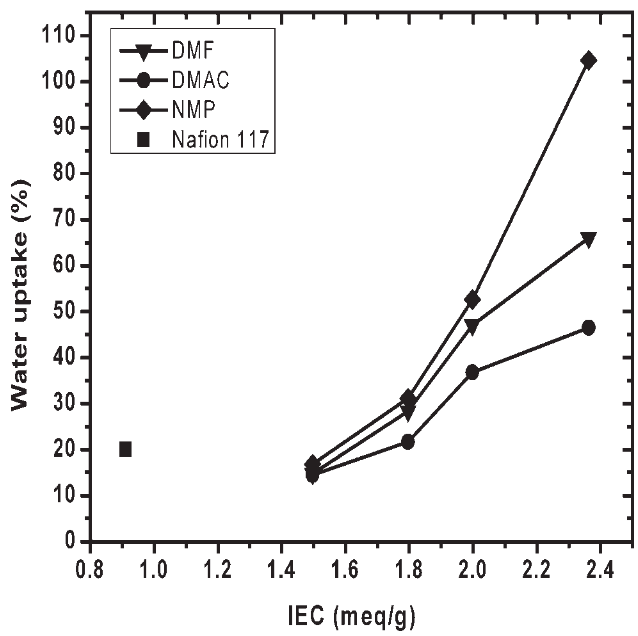


Figure 3 Water uptake of homo-sPEEK membranes at room temperature. Membranes were prepared using different types of solvents of DMF, DMAc, and NMP, respectively.

TABLE I
Amount of Solvents Remained in Membrane After Drying Process

Samples	Amount of solvents (g)
DMF-60%-sPEEK membrane	0.0729
DMF-68%-sPEEK membrane	0.0646
DMF-83%-sPEEK membrane	0.0506
DMAC-60%-sPEEK membrane	0.0613
DMAC-68%-sPEEK membrane	0.0643
DMAC-83%-sPEEK membrane	0.0622
NMP-60%-sPEEK membrane	0.1018
NMP-63%-sPEEK membrane	0.0778
NMP-83%-sPEEK membrane	0.0828

cies.[19] Therefore, it is important to select the suitable ratio of H_2SO_4/MSA for homogeneous sulfonation method. The values of DS and IEC of sPEEK at room temperature for $r = 8$ are presented in Figure 1. The sPEEKs with various DS were obtained by sulfonating the PEEK for 0–220 h. It is shown that both the DS and IEC of sPEEK increase monotonically with the progress of sulfonation reaction.

Membrane morphology

Choosing the appropriate drying temperature is another important factor in preparation of good membranes. According to Robertson et al.,[16] the ion conductivity of membranes depended on the treatment (drying) temperature. The sPEEK membranes dried at 90°C provided higher ion conductivity than those at 60 or 25°C, because the retained solvents in membranes decreased the proton conductivity. In preparation of membranes, the solvent should be slowly vaporized so that all polymer molecules are arranged into a good relaxation, while the boiling temperatures of solvents are 153°C for DMF, 166°C for DMAC, and 202°C for NMP.

The surface morphologies of the sPEEK membranes prepared with DMF, DMAC, and NMP at different treatment temperatures are shown in Figure 2. While the membrane with the clean surface was obtained when the drying temperature was lower than the boiling point of solvent and T_g of PEEK, the blur-white-bars appeared on the membrane surface at 160°C (which is around the boiling point of DMF/DMAC) and at 200°C (which is around the boiling point of NMP) due to the rapid evaporation of solvent.

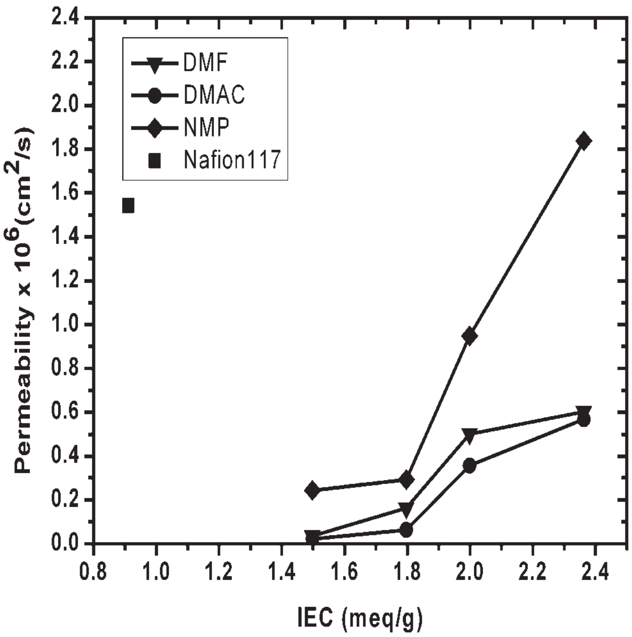


Figure 4 Methanol permeability of homo-sPEEK membranes at room temperature. Membranes were prepared using different types of solvents of DMF, DMAc, and NMP, respectively.

Water uptake

In Figure 3, the water uptake of homo-sPEEK membrane increased with the increase of DS due to the introduction of more hydrophilic SO_3H groups, and showed even higher values than that of Nafion 117 membrane. Introduction of water increases the size of hydrophilic clusters associated with the congregation of ionic groups being separated from the hydrophobic PEEK matrix phase. Imbibe of more water eventually provides water passages among ionic clusters, which is the so-called percolation, where

TABLE II
Methanol Uptake of Homo-sPEEK and Nafion® Membranes

Samples	Water uptake (%)	Methanol uptake, 2*M* concentration (%)	Methanol uptake, 100% concentration (%)
DMF-48%-sPEEK membrane	14.8	10.6	10.3
DMF-60%-sPEEK membrane	28.3	18.1	16.8
DMAC-48%-sPEEK membrane	14.5	16.0	16.0
DMAC-60%-sPEEK membrane	21.7	26.2	26.8
NMP-48%-sPEEK membrane	16.8	17.2	17.8
NMP-60%-sPEEK membrane	31.1	22.6	–
Nafion® 117 membrane	21.0	25.0	53.0

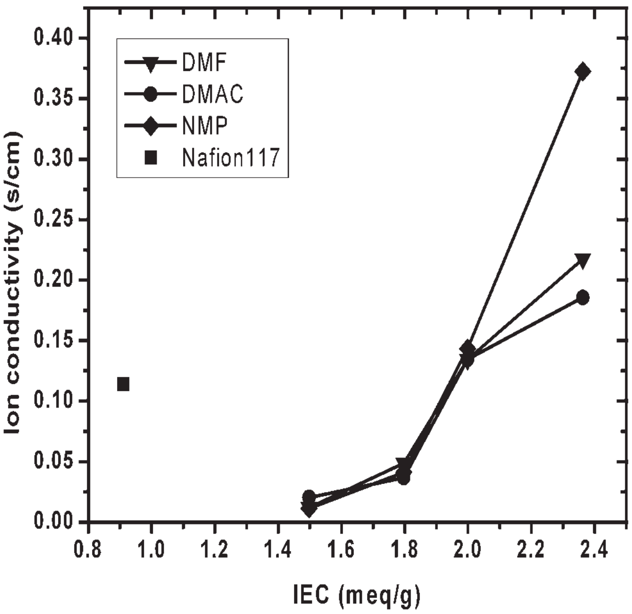


Figure 5 Proton conductivity of homo-sPEEK membranes at room temperature. Membranes were prepared using different types of solvents of DMF, DMAc, and NMP, respectively.

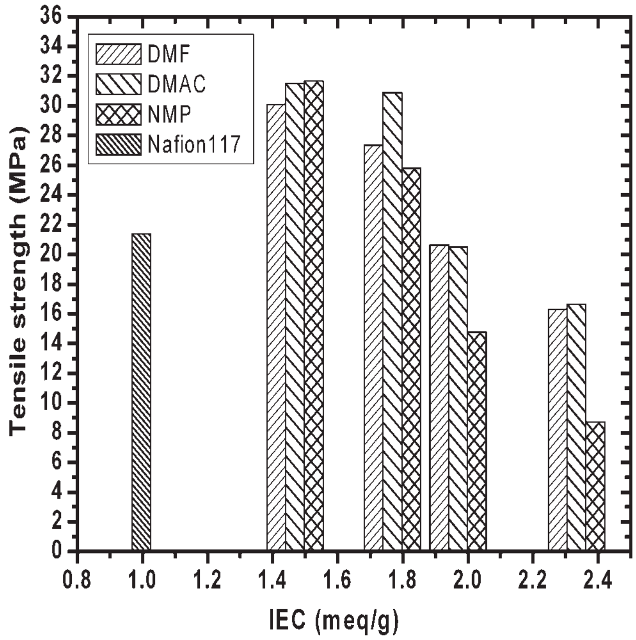


Figure 6 Tensile strength of fully hydrated membranes. Tensile strength of fully hydrated membranes prepared using different types of solvents of DMF, DMAc, and NMP, respectively.

the equilibrium water uptake takes place. The influence of solvents on the water uptake was not considerable when the DS of membrane was lower than 80%. On the other hand, when the DS was higher than 80%, for example, 83% in this study, there was a huge difference in water uptake between DMF/DMAC-sPEEK and NMP-sPEEK membranes. The amount of solvents remained in the membrane after drying is shown in Table I. Although treated at 140°C for 2 days, a little amount of solvent still remained in the membrane and it affected the water uptake property. The H-bonding between solvent and PEEK kept DMF/DMAC retained in the membrane and thus prevented the SO_3H groups from absorbing water.[16,17]

MeOH permeability

The methanol permeability data are shown in Figure 4. Methanol permeation increased with increasing DS for all solvents. However, DMF/DMAC-sPEEK membranes showed lower permeation than NMP-sPEEK membranes. The higher water content of NMP-sPEEK membrane led to higher methanol permeation. In comparison with the Nafion membrane with the same water uptake, around 20–25%, all of the present sPEEK membrane around 48–60% DS showed lower methanol permeability. Aside from the reason that water channels of sulfonated PEEK were narrower than that of Nafion membrane, there was another reason that the Nafion membrane trended to absorb more methanol than sPEEK membrane. As showed in Table II, the Nafion membrane absorbed 25% 2*M* methanol and 53% pure methanol solution while the absorption tendency of sPEEK membranes was lessened with the increase of methanol concentration, resulting in lower methanol permeability.

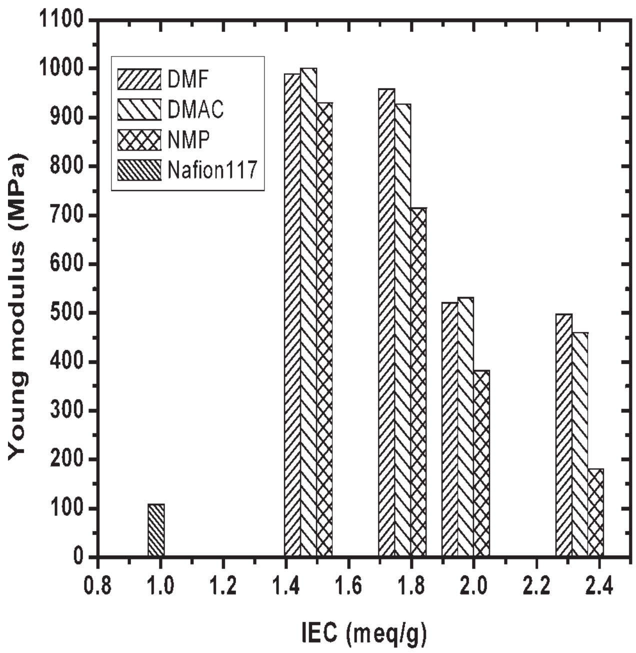


Figure 7 Young's moduli of fully hydrated membranes prepared using different types of solvents of DMF, DMAc, and NMP, respectively.

TABLE III
Characteristic Factors of Homo-sPEEK Membranes Prepared Using Different Types of Solvents of DMF, DMAc, and NMP

	IEC (mequiv/g)			
CF [10^{-3} S/Ω cm^3]	DMF-sPEEK membrane	DMAC-sPEEK membrane	NMP-sPEE membrane	Nafion117 membrane
0.91	86.857	217.055	46.285	74.073
1.49 (48%DS)	301.172	369.300	141.432	
1.79 (60%DS)	268.273	377.423	151.236	
1.99 (68%DS)	360.541	326.943	202.715	
2.36 (83%DS)	86.857	217.055	46.2856	

Proton conductivity

As shown in Figure 5, the proton conductivity of the sPEEK membrane increased with the increment of DS. The influence of solvents on conductive properties was not significant at the DS lower than 80%. However, when the DS was higher than 80%, NMP-sPEEK membrane showed much higher conductivity than DMF/DMAC-sPEEK membrane, as the hydrogen bonding between DMF/DMAC and SO_3H groups in sPEEK reduced the polymeric chain mobility and water uptake required for easy proton transportation.

Mechanical properties

The tensile strength and Young's modulus of fully hydrated membranes are shown in Figures 6 and 7, respectively. These values decreased with increasing DS because of the increase of water uptake. The presence of more water induced more free volume, and thus gradually damaged the mechanical property of the membrane by plasticization effect. The tensile strength and Young's modulus were reduced more promptly in NMP-sPEEK membranes, as its water content was higher than those in DMF/DMAC-sPEEK membranes at the same DS.

Characteristic factor

The membrane performance in DMFCs is usually indicated by the characteristic factor (CF), the ratio of the proton conductivity to the methanol permeability. In general, the membrane with too high or too low DS is not applicable for DMFC. At very high DS (higher than 80%), the membrane was too highly swollen in water, leading to too high methanol permeability or too low mechanical strength. At very low DS, not enough proton transportation. As shown in Table III, the CF values of DMAC-sPEEK membranes were the highest among three kinds of solvent systems, especially the sample with 60 and 68% DS. It means the hydrogen-bonding effect on the methanol crossover is much stronger than on the ion conductivity, even though both proton conductivity and methanol permeability were reduced by it.

CONCLUSIONS

The homogeneous method was used to postsulfonate PEEK, and the effect of types of casting solvents during the fabrication of membrane on its morphology and properties was investigated. Water uptake, methanol permeability, and ion conductivity were highly affected by the type of solvents, especially when the DS was over 80%. Among three types of solvent systems, DMF, DMAC, and NMP, the NMP-sPEEK membrane system resulted in the highest in each of those properties, because the strong interaction associated with the hydrogen bonding between DMF/DMAC and SO_3H groups of sPEEK reduced both the mobility of polymeric chains and the dissociation strength of sulfonic acid groups. Considering the mechanical strength and the CF, the ratio of ion conductivity to methanol permeability together, the DMAC-sPEEK membrane showed the best performance for DMFC application. Although DMAC-sPEEK membrane has the hydrogen bonding, its effect on the methanol crossover was much stronger than the ion conductivity. The effect of treatment (drying) temperature on the membrane morphology was also studied. As the rapid drying around or above the boiling point of the solvent caused the distortion of DMF/DMAC-sPEEK membrane surface, the drying temperature had better be chosen below the boiling temperature of solvent.

References

1. Kerres, J.; Zhang, W.; Jörissen, L.; Gogel, V. J New Mater Electrochem Syst 2002, 5, 97.
2. Jörissen, L.; Gogel, V.; Kerres, J.; Gacher, J. J Power Sourc 2002, 105, 267.
3. Gurau, B.; Smotkin, E. S. J Power Sourc 2002, 112, 339.
4. EG&G Services, Parsons, Inc. Science Applications International Corporation, Fuel cell Handbook.
5. Kreuer, K. A. J Membr Sci 2001, 185, 3.
6. Cruickshank, J.; Scott, K. J Power Sourc 1998, 70, 40.

7. Kalhammer, F. R.; Prokopius, P. R.; Voecks, V. P. Status and Prospects of Fuel Cells as Automobile Engines; State of California Air Resources Board: California, 1998.
8. Jin, X.; Bishop, M. T.; Ellis, T. S.; Karasz, F. Br Polym J 1985, 17, 4.
9. Mikhailenko, S. D.; Zaidi, S. M. J.; Kaliaguine, S. Catal Today 2001, 67, 225.
10. Kobayashi, T.; Rikukawa, M.; Sanui, K.; Ogata, N. Solid State Ionics 1998, 106, 219.
11. Zaidi, S. M. J.; Mikailenko, S. D.; Robertson, G. P.; Guiver, M. D.; Kaliaguine, S. J Membr Sci 2000, 173, 17.
12. Cui, W.; Kerres, J.; Eigenberger, G. Separ Purif Technol 1998, 14, 145–154.
13. Ise, M.; Kreuer, K. D.; Maier, J. Solid State Ionics, 1999, 125, 213.
14. Bonnet, B.; Jones, D. J.; Roziere, J.; Tchicaya, L.; Alberti, G.; Casciola, M.; Massinelli, L.; Bauer, B.; Peraio, A.; Ramunni, E. J New Mater Electrochem Syst 2000, 3, 87–92.
15. Xing, P.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Wang, K.; Kaliaguine, S. J Memb Sci 2004, 229, 95–106.
16. Roberson, G. P.; Mikhailenko, S. D.; Wang, K.; Xing, P.; Guiver, M. D.; Kaliaguine, S. J Membr Sci 2003, 219, 113–121.
17. Kaliaguine, S.; Mikhailenko, S. D.; Wang, K. P.; Xing, P.; Robertson, G.; Guiver, M. Catal Today 2003, 82, 213–222.
18. Jin, X.; Bishop, M. T.; Ellis, T. S.; Karasz, F. E. Br Polym J 1985, 17, 4.
19. Bailly, C.; Williams, D. J.; Karasz, F. E.; Macknight, W. J. Polymer 1987, 28, 1009–1016.
20. Huang, R. Y. M.; Shao, P.; Burns, C. M.; Feng, X. J Appl Polym Sci 2001, 82, 2651–2660.
21. Silva, V. S.; Weisshaar, S.; Reissner, R.; Ruffman, B.; Vetter, S.; Mendes, A.; Madeira, L. M.; Nunes, S. P. J Power Sourc 2005, 145, 485.