Influence of Casting Conditions on the Properties of Sulfonated Poly(ether ether ketone ketone)/Phosphotungstic Acid Composite Proton Exchange Membranes

Xianfeng Li, Dan Xu, Gang Zhang, Zhe Wang, Chengji Zhao, Hui Na

Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China

Received 27 November 2005; accepted 24 July 2006
DOI 10.1002/app.25543
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The sulfonated poly(ether ether ketone ketone)/phosphotungstic acid (SPEEKK/PWA) composite membranes were researched for proton exchange membranes. The effect of casting condition on the properties of membranes was studied in detail. The study showed that the casting condition has great influence on the membrane properties because of the hydrogen bond between the SPEEK and PWA and the interaction between the SPEEKK and dimethylformamide (DMF). The PWA particles are well crystallized on the surface when the velocity of the solvent volatilization is very slow under the SEM. The study will favor further research on excellent composite membranes for proton exchange membrane fuel cells. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 4020–4026, 2007

Key words: composite membranes; phosphotungstic acid; proton exchange membranes; sulfonated poly(ether ether ketone ketone)

INTRODUCTION

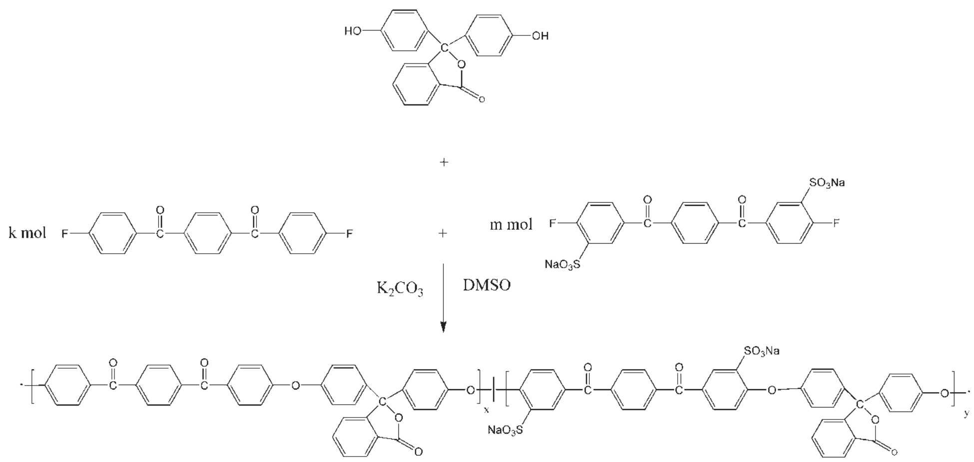
Proton exchange membrane fuel cells (PEMFC) are receiving high attention as the most practical fuel cell candidates because of their nonproduction of CO_2, low operating temperatures, and suitability for electric vehicles.[1–3] However, the current industry standard perfluorosulfonic polymers such as Nafion are limited by (1) high cost, (2) high methanol permeability, and (3) loss performance of membranes at evaluated temperatures. Novel proton exchange membranes should be developed.

In recent works, it has been shown that poly(aryl ether ketone)s (PAEKs) are of particularly significant promise, as they possess good thermal stability, appropriate mechanical properties, and some conductivity when sulfonated. Sulfonated poly(arly ether ketone)s (SPAEKs) are usually prepared via two methods: post sulfonating polymers and direct synthesis from sulfonated monomers.[4,5] The latter method has been proven to be more advantageous than post sulfonating polymers because of its avoiding the crosslinking and other side reactions, which may result in better thermal ability and mechanical properties. In our previous work (series on SPEEK) sulfonated poly(ether ether ketone ketone) (SPEEKK) was developed for proton exchange membranes.[5–8] Although they show relatively good properties, the proton conductivity of membranes with low sulfonated degrees is not sufficient to meet the requirement for proton exchange membranes. The composite membrane is one of the ways to improve the proton exchange membrane properties, as it can presumably combine the assets of the components.[9,10] Heteropolyacids (HPAs) are the most attractive inorganic modifiers, because these inorganic materials in crystalline form have been demonstrated to be highly conductive and thermally stable. They can also be dissolved in polar solvents such as dimethylformamide (DMF), dimethylacetamide (DMAC), etc. HPAs are known to have different hydrated structures depending on the environment,[11] and the proton conductivity of the HPA with different hydrated structures is very different. For example, proton conductivity of phosphotungstic acid (PWA) at 29 and 6 hydrated water molecules decreases from 1.8×10^{-2} s/cm to 6×10^{-5} s/cm. Moreover, the existence of interaction between the sulfuric acid groups and HPA will affect the properties of the membranes. In this article, we mainly focus on the influence of the different casting conditions on the properties of membranes.

The object of the present work is to explore the possibility of using PWA as filler in sulfonated PEEKKs with low ion exchange capacity. On the basis of the study of the morphology and properties of the membranes that were cast at different condi-

Correspondence to: H. Na (huina@jlu.edu.cn).

Journal of Applied Polymer Science, Vol. 103, 4020–4026 (2007)



Scheme 1 The preparation of sulfonated polymers.

tions, we expect to establish the relationship between casting conditions and membrane properties. This work will favor further research on proton exchange membranes.

EXPERIMENTAL

Material

Sulfonated poly(ether ether ketone ketone) (SPEEKK) was prepared as described in our previous publication.[6] The chemical structure and the preparation of SPEEKK are shown in Scheme 1. The sulfonated degree of SPEEKK was controlled by adjusting the ratio of sulfonated monomer to nonsulfonated monomer (m/k). The detailed procedure was reported previously.[6]

PWA was obtained from Chemical plants in Shanghai China and was used as received.

Membrane preparation

Pure SPEEKK and SPEEKK/PWA composite membranes were prepared by solution casting. The SPEEKK and PWA were dissolved in DMF to form a 10% solution. The resulting mixture was stirred for about 6 h and was cast onto a glass plate. Then, the resultant solutions were, respectively, dried at 45 and 70°C for about 48 h and were peeled off to obtain the membranes.

Scanning electron microscopy

The morphology of the membranes was studied by scanning electron microscopy (SEM) using SHIMADZU SSX-550. The membranes were gold-coated prior to SEM measurements.

Water uptake of membranes

Measurement of water uptake was determined from the difference in weight (W) between the drying and the swollen membranes.[7,8] The weight (W_{drying}) of the drying membrane was weighed and was then soaked in water until the weight remained constant. It was then taken out, wiped with blotting paper, and the weight (W_{wet}) of the membrane was weighed again. The water uptake was calculated as

$$\text{Water uptake } = (W_{wet} - W_{drying})/W_{drying} \times 100\%$$

Ion-exchange capacity

Ion-exchange capacity (IEC) was determined through titration.[7,8] The membranes in acid forms (H^+) were converted to sodium forms by immersing in 0.5M NaCl solutions for 24 h to liberate the H^+ ions (the H^+ ions in the membrane were replaced by Na^+ ions). The H^+ ions now in solution were then titrated with 0.01M NaOH.

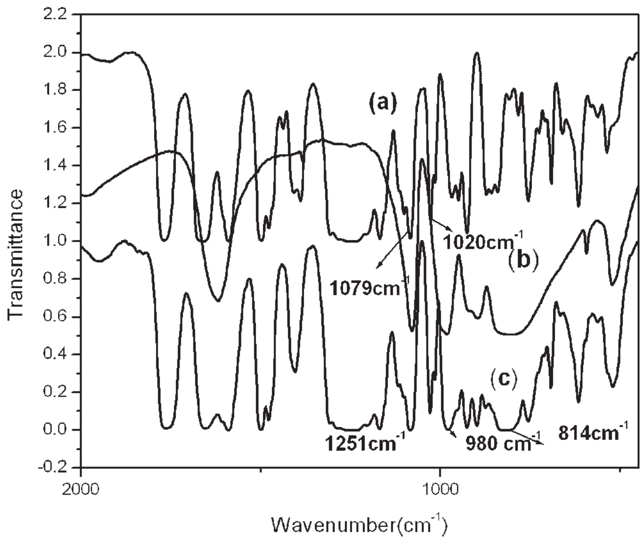


Figure 1 The FTIR of SPEEKK and PWA–SPEEKK composite membranes; (a) SPEEKK membrane, (b) PWA powder, and (c) PWA–SPEEKK composite membrane.

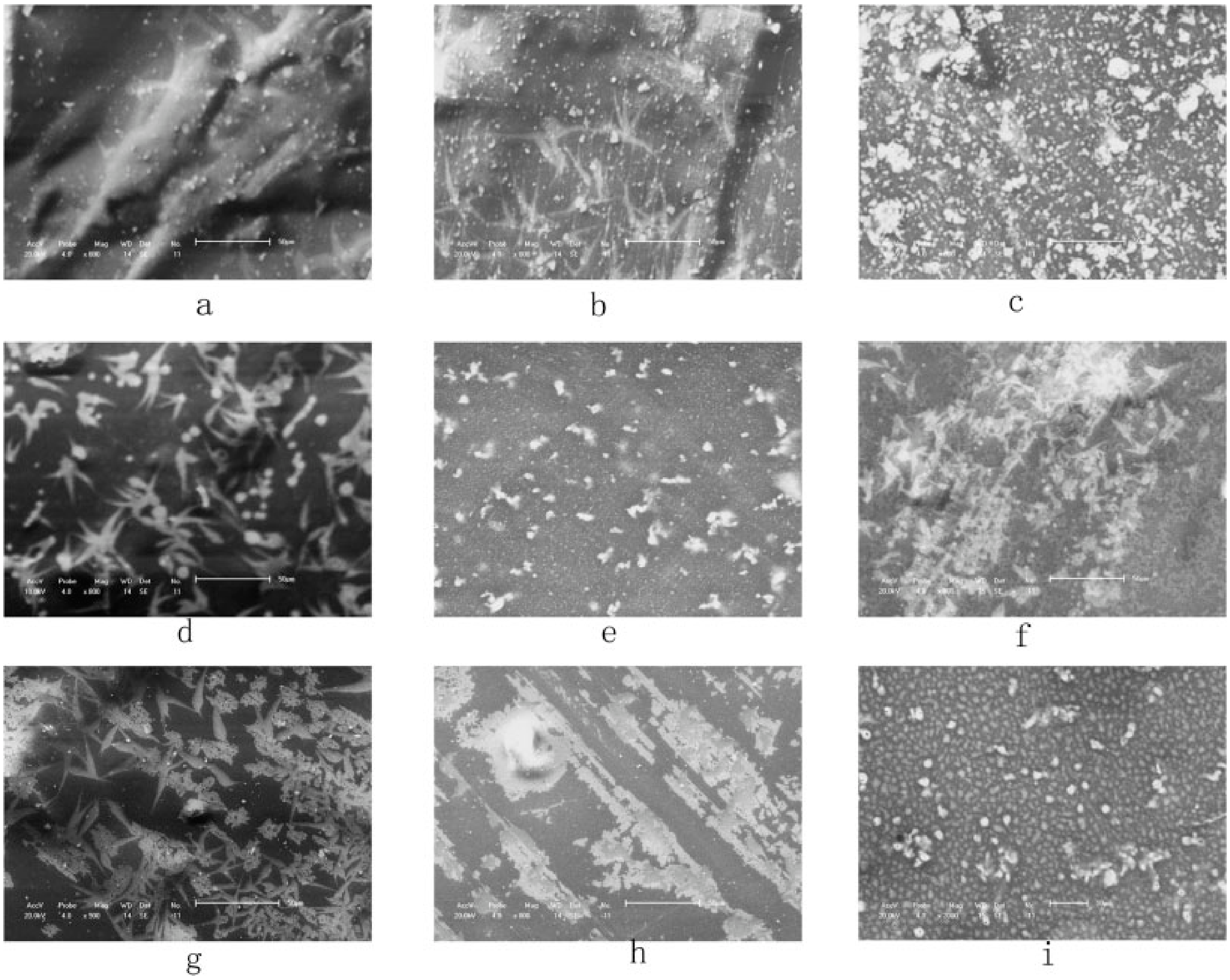


Figure 2 SEM of PWA–SPEEKK composite membranes; (a) 10% 25°C, (b) 20% 25°C, (c) 30% 25°C, (d) 10% 45°C, (e) 20% 45°C, (f) 30% 45°C, (g) 10% 70°C, (h) 20% 70°C, (i) 30% 70°C.

Methanol diffusion

Methanol diffusion coefficient was determined using a cell basically consisting of two half-cells separated by the membrane, which was fixed between two rubber rings. Methanol was placed on one side of the diffusion cell and water was placed on the other side. Magnetic stirrers were used on each compartment to ensure uniformity. The concentration of the methanol was measured by using SHIMADU GC-8A chromatograph. Peak area was converted to methanol concentration with a calibration curve. The methanol diffusion coefficient was calculated by the reference report.[12]

Proton conductivity

The measurement of proton conductivity of the membranes was carried out using Philips 1260 impedance/gain-phase analyzer over a frequency range from10 Hz to 1 MHz. Conductivity measurement of fully hydrated membranes was carried out with the cell immersed in liquid water. The membrane conductivity was determined with the test cell similar to the one employed by Zawodzinski et al.[13] The proton conductivity was calculated as

$$\sigma = L/R\ A$$

where L is the distance between the two electrodes, R is the membrane resistance, and A is the cross-sectional area of membrane.

RESULTS AND DISCUSSION

The preparation and characterization of composite membranes

SPEEKKs polymers were prepared in our previous work.[6] The polymers were synthesized via two steps: monomer synthesis and polymer preparation. The sulfonated degree of the polymer used in this article is 0.6. The intrinsic viscosity of the polymer, which

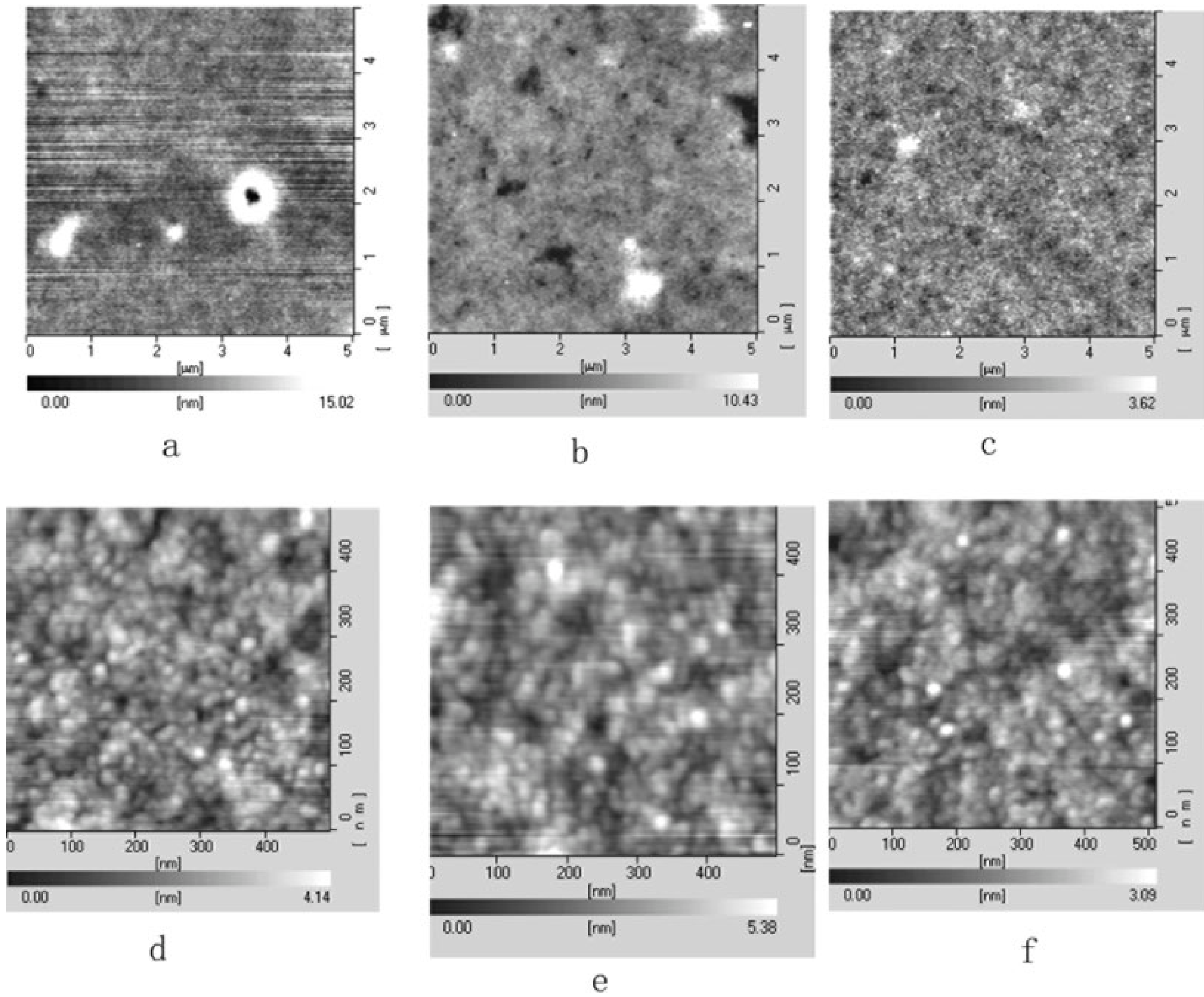


Figure 3 The AFM of composite membranes; scale, 5 × 5 um^2; (a) 10%, (b) 20%, (c) 30%; scale, 500 × 500 nm^2; (d) 10%, (e) 20%, (f) 30%.

was measured in DMF at 25°C ± 1°C with a polymer concentration of 5.0 g/dL, is 1.18. The ion exchange capacity of the membrane is 0.73 meq/g.

FTIR was carried out to confirm the structures of SPEEKK and its composite membranes (Fig. 1). The major vibration structures associated with SPEEKK are found in the two membrane samples. The peaks observed at 1020 cm^{-1}, 1079 cm^{-1}, and 1251 cm^{-1} are attributed to the stretching vibrations of SO_3Na groups.[6] The obvious peaks that are noted at 814 and 980 cm^{-1} in SPEEK/PWA membrane are due to the W—O—W stretching vibrations.[9]

Morphology of the composite membranes cast at different temperatures

The surface morphology of PWA–SPEEKK composite recast membranes at different temperatures is shown in Figure 2. It can be seen that the solid PWA is uniformly dispersed in the SPEEKK membranes. Moreover, the PWA in the SPEEKK membrane shows good crystallinity at 25, 45, and 70°C. In addition, with increasing temperatures, PWA becomes entirely crystalline. For example, the composite membranes cast at 25°C showed less crystallinity of PWA when the weight ratio of PWA was kept at 10 and 20%. When composite membranes with 10 and 20% PWA were cast at 45°C, there were many PWA particles around the PWA crystals. But when the cast temperature was increased to 70°C, almost all the PWAs in SPEEKK membranes were crystalline. The influence of the concentration of PWA on the morphology of the composite membranes shows the same tendency as well. Expect for the membranes that were cast at 70°C and with the weight ratio of the PWA at 30%, the shapes of the PWA crystals were very similar.

The velocity of solvent volatilization may have a great influence on the surface morphology of the

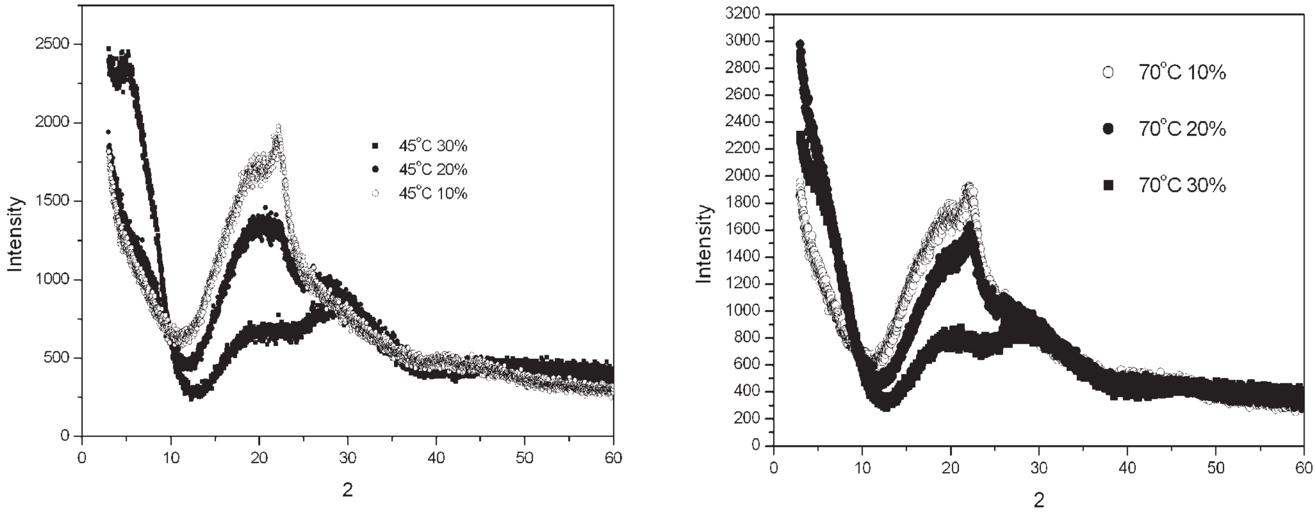


Figure 4 The XRD of composite membranes.

composite membranes. To study this, we prepared membranes with different weight ratios of PWA by spin-coating a polymer solution in DMF (the concentration is still 10%) onto a freshly cleaned silicon wafer at 3000 rpm for 50 s at room temperature. The morphology of the membranes was determined by AFM. The topography of the composite membranes is shown in Figure 3. The PWA particles were distributed very uniformly in SPEEKK matrix. The size of the particles is much less than that of the membranes prepared by the usual method. Also PWA crystallinity was not found in SPEEKK membranes prepared by this method.

The diffractograms of the recast SPEEKK/PWA membranes are shown in Figure 4. Figure 4(a) shows the diffractograms of the composite membranes that were cast at 45°C, while Figure 4(b) indicates the diffractograms of the ones cast at 70°C. The composite membranes that contain the same weight ratio of PWA show similar WAXD profiles, although they were cast at different temperatures. From the WAXD result, all the membranes show a diffraction feature at about 20°. Expect for the membranes with 30% PWA, all the composite membranes show similar diffractograms. The membranes containing 30% PWA show two diffraction features at $2\theta = 20°$ and $2\theta = 30°$ from the XRD; one can safely conclude that the PWA crystalline in SPEEKK may be influenced mostly by the solution concentration.

Membrane properties

Thermal stability

The thermal stability of the SPEEKK/PWA was investigated by thermogravimetric analysis. Figure 5 shows the TGA curves of the representative membranes in nitrogen. All the membranes show two weight loss steps. The first one at about 200–300°C is attributed to the splitting-off of sulfonic acid groups of SPEEK. The second weight loss step at about 450°C corresponds to the decomposition of the main polymer chain. Although the membranes show similar profiles of the TG curves, the temperatures corresponding to the onset of thermal degradation and the slope of mass loss are different. Compared to the SPEEKK membranes, the composite membranes show relatively high onset temperatures. In addition, SPEEKK lost about 25% by weight at 550°C after thermal decomposition, while SPEEK/PWA composite membranes lost about 25% by weight at higher temperatures. This may be due to the interaction between the SPEEKK and PWA. It is interesting to

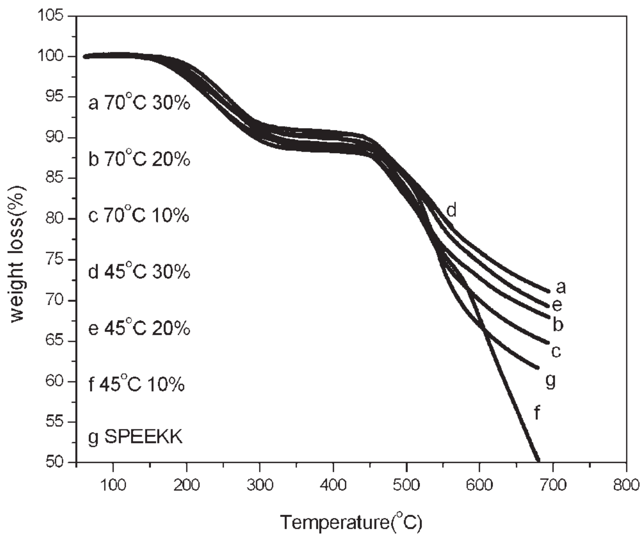


Figure 5 The TGA curves of SPEEKK and its composite membranes.

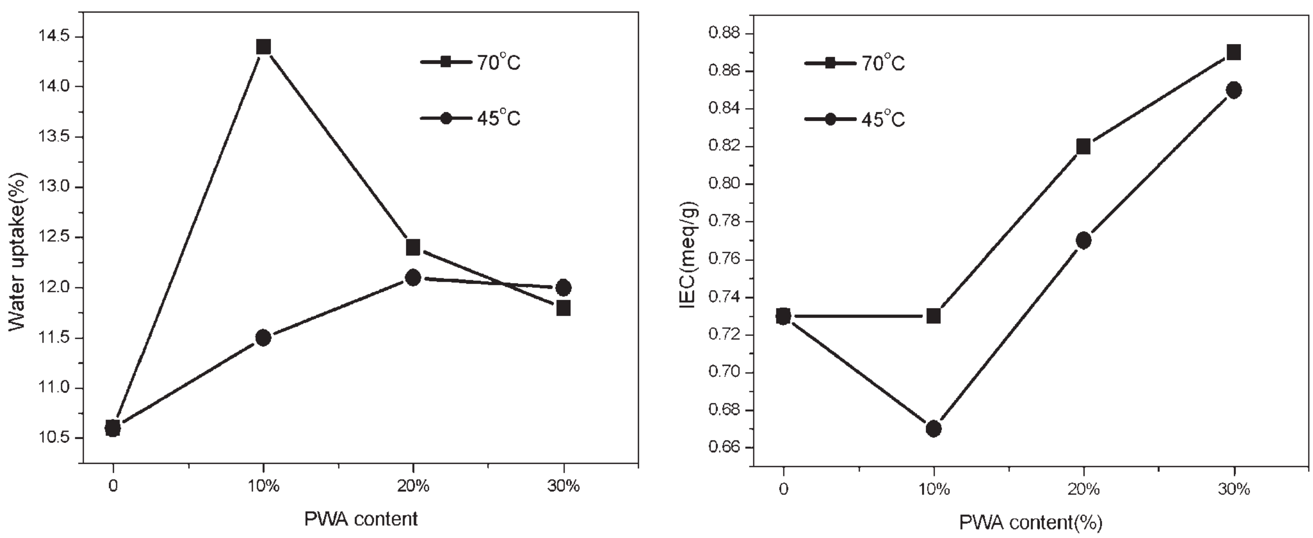


Figure 6 The water uptake and IEC of composite membranes.

note that the membranes that are cast at 70°C show much lower temperatures for the degradation of sulfonic groups than the ones that are cast at 45°C.

There may be two significant interactions that influence the degradation temperature of sulfonic groups. One is the interaction between the solvent (DMF) and SPEEK[9] and the other is the hydrogen bond between the SPEEKK and PWA.[14] When the membranes were cast at 45°C, the hydrogen bond between the SPEEK and PWA and the interaction between the SPEEKK and DMF may be more easily formed than those cast at 70°C. The strong interaction will lead to the improved thermal stability of sulfuric groups.

Water uptake and ion exchange capacity of the composite membranes

Water uptake plays a very important role in PEM. Proton transport in SPEEKK membranes is large influenced by the water content of membranes. The proton exchange reaction requires a significant amount of water to coordinate with proton as it moves through the membrane. Ionic membranes behave like insulator in dry state but become conductive as function water content when hydrated. The water uptake of the composite membranes is shown in Figure 6. The composite membranes show the opposite tendency with the addition of PWA to the SPEEKK matrix. The membranes cast at 70°C show decreasing tendency with the increase of PWA; however, the ones cast at 45°C show contrary tendency. But compared with the pure SPEEKK membranes, all the composite membranes show much higher water uptake. The water uptake may be influenced by many factors in this system, including PWA loss due to solubility of PWA in water, the interaction or the hydrogen bond between PWA and SPEEKK, the interaction between DMF and SPEEKK, and the hydrophilic property of PWA, etc. When the membranes were cast at 70°C, the interaction was much weaker than that of the membranes cast at 45°C, and the PWA may be more easily soluble in water. So, the water uptake of composite membranes decreases with the increase of PWA. For example, the water uptake of PWA/SPEEKK composite membranes cast at 70°C with 10, 20, and 30% HPA is 14.4%, 12.4%, and 11.8%, respectively. However, when the membranes were cast at 45°C, the water uptake decreased because of the hydrogen bond between SPEEKK and PWA and the interaction between SPEEKK and rudimental DMF. Compared with the pure SPEEKK membrane, the composite membranes show much higher water uptake due to the hydrophilic property of PWA. IEC provides an indication of the ion exchangeable groups present in a polymer matrix, which are responsible for the conduction of protons and thus is an indirect and reliable approximation of proton conductivity. The IEC of the composite membranes shows increasing tendency with the increase in the content of PWA. Despite the sulfonic acid groups, the PWA may participate in the exchange process. The membranes cast at 70°C show much higher IEC than the ones that were cast at 45°C, due to the hydrogen bond between SPEEKK and PWA and the interaction between SPEEKK and rudimental DMF at different temperatures.

Methanol permeability and proton conductivity

Two transport properties have great influence on the cell performance of PEMFC especially for direct

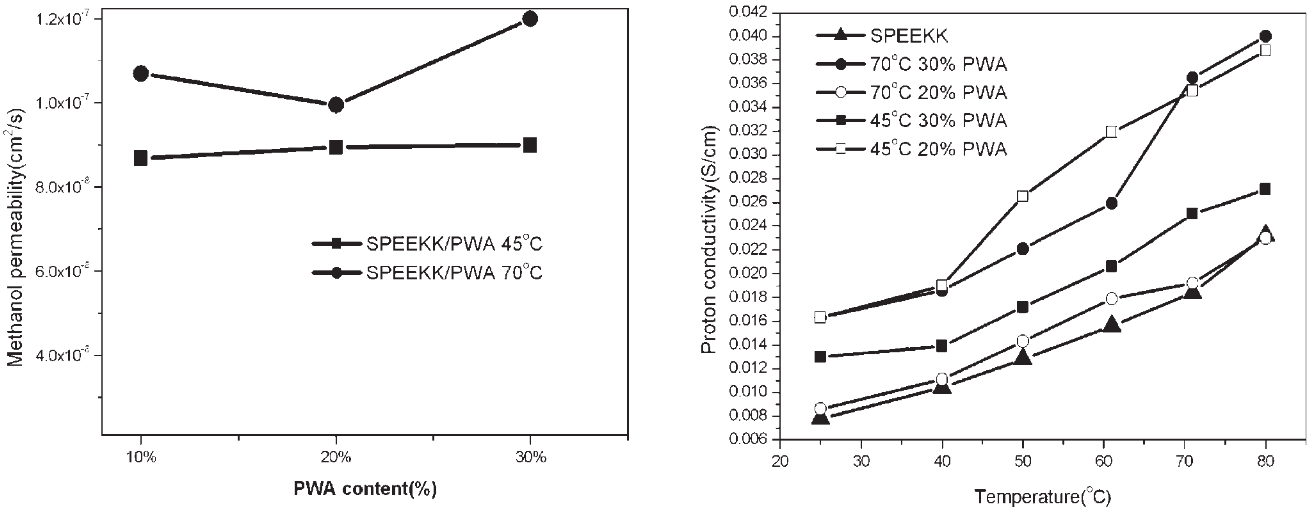


Figure 7 The methanol permeability and proton conductivity of SPEEKK and its composite membranes.

methanol fuel cells (DMFC). A good performance needs high proton conductivity and low methanol permeability. The methanol permeability of SPEEK and its composite membranes is shown in Figure 7. With the introduction of PWA, the methanol permeability increased. This may be explained by the fact that PWA can be easily soluble in water and methanol. After the membranes are immersed in methanol and water, the PWA on the surface of the membranes dissolve which will leave many holes in the membranes.[9] The holes in membranes make the membranes' structures looser, further leading to the increasing transport properties. In addition, the membranes that were cast at 70°C show relatively higher methanol permeability than those cast at 45°C, which conforms to the results of water uptake and IEC. The proton conductivity of membranes is shown in Figure 7. The proton conductivity of the composite membranes was found to increase with both the temperatures and PWA content. Compared with pure SPEEKK membranes, SPEEKK/PWA membranes show much higher proton conductivity, because of the proton conductive ability of PWA. The membranes, which were cast at 45°C show a little higher proton conductivity than those that were cast at 70°C. All the composite membranes show room-temperature proton conductivity higher than 10^{-2} S/cm, which is the lowest value of practical interest for use as PEMs in fuel cells. All the composite membranes show good proton conductive ability and good potential usages in PEMFC.

CONCLUSIONS

SPEEKK/PWA composite membranes cast at different temperatures were researched for PEMFC. The influence of the cast temperatures on the properties of the membranes was studied. The results showed that the cast condition of the composite membranes have great influence on the membrane properties, due to the existence of the hydrogen bond between the SPEEK and PWA and the interaction between the SPEEKK and DMF. When the membranes were cast at high temperatures, the interactions were easily destroyed, and the membranes showed higher conductivity, water uptake, and IEC. The proton conductivity of the composite membranes was greatly improved when compared with that of SPEEKK. The composite membranes show good potential usages in PEMFC.

References

1. Shoesmith, J. P.; Collins, R. D.; Oakley, M. J.; Stevenson, D. K. J Power Sources 1994, 49, 129.
2. Kreuer, K. D. Solid State Ionics 1997, 97, 1.
3. Wang, H. T.; Holmberg, B. A.; Huang, L. M.; Wang, Z. B.; Mitra, A.; Norbeck, J. M.; Yan, Y. S. J Mater Chem 2002, 12, 834.
4. Xing, P. X.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Wang, K. P.; Kaliaguine, S. J Membr Sci 2004, 229, 95.
5. Gil, M.; Ji, X. L.; Li, X. F.; Na, H. Hampsey, J. E.; Lu, Y. F. J Membr Sci 2004, 234, 75.
6. Li, X. F.; Na, H.; Lu, H. Chem J Chin Univ 2004, 25, 1563.
7. Li, X. F.; Liu, C. P.; Lu, H.; Zhao, C. J.; Wang, Z.; Xing, W.; Na, H. J Membr Sci 2005, 255, 149.
8. Li, X. F.; Zhao, C. J.; Lu, H.; Wang, Z.; Na, H. Polymer 2005, 46, 5820.
9. Kim, Y. S.; Wang, F.; Hickner, M.; Zawodzinski, T. A.; McGrath, J. E. J Membr Sci 2003, 212, 263.
10. Shao, Z. G.; Joghee, P.; Hsing, I.-M. J Membr Sci 2004, 229, 43.
11. Janik, M. J.; Davis, R. J.; Neurock, M. J Phys Chem B 2004, 108, 12292.
12. Jung, B.; Kim, B. Y.; Yang, J. M. J Membr Sci 2004, 245, 61.
13. Zawodzinski, T. A.; Neeman, J. M.; Sillerud, L. O.; Gottesfeld, S. J Phys Chem 1991, 95, 6040.
14. Robertson, G. P.; Mikhailenko, S. D.; Wang, K. P.; Xing, P. X.; Guiver, M. D.; Kaliaguine, S. J Membr Sci 2003, 219, 113.