JOURNAL OF Applied Polymer SCIENCE

Effects of Microstructural Functional Polyaniline Layers on SPEEK/HPW Proton Exchange Membranes

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ABSTRACT: In this study, a method is developed to fabricate sulfonated poly (ether ether ketone)/phosphotungstic acid-polyaniline (SPEEK/HPW-PANI) membranes by *in situ* polymerization of aniline for the purpose of decreasing the weight loss of HPW in the membranes. The synthesis involves the production of a SPEEK/HPW hybrid membrane followed by different layer of PANI coatings on the membrane surface, and subsequent treatment using drying in vacuum procedures. The scanning electronic microscopy images showed that HPW had good compatibility with SPEEK polymers and energy dispersive X-ray spectroscopy revealed the successfully doping with HPW and polymerization of PANI. The surface of SPEEK/HPW-PANI becomes more compact than that of SPEEK/HPW and pure SPEEK, which may lead to reduce the water uptake and swelling property. The proton conductivity was found for the SPEEK/HPW-PANI-5 composite membrane (91.53 mS/cm at 80°C) higher than that of pure SPEEK membrane (68.72 mS/cm at 80°C). Better thermal stability was determined in both SPEEK/HPW and SPEEK/HPW-PANI membranes than pristine SPEEK membrane. Therefore, PANI is a good potential coating for organic–inorganic hybrid e.g. SPEEK/HPW membrane materials to improve their hydrothermal stable properties and SPEEK/HPW PANI is a material that shows promise as a proton exchange membranes. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41033.

KEYWORDS: batteries and fuel cells; conducting polymers; membranes

Received 26 February 2014; accepted 15 May 2014
DOI: 10.1002/app.41033

INTRODUCTION

Proton-exchange membrane fuel cells (PEMFC) have gained much attention recently due to their high efficiency and power density compounded with low environmental impact.[1–4] As one of the most important components of the PEMFC, suitable proton exchange membranes (PEM) with high proton conductivity, good mechanical stability are required to satisfy the application in PEMFC. Although Nafion® as perfluorosulfonated ionomer, has been currently employed as the membrane in fuel cells, the limitations including low conductivity at elevated temperatures, high cost prohibit its wide usages.[5–8] Thus, the main limitations to the commercialization of the PEM technology based on perfluorosulfonic acid membranes stimulated the need for non-fluorinated PEM.[3,9–11] In this regard, sulfonated poly (ether ether ketone) (SPEEK) is definitely one of the most fascinating non-fluorinated aromatic ionomers emerging in most recent decades due to its high proton conductivity, high thermal stability, good mechanical properties, and low cost.[11–22] However, SPEEK also has some drawbacks in its practical application. The SPEEK membranes show very low conductivity in low degree of sulfonation (DS) and in high DS absorb too much water and thus swell a lot, sometimes leading to dissolution in contact with water especially at elevated temperatures. Hence, it is important to develop the SPEEK membranes possessing not only high proton conductivity but also dimensional stability associated swelling led by moderate water uptake even at elevated temperatures.

Several routes have been reported for the synthesis of SPEEK-based membrane with high proton conductivity. Apart from the cross-linking or blend with base molecules methods,[23–27] inorganic proton conducting materials doping chemical methods have also been reported.[28–33] For instance, sulfonated SiO_2, sulfonated TiO_2, Montmorillonite clay, $AlPO_4$, etc. have been investigated. Another strategy to solve this problem relative to high proton conductivity is the approach that includes mixing heteropolyacids (HPAs), a kind of super ionic proton conductors in their fully hydrated states with high DS of SPEEK.[34–36] Phosphotungstic acid ($H_3PW_{12}O_4$, HPW) is one of the strongest acids with the highest conductivity in the Keggin-type HPAs. Many researchers have studied the application of HPW in fuel cells.[37–43] However, these investigations have shown that the cell output and stability greatly decay owing to the leakage of HPW in water.[44] Therefore, it urgently needs to explore the efficient assembly methods to decrease the leakage of HPW and swelling ratio from high DS.

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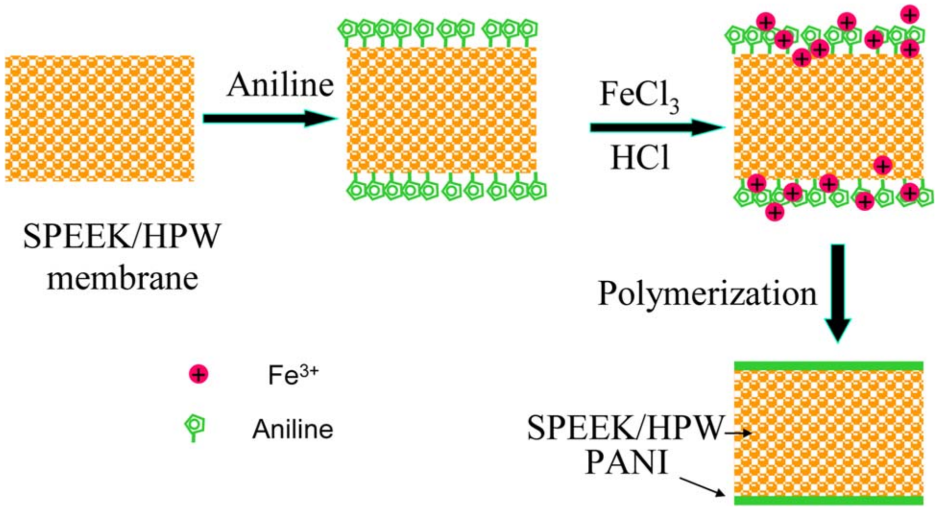


Scheme 1. Process of surface-modification by *in situ* polymerization of PANI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

We have conducted surface modification for SPEEK membranes using Nafion solution for direct methanol fuel cells.[12] Recently, conducting polymer, especially polyaniline (PANI), has received much attention for PEM because of their high chemical and electrochemical stability, high conductivity, easy synthesis, benign environmental effect, good adhesion, and high hydrophilic property.[45–51] Furthermore, it has been recently reported that PANI nanosheets can be simply synthesized in solution in the presence of Fe^{3+} as catalyst. Particularly, Nagarale et al.[45] report recently that using chemical polymerization of a thin layer of PANI in the presence of a high oxidant concentration on a single surface of SPEEK, PANI can coat on SPEEK surface and efficiently keep SPEEK from swelling and methanol permeability. However, the proton conductivity of SPEEK/PANI composites is not as high as expected and coating is not uniform. Therefore, it is a challenge to realize the fabrication of orderly PANI coating on SPEEK/HPW composites because of the difficulties involved in controlling the nucleation and growth of nanostructures in the presence of different precursors with various reduction kinetics.

In the present work, a SPEEK-based composite membrane is investigated, of which the DS is around 51.26 mol. %. After a small amount of HPW incorporated, the SPEEK/HPW hybrid membrane was coated with multilayer of PANI on surfaces. The preparation scheme of the composite membranes is displayed in Scheme 1. The composite membranes are examined by scanning electronic microscopy (SEM), proton conductivity, water uptake, dimensional change, and swelling properties to identify the effects of PANI layer on the prepared SPEEK/HPW-PANI composite membranes.

EXPERIMENTAL

Materials

PEEK (Changchun Jilin University Super Engineering Plastics research Co, Ltd, China) was dried for 24 h in a vacuum box at 120°C before sulfonation reaction. H_2SO_4, HCl, NaOH, NaCl, $FeCl_3$, N-methyl-2-pyrrolidinone (NMP), HPW (Bejing chemical works, China) were used as received. Aniline (Bejing chemical works, China) was distilled before using.

Preparation of SPEEK

Sulfuric acid (120 mL; 98%) was first transferred into a three-neck round bottom flask after N_2 purging for 30 min at room temperature. Twelve gram of PEEK was slowly added under vigorously stirring at room temperature until the polymers were completely dissolved and then speedily stirring at 50°C for 3 h. After a period of sulfonation reaction, the obtained brown–yellow polymer solution was gradually precipitated into ice-cold water under mechanical agitation to form SPEEK fibers. The fibers were filtered, washed several times with deionized water until the pH was neutral and dried at 80°C for 48 h in a vacuum oven. The DS of SPEEK was obtained about 51.26 mol % using a titration method.[52]

Membrane Preparation

SPEEK/HPW Hybrid Membranes. The fabrication of hybrid membranes was made by a solution-casting method. The SPEEK and HPW were added into NMP with the ratio of 10% in total weight and volume, and stirred constantly for 4 h at room temperature. Then a pale yellow transparent homogeneous solution was obtained. The weight ratio of HPW to the mixture of SPEEK and HPW was 7 : 3. The solutions were cast in the form of thin film on a glass plate, dried at 60°C for 48 h, and then dried at 80°C for 15 h in vacuum.

SPEEK/HPW-PANI Composite Membranes. The surface modification of SPEEK/HPW hybrid membranes was carried out by *in situ* polymerization, as shown in Scheme 1. Typically, the hybrid membranes were firstly immersed in 50 mL of aqueous solution including 0.04M aniline for 10 min. Then, they were removed from the solution and washed with deionized water to remove the weakly bonded aniline monomer. Polymerization of aniline was induced by immersing the washed membrane in another 50 mL solution containing 0.01M $FeCl_3$ and 0.01M HCl at room temperature for 30 min. Then, the membrane was taken out and washed with distilled water. All these steps were repeated for n ($n = 1–5$) times in order to obtain multilayer coating composite membranes. SPEEK/HPW-PANI-n refers that SPEEK/HPW based membrane is coated with n layer of PANI.

Characterization Methods

Morphological Characterization. Morphological characterization was performed using SEM (QUANTA450) combined with energy dispersive X-ray spectroscopy (EDS) on the horizontal surface and cross-section of composite membranes after freeze-fracture in liquid nitrogen and operated at 1.5 kV. All samples were measured after gold sputter coating.

Proton Conductivity. Proton conductivity of the membranes was measured by the standard four-electrode method via the ac impedance spectroscopy using electrochemical workstation (A08001 Netherlands Ivium Technologies Company) from 1 Hz to 10^5 Hz. The test was kept at elevated temperatures and 100% RH. The proton conductivity (σ) was calculated by the following expression (1)

$$\sigma = \frac{L}{RA} \tag{1}$$

where R is the membrane resistance (Ω), A is the membrane area (cm^2), L is the thickness of the membrane (μm), σ is the proton conductivity (mS/cm).

Water Uptake. For water uptake, the measurements were carried out in quadruplicate. Membranes were first immersed in water at four different temperatures, that is, at 25°C, 40°C, 60°C, and 80°C, for 12 h to promote water uptake up to equilibrium. After the removal of surface water immediately, the membranes were weighed. The water uptake was calculated using eq. (2)

$$\text{Uptake}(\%) = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100 \tag{2}$$

here, W_{wet} and W_{dry} are weights of wet and dry membranes, respectively.

Swelling Ratio. Swelling experiment was conducted by measuring the volume of membrane specimens under fully hydrated and completely dried conditions. Firstly, the membrane was cut into a strip with predetermined dimensions (1 cm in width and 4.5 cm in length) and equilibrated in distilled water at the target temperature for 12 h to obtain the wet volume (V_{wet}). The extent of water swelling (WS) of the membrane was calculated as the eq. (3)

$$\text{WS}(\%) = (V_{\text{wet}} - V_{\text{dry}})/V_{\text{dry}} \times 100 \tag{3}$$

here, V_{wet} and V_{dry} are the volumes of wet and dry membranes, respectively.

Thermogravimetric Analysis. Thermal transition behaviors of the membranes were determined by using TA instruments (thermogravimetric analysis [TGA-Q50]). The heating rate was 10°C/min. The temperature ranged from 25°C to 800°C and the nitrogen flow rate was 50 ml/min. Before analysis the samples were dried at 80°C for 24 h in vacuum.

Weight Loss Ratio of HPW. For investigation of the weight loss ratio of HPW in the polymer matrix, the known weight membranes were immersed in distilled water at target temperature for 20 days. Then the membranes were completely dried at 120°C until no weight loss was obtained. The weight loss ratio of HPW was calculated as the formula (4)

$$\text{Weight loss ratio}(\%) = (W_1 - W_2)/W_2 \times 100 \tag{4}$$

where W_1 is the dry weight of membranes before immersed in water, W_2 is the dry weight of membranes after immersed in water.

RESULTS AND DISCUSSION

Morphological Characterization

Figure 1 shows the surface and cross-section morphologies of membranes. SEM images of the surface and cross-section of SPEEK matrix were uniform and dense as shown in Figure 1(a,b). When HPW was introduced into the SPEEK matrix, the surface of the SPEEK/HPW hybrid membrane became spongy because of the leakage of small amounts of HPW during treatment in water as shown in Figure 1(c). It is important to note that no large agglomerates are observed both on the surface and the cross-section which means that HPW is uniformly distributed in the SPEEK matrix [Figure 1(c,d)]. With increasing the PANI layers by *in situ* polymerization on the surface of SPEEK/HPW hybrid membrane, the surface of the composite membranes became more and more compact. The PANI layer with the thickness of about 5 μm is obviously observed from Figure 1(e).

EDS images of SPEEK, SPEEK/HPW and SPEEK/HPW-PANI composite membranes are shown in Figure 2. The SPEEK membrane exhibits carbon, oxygen, sulfur, main elements of SPEEK chain, as shown in Figure 2(a). Compared Figure 2(b) with Figure 2(a), the SPEEK/HPW hybrid membrane in Figure 2(b) not only exhibited carbon, oxygen, sulfur (the main elements of SPEEK) but also tungsten, which indicated that the HPW was successfully incorporated in the SPEEK/HPW. As shown in Figure 2(b,c), the content of carbon in SPEEK/HPW-PANI was higher than that of SPEEK/HPW indicating that PANI was uniformly distributed on the surface of membrane because that the main element of PANI was carbon.

Proton Conductivity

Figure 3 shows the proton conductivity of SPEEK, SPEEK/HPW, and SPEEK/HPW-PANI at elevated temperatures under 100% RH. Proton conductivity increased much with the temperature increased as the mobility of proton migrated or exchanged more quickly.[53–55] The introduction of HPW into SPEEK led to the increase of water uptake as the HPW was hydrophilic, and thus increased the proton conductivity.[56] Calculated using expression (1), the proton conductivity of hybrid membrane containing 3% (*w/v*) of HPW at 80°C was the maximum, 63.57 mS/cm at 25°C and 165.01 mS/cm at 80°C under 100% RH, more than 2.4 times higher than that of SPEEK membrane at 80°C as shown the uppermost curve in Figure 3. As for the surface-coating, the surface became compact and the water uptake of composite membranes decreased which resulted in reduction of proton conductivity. As shown in Figure 3, the proton conductivity declined with the increasing in the aggregation layer of PANI. The conductivities of SPEEK/HPW-PANI-3 and SPEEK/HPW-PANI-5 composite membranes were 110.38 mS/cm and 91.53 mS/cm at 80°C under 100% RH, respectively.

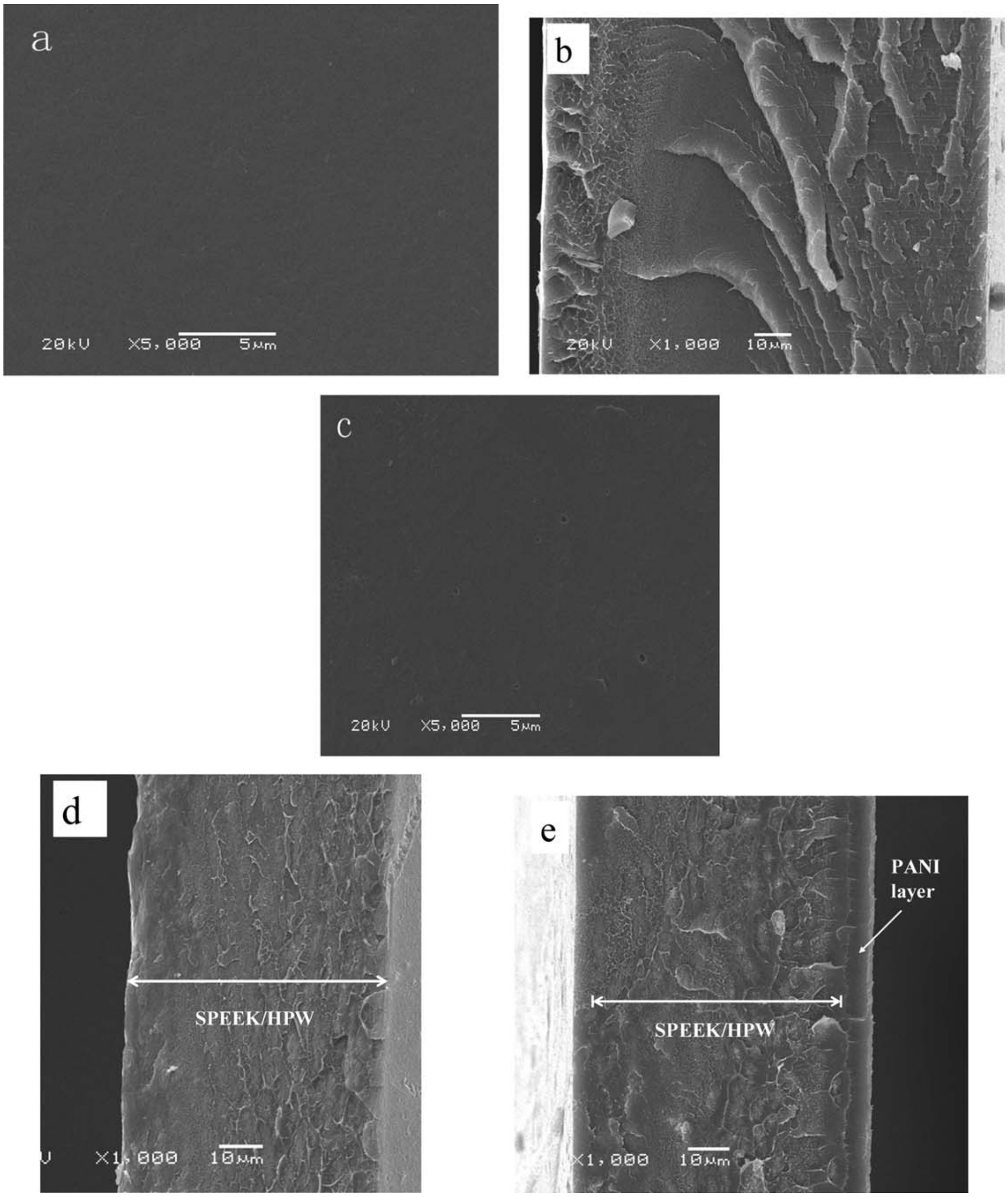
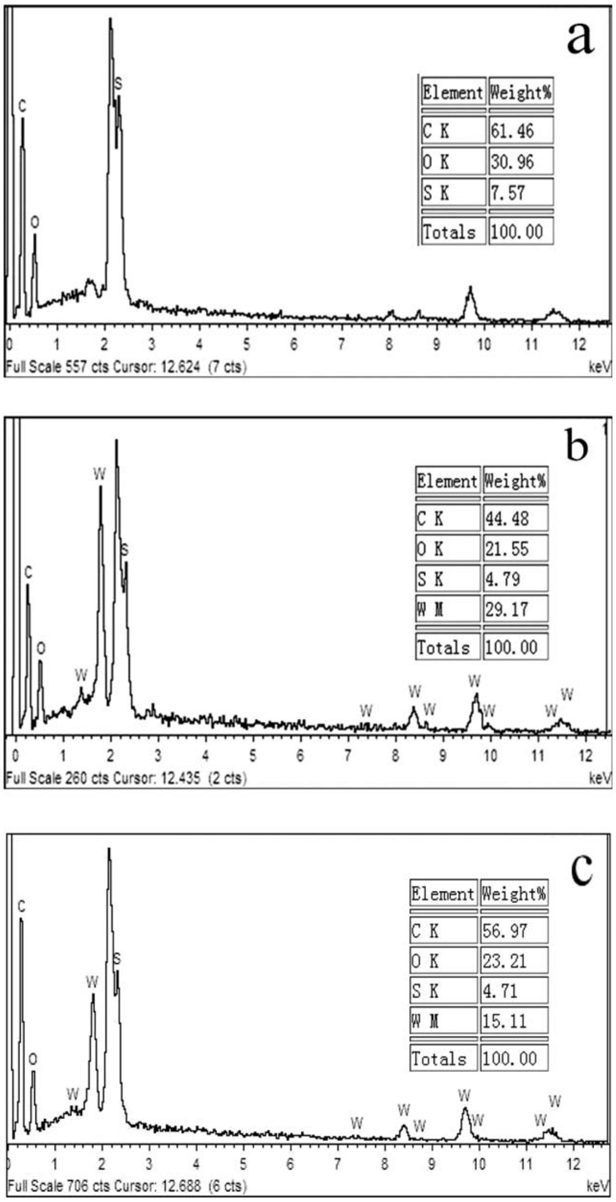


Figure 1. SEM images of surface of SPEEK (a), cross-section of SPEEK (b), surface of SPEEK/HPW-PANI-1 (c), cross-section of SPEEK/HPW (d), and cross-section of SPEEK/ HPW-PANI (e).

However, the proton conductivity of SPEEK/HPW-PANI-5 was still higher than the pure SPEEK membranes at 80°C.

Water Uptake

The water uptake of SPEEK, SPEEK/HPW and SPEEK/HPW-PANI at elevated temperatures of the membranes calculated using eq. (2) is illustrated in Figure 4. Water uptake of all the obtained membranes increased with the increasing temperature because the mobility of polymer chains and the free volume for water absorption increased with temperature.[53] The introduction of HPW to SPEEK increased the water uptake as HPW was hydrophilic.[36] Thus, the water uptake of SPEEK/HPW was higher than that of the pure SPEEK and SPEEK/HPW-PANI membranes. Figure 4 also shows the decreased tendency with the increasing of PANI layers. This may be due to the formation of hydrogen bond between the SPEEK and PANI and the hydrogen bonds made the surface more uniform and compact.[45] For example, the membranes with the PANI layers from 1 to 5, respectively, show the water uptake of 68.53%, 68.15%, 67.71%, 62.74% and 59.68% at 80°C. However, the water uptake of composite membranes with one layer to three layers was still higher than that of SPEEK (64.13% at 80°C).



Element	Weight%
C K	61.46
O K	30.96
S K	7.57
Totals	100.00

Element	Weight%
C K	44.48
O K	21.55
S K	4.79
W M	29.17
Totals	100.00

Element	Weight%
C K	56.97
O K	23.21
S K	4.71
W M	15.11
Totals	100.00

Figure 2. EDS images of SPEEK (a), SPEEK/HPW (b), and SPEEK/HPW-PANI-5 composite membrane (c).

Swelling Ratio

Figure 5 shows the swelling ratio of SPEEK, SPEEK/HPW and SPEEK/HPW-PANI membranes calculated as the eq. (3). The swelling ratio in volume of all membranes investigated increased with the elevated temperature due to the motion of molecules,[53] but there are different in detail. For SPEEK membrane, the swelling ratio varied from 41.50% at 25°C to 67.82% at 80°C. When the HPW was introduced to the SPEEK membranes, the swelling ratio of SPEEK/HPW increased from 74.88% at 25°C to 110.13% at 80°C. It was noting that the swelling ratio of composite membranes decreased with the increase of PANI layers, which may be because of the compact PANI coating decreasing the water uptake. As shown in Figure 5, the swelling ratios of SPEEK/HPW-PANI-4 and SPEEK/HPW-PANI-5 were lower than that of pristine SPEEK membranes. Therefore, the PANI coating of SPEEK/HPW significantly decreased the swelling ratio and increased the dimensional stability.

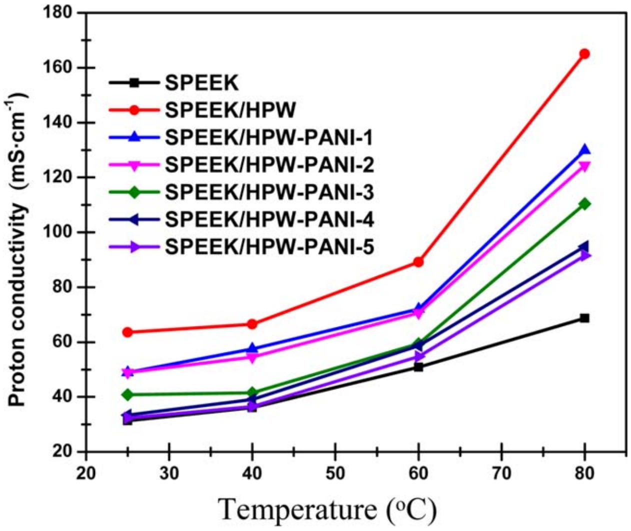


Figure 3. Proton conductivity of SPEEK, SPEEK/HPW, and SPEEK/HPW-PANI as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TGA

Figure 6 shows the TGA curves of membranes. These curves exhibited three main degradation steps. The first step was below 200°C and was attributed to loss of physically and chemically bound water.[57–61] The second step was between 300°C and 400°C and corresponded to the decomposition of sulfonic acid groups.[57–61] The third step was below 500°C due to the main chain degradation of SPEEK.[57–61] Although the weight loss ratio of SPEEK/HPW and SPEEK/HPW-PANI was lower than that of pristine SPEEK, there are similar tendency in the thermal stability curves to both of them. As for the thickness of PANI layer of SPEEK/HPW-PANI-5 was 5μm, much thinner than that of

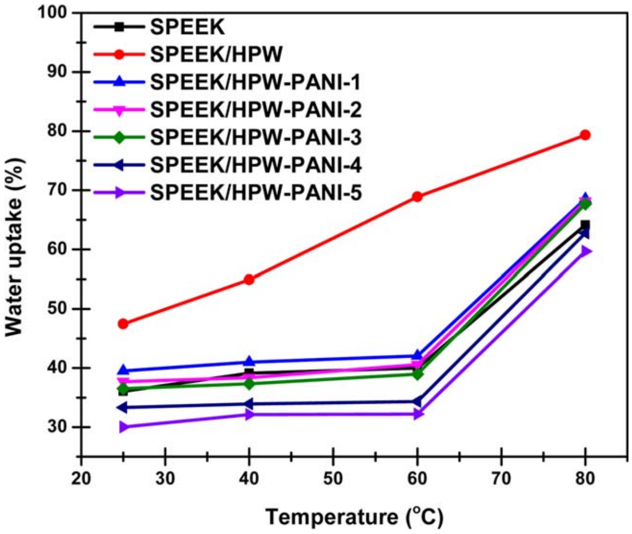


Figure 4. Water uptake of SPEEK, SPEEK/HPW, and SPEEK/HPW-PANI as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

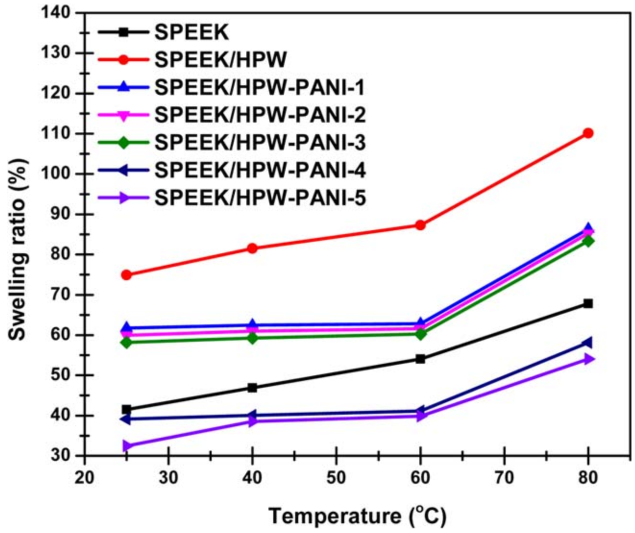


Figure 5. Swelling ratio of SPEEK, SPEEK/HPW, and SPEEK/HPW-PANI as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SPEEK/HPW, so PANI layer has little influence on the thermostability of composite membranes. From those TGA curves, it is concluded that the thermal stability of membranes is significantly enhanced by introduction of HPW and PANI.

Weight Loss Ratio of HPW

Table I shows the weight loss ratio of SPEEK, SPEEK/HPW and SPEEK/HPW-PANI membranes after immersing in water for 20 days at different temperature calculated as the eq. (4). From Table I, the weight loss ratios of all obtained membranes were much lower under 25°C than that under 80°C. The weight loss ratio of SPEEK/HPW reached the maximum of 2.07% at 25°C and 28.93% at 80°C. With the increase of surface-polymerization times, the weight loss ratio declined a lot. And the weight loss ratio of SPEEK/HPW-PANI-5 was 1.29% at 25°C and 19.84% at 80°C, which was 2.07% and 28.93% of SPEEK/HPW hybrid membrane, respectively.

Figure 7 shows the proton conductivity of SPEEK, SPEEK/HPW and SPEEK/HPW-PANI membranes after 20 days immersing in water at different temperature calculated as the eq. (1). After immersing in water for 20 days, the proton conductivity of all the investigated membranes declined a lot at 80°C than at 25°C. As for the surface-modification by PANI, the proton conductivity of composite membranes decreased a little than that of hybrid membranes. The proton conductivity of SPEEK/HPW-PANI-5 was 68.46 mS/cm at 80°C compared with the SPEEK/HPW hybrid membrane (63.65 mS/cm at 80°C), which was still higher than that of pure SPEEK membrane.

Table I. Weight Loss Ratio of SPEEK, SPEEK/HPW, and SPEEK/HPW-PANI Membranes after 20 Days Immersing in Water at Different Temperatures

Membranes	Weight loss ratio (%) at 25°C	Weight loss ratio (%) at 80°C
SPEEK	1.68	2.38
SPEEK/HPW	2.07	28.93
SPEEK/HPW-PANI-1	2.00	28.61
SPEEK/HPW-PANI-2	1.94	28.41
SPEEK/HPW-PANI-3	1.73	27.51
SPEEK/HPW-PANI-4	1.55	21.45
SPEEK/HPW-PANI-5	**1.29**	**19.84**

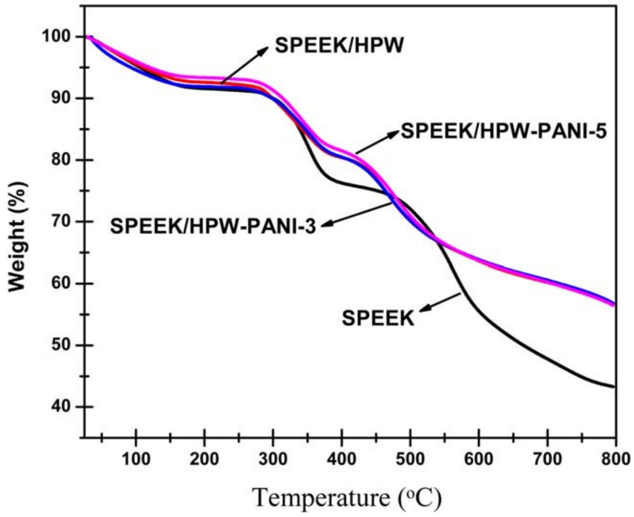


Figure 6. TGA curves of SPEEK, SPEEK/HPW, and SPEEK/HPW-PANI in a temperature range from 25 to 800°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

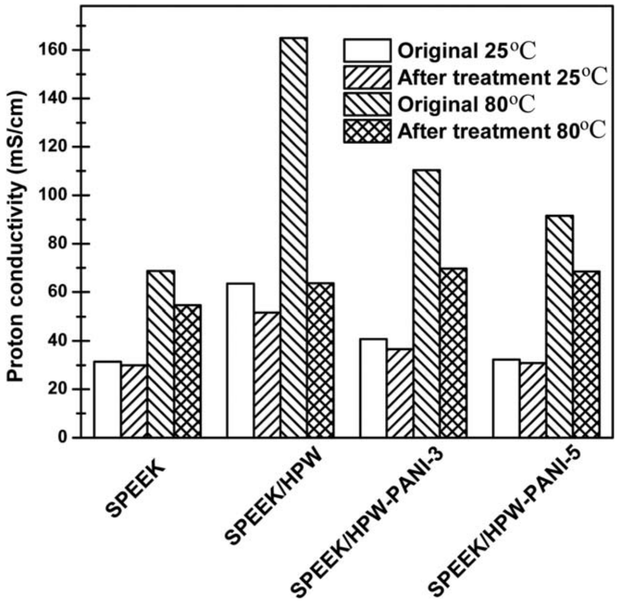


Figure 7. Proton conductivity of SPEEK, SPEEK/HPW, and SPEEK/HPW-PANI membranes after 20 days immersing in water at different temperatures.

CONCLUSIONS

A series of composite membranes were prepared by *in situ* polymerization of different thickness of PANI layers on the surface of SPEEK/HPW membranes. The SEM images show that PANI layer is compact and dense on surface and cross-section. The PANI layers can reduce the weight loss ratio of HPW in the SPEEK/HPW hybrid membranes. The proton conductivity of SPEEK/HPW reached the maximum and all of the SPEEK/HPW-PANI membranes showed higher conductivities than pure SPEEK membranes. Water uptake and swelling ratio in volume of membranes decreased with increasing the PANI layers. The thermal stability of SPEEK/HPW and SPEEK/HPW-PANI membranes slightly increased, as for the pure SPEEK membrane from TGA. Weight loss of ratio of HPW was significantly decreased by increasing PANI layers and also, the proton conductivity of SPEEK/HPW-PANI membranes was much higher than that of SPEEK membrane after 20 days immersing in water at 80°C. Therefore, PANI layers on the prepared SPEEK/HPW composite membranes have important effects on decreasing weight loss ratio of HPW, lower water uptake and swelling ratio. The composite membrane SPEEK/HPW-PANI seems to be a promising candidate for PEMFC applications.

ACKNOWLEDGMENTS

Support of this work by the National Natural Science Foundation of China (Grant Nos. 21036006, 21137001) is gratefully acknowledged.

REFERENCES

1. Kreuer, K. D. Fuel Cells: Selected Entries from the Encyclopedia Of Sustainability Science and Technology; Springer Science Business Media, **2013**, 1.
2. Steele, B. C. H.; Heinzel, A. *Nature* **2001**, *414*, 345.
3. Peighambardoust, S. J.; Rowshanzamir, S.; Amjadi, M. *Int. J. Hydrogen Energy* **2010**, *35*, 9349.
4. Iulianelli, A.; Basile, A. *Int. J. Hydrogen Energy* **2012**, *37*, 15241.
5. Helen, M.; Viswanathan, B.; Murthy, S. S. *J. Power Sources* **2006**, *163*, 433.
6. Jin, Y.; Diniz da Costa, J. C.; Lu, G. Q. *Solid State Ionics* **2007**, *178*, 937.
7. Shahi, V. K. *Solid State Ionics* **2007**, *177*, 3395.
8. Delhorbe, V.; Thiry, X.; Cailleteau, C.; Mourier, E.; Bathfield, M.; Chikh, L.; Fichet, O.; Ameduri, B.; Mercier, R.; Vidal, S.; Augier, L.; Espuche, E.; Gouanvé, F.; Gebel, G.; Morin, A. *J. Membr. Sci.* **2012**, *389*, 57.
9. Kreuer, K. D. *J. Membr. Sci.* **2001**, *185*, 29.
10. Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem. Rev.* **2004**, *104*, 4587.
11. Zhang, H. W.; Shen, P. K. *Chem. Rev.* **2012**, *112*, 2780.
12. Ren, S. Z.; Li, C. N.; Zhao, X. S.; Wu, Z. M.; Wang, S. L.; Sun, G. Q.; Xin, Q.; Yang, X. F. *J. Membr. Sci.* **2005**, *247*, 59.
13. Gil, M.; Ji, X. L.; Li, X. F.; Na, H.; Hampsey, J. E.; Lu, Y. F. *J. Membr. Sci.* **2004**, *234*, 75.
14. Rikukawa, M.; Sanui, K. *Prog. Polym. Sci.* **2000**, *25*, 1463.
15. Xing, P. X.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S.D.; Wang, K. P.; Kaliaguine, S. *J. Membr. Sci.* **2004**, *229*, 95.
16. Li, L.; Zhang, J.; Wang, Y. X. *J. Membr. Sci.* **2003**, *226*, 159.
17. Zhao, C. J.; Li, X. F.; Wang, Z.; Dou, Z. Y.; Zhong, S. L.; Na, H. *J. Membr. Sci.* **2006**, *280*, 643.
18. Ye, G.; Janzen, N.; Goward, G. R. *Macromolecules* **2006**, *39*, 3283.
19. Do, K. N. T.; Kim, D. *J. Power Sources* **2008**, *185*, 63.
20. Maab, H.; Nunes, S. P. *J. Power Sources* **2010**, *195*, 4036.
21. Lafi, A. G. A.; Hay, J. N. *J. Appl. Polym. Sci.* **2013**, *128*, 3000.
22. Marani, D.; Di Vona, M. L.; Traversa, E.; Licoccia, S.; Beurroies, I.; Llewellyn, P. L.; Knauth, P. *J. Phys. Chem. B* **2007**, *110*, 15817.
23. Kerres, J. *Fuel Cells* **2006**, *6*, 251.
24. Luo, H. Z.; Vaivars, G.; Mathe, M. *Int. J. Hydrogen Energy* **2009**, *34*, 8616.
25. Mikhailenko, S. D.; Zaidi, S. M. J.; Kaliaguine, S. *J. Polym. Sci. Part B: Polym. Phys.* **2000**, *38*, 1386.
26. Zhang, H. Q.; Li, X. F.; Zhao, C. J.; Fu, T. Z.; Shi, Y. H.; Na, H. *J. Membr. Sci.* **2008**, *308*, 66.
27. Wilhelm, F. G.; Punt, I. G. M.; van der Vegt, N. F. A.; Strathmann, H.; Wessling, M. *J. Membr. Sci.* **2002**, *199*, 167.
28. Roelofs, K. S.; Hirth, T.; Schiestel, T. *J. Membr. Sci.* **2010**, *346*, 215.
29. Hasani-Sadrabadi, M. M.; Emami, S. H.; Ghaffarian, R.; Moaddel, H. *Energy Fuel.* **2008**, *22*, 2539.
30. Rani, G. S.; Beera, M. K.; Pugazhenthi, G. *J. Appl. Polym. Sci.* **2012**, *124*, E45.
31. Zhang, Y.; Zhang, H.; Zhu, X.; Bi, C. *J. Phys. Chem. B* **2007**, *111*, 6391.
32. Du, L.; Yan, X.; He, G.; Wu, X.; Hu, Z.; Wang, Y. *Int. J. Hydrogen Energy* **2012**, *37*, 11853.
33. Rangasamy, V. S.; Thayumanasundaram, S.; Greef, N. D.; Seo, J. W.; Locquet, J. P. *Solid State Ionics* **2012**, *216*, 83.
34. Horky, A.; Kherani, N.; Xu, G. *J. Electrochem. Soc.* **2003**, *150*, A1219.
35. Kozhevnikov, I. V. *Chem. Rev.* **1998**, *98*, 171.
36. Lee, K. H.; Chu, J. Y.; Kim, A. R.; Nahm, K. S.; Kim, C. J.; Yoo, D. J. *J. Membr. Sci.* **2013**, *434*, 35.
37. Rhoden, S. L. N. H.; Linkous, C. A.; Mohajeri, N.; Diaz, D. J.; Brooker, P.; Slattery, D. K.; Fenton, J. M. *J. Electrochem. Soc.* **2010**, *157*, B1095.
38. Xu, W.; Lu, T.; Liu, C.; Xing, W. *Electrochim. Acta* **2005**, *50*, 3280.
39. Lin, C.; Thangamuthu, R.; Chang, P. *J. Membr. Sci.* **2005**, *254*, 197.
40. Wu, H.; Shen, X.; Cao, Y.; Li, Z.; Jiang, Z. *J. Membr. Sci.* **2004**, *451*, 74.
41. Xiang, Y.; Yang, M.; Zhang, J.; Lan, F.; Lu, S. *J. Membr. Sci.* **2011**, *368*, 241.

42. Xu, D.; Zhang, G.; Zhang, N.; Li, H.; Zhang, Y.; Shao, K.; Han, M.; Lew, C. M.; Na, H. *J. Mater. Chem.* **2010**, *20*, 9239.
43. Yamada, M.; Honma, I. *J. Phys. Chem. B* **2006**, *110*, 20486.
44. Aparicio, M.; Mosa, J.; Etienne, M.; Durán, A. *J. Power Sources* **2005**, *145*, 231.
45. Nagarale, R. K.; Gohil, G. S.; Shahi, V. K. *J. Membr. Sci.* **2006**, *280*, 389.
46. Qaiser, A. A.; Hyland, M. M.; Patterson, D. A. *J. Membr. Sci.* **2011**, 385, *67*.
47. Wu. G.; More, K. L.; Johnston, C. M.; Zelenay, P. *Science* **2011**, *332*, 443.
48. Gao, W.; Sattayasamitsathit, S.; Orozco, J.; Wang, J. *J. Am. Chem. Soc.* **2011**, *133*, 11862.
49. Wang, A. L.; Xu, H.; Feng, J. X.; Ding, L. X.; Tong, Y. X.; Li, G. R. *J. Am. Chem. Soc.* **2013**, *135*, 10703.
50. Wu, G.; Li, D.; Dai, C.; Wang, D.; Li, N. *Langmuir* **2008**, *24*, 3566.
51. Tu, J. G.; Hu, L. W.; Wang, W.; Hou, J. G.; Zhu, H. M.; Jiao, S. Q. *J. Electrochem Soc.* **2013**, *160*, A1916.
52. Gupta, D.; Choudhary, V. *Int. J. Hydrogen Energy* **2011**, *36*, 8525.
53. Knauth, P.; Sgreccia, E.; Donnadio, A.; Casciola, M.; Di Vona, M. L. *J. Electrochem. Soc.* **2011**, *158*, B159.
54. Wang, C. M.; Chalkova, E.; Lee, J. K.; Fedkin, M. V.; Komarneni, S.; Lvov, S. N. *J. Electrochem. Soc.* **2011**, *158*, B690.
55. Miyatake, K.; Chikashige, Y.; Higuchi, E.; Watanabe, M. *J. Am. Chem. Soc.* **2007**, *129*, 3879.
56. Grosmaire, L.; Castagnoni, S.; Huguet, P.; Sistat, P.; Boucher, M.; Bouchard, P.; Bebin, P.; Deabate, S. *Phys. Chem. Chem. Phys.* **2008**, *10*, 1577.
57. Fu, T.; Wang, J.; Ni, J.; Cui, Z.; Zhong, S.; Zhao, C.; Na, H.; Xing, W. *Solid State Ionics* **2008**, *179*, 2265.
58. Tripathi, B. P.; Shahi, V. K. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2009**, *340*, 10.
59. Luu, D. X.; Kim, D. *J. Membr. Sci.* **2011**, *371*, 248.
60. Luo, Y. F.; Huo, R. Z.; Jin, X. G.; Karasz, F. E. *J. Anal. Appl. Pyrol.* **1995**, *34*, 229.
61. Brooker, R. P.; Bonville, L. J.; Slattery, D. K. *J. Electrochem. Soc.* **2013**, *160*, F75.