A Modified Poly(aryle ether ketone sulfone) Proton Exchange Membrane with *In Situ* Polymerized Polypyrrole for the Direct Methanol Fuel Cells

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ABSTRACT: To meet with the requirement of proton exchange membrane in direct methanol fuel cells (DMFCs), sulfonated poly(aryle ether ketone sulfone)/ polypyrrole (SPAEKS/Ppy) composite membranes with different contents of Ppy were prepared by chemically *in situ* polymerization. FT-IR spectra suggested that the sulfonic groups on SPAEKS copolymers interacted with N groups of Ppy. SEM pictures showed that the Ppy particles were uniformly distributed throughout the SPAEKS membranes matrix. The composite membranes showed good thermal stability, low water uptake, and high proton conductive capability. The methanol diffusion coefficient (1.18×10^{-7} cm^2/s) of the composite membrane with 15% Ppy was much lower than that of pure SPAEKS membrane (8.52×10^{-7} cm^2/s). The composite membranes showed very good potential usage in direct methanol fuel cells (DMFCs). © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 914–920, 2011

Key words: sulfonated poly(aryle ether ketone sulfone); polypyrrole; DMFC; composite proton exchange membrane

INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) is one of the most promising efficient and environmental friendly power generation systems because of its low noise, low pollution, and high working efficiency.[1,2] Direct methanol fuel cell (DMFC) is a type of PEMFC, which is potentially suitable for applications in automobiles (cars, trucks and buses) or portable applications (cell phones and laptops) because of its simple fueling (easy storage of methanol, no reformer required), low emissions, and low operating temperatures.[3] The key component of a PEMFC is proton exchange membrane (PEM) material, which acts as a separator to prevent the mixing of the fuel and the oxidant, as well as an electrolyte to transfer protons from the anode to the cathode.

Therefore, during the current years, studies on alternative membrane materials to Nafion membranes such as sulfonated poly(aryl ether ketone)s (SPAEKs),[4] sulfonated poly(aryl ether sulfone)s (SPAES)[5] and sulfonated polyimide (SPI),[6] and their composite membranes[7–9] are being widely undertaken. Our research groups have synthesized a series of sulfonated poly(aryl ether ketone sulfone) proton exchange membrane materials, which show extremely good mechanical properties, thermochemical stability, high proton conductivity, and low relatively methanol diffusion coefficient. However, the PEMs with high sulfonation degree (DS, which is the number of sulfonate groups per repeating unit) still have the problem of high methanol diffusion coefficient, which limits it further usage in DMFCs.

In this article, to decrease the methanol diffusion coefficient of membranes, polypyrrole has been introduced into SPAEKS membranes through *in situ* polymerization method. It is hoped to enhance the densification of membranes with high DS and finally reduce the methanol permeability by means of the interaction between the sulfonic groups of SPAEKS membranes and N groups of polypyrrole. This method not only can overcome the phenomenon of blending-induced agglomeration when using traditional methods, but also can change the content of monomer pyrrole for a more flexible adjustment of Ppy content.

EXPERIMENTAL

Materials

SPAEKS copolymers were synthesized by direct aromatic nucleophilic substitution polymerization. The synthesis procedure and characterization of these copolymers were described in detail in our previous work.[10] The sulfonation degree of SPAEKS used in this article is 1.0. The structure of SPAEKS is shown in Scheme 1. Hydrogen peroxide (H$_2$O$_2$), pyrrole
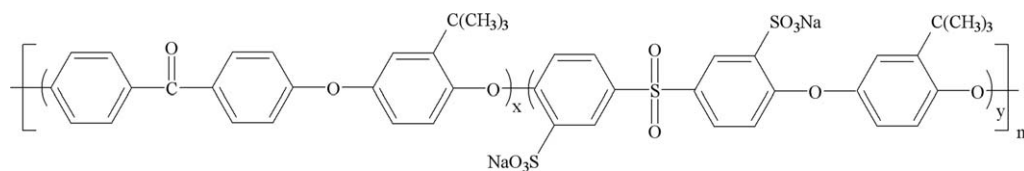
Scheme 1 The structure of SPAEKS copolymers.

and other organic solvents were obtained commercially and used without further purification.

The preparation of the Spaeks/Ppy composite membranes

The SPAEKS copolymers were treated by first immersing themselves in 2*M* HCl solution for 24 h to change the SPAEKS copolymers into an acidic form. Then the prepared copolymers were washed with deionized water until the pH reached 6–7 and finally dried at 80°C for 48 h for further using.

The SPAEKS/Ppy composite membranes were prepared by the polymerization of pyrrole monomers in SPAEKS solutions. Above all, a fixed weight ratio of pyrrole monomer and SPAEKS copolymers were dissolved in DMF solutions and stirred for 2 h. Then 30 wt % H_2O_2 was slowly dripped into the solutions and allowed to stir for another 4 h. The solutions were then cast onto glass plates, dried at 100°C for about 24 h, obtained 80–90 μm thick membranes. After the *in situ* polymerization, the modified membranes were post-treated with methanol to remove the unreacted pyrrole monomers.

The characterization of membranes

The Fourier transform infrared spectroscopy (FT-IR) spectra of SPAEKS and SPAEKS/Ppy thin films were recorded on a Bruker Vector 22 FT-IR spectrometer and 32 scans were recorded with a resolution of 4 cm^{-1} in transmittance mode. The SEM (SHIMADZU SSX-550) was used to observe the surface morphology of the membranes. The membranes were gold-coated prior to SEM measurements. The cross-sectional SEM measurements were performed by fracturing membranes in liquid nitrogen and the fractured surfaces were also sputter-coated with Au prior to SEM measurements. A Pyris 1 thermogravimetric analyzer (TGA, Perkin–Elmer) was performed to study the thermal stability behavior of the SPAEKS membrane and SPAEKS/Ppy composite membranes. About 5 mg samples of the membranes were heated to 120°C and kept at that temperature for 15 min to remove any water absorbing from the air before the test. The samples were cooled to 50°C and then reheated to 700°C at a rate of 10°C/min under the protection of N_2. The temperature at 5% weight loss ($T_{d5\%}$) occurred for each sample was recorded.

The performance measurement of membranes

The water uptake of membranes was calculated by measuring the weight difference between the dried and hydrated membranes. The dried membranes were weighed and the weights of membrane were recorded as W_{dry}. After that, they were immersed in water until the weight remained constant. Water on the surface of the hydrated samples was removed with filter paper, immediately transferred to weighting dishes and then weighed (W_{wet}). The water uptake of membranes was calculated by $(W_{wet} - W_{dry})/W_{dry} \times 100\%$.

The water diffusion coefficient measurements of composite membranes were accomplished by a Pyris 1TGA (Perkin–Elmer). During the process of measurement, the temperature was kept at 80°C and constant pressure (0.1 MPa) for 60 min, to determine the weight change of the sample with time. Water diffusion coefficient was calculated as follows (eq. 1).[11]

$$\frac{Mt}{M\infty} = 4\left(\frac{Dt}{\Pi L^2}\right)^{1/2} \quad (1)$$

where D is the water diffusion coefficient, M_t/M_∞ is the water desorption, and L is the membrane thickness.

The proton conductivity of the membranes was determined by Ac impedance spectroscopy using a Princeton Applied Research Model 273A potentiostat with a Model 5210 Frequency Response Detector (EG and G PARC, Princeton, NJ) from 100 MHz to 100 KHz. All membranes were initially hydrated by immersion in deionized water for 24 h at room temperature. Measurement of the conductivity of fully hydrated membranes was performed with the cell immersed in water. All impedance measurements were performed both at 25°C and 80°C in deionized water. Proton conductivity (s) of membranes in the acidic form was calculated from the resistance according to Eq. (2).

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

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

Methanol permeability was measured by means of a U-shaped steel-made diffusion cell in the literatures.[12,13] The diffusion cell consisting of two

compartments was separated by a vertical membrane, which was fixed between two rubber rings. One compartment of the cell was filled with deionized water. The other compartment was filled with a mixture solution of methanol and deionized water (5/5, v/v). The compartments were stirred continuously during permeability measurement. The methanol concentration in the water compartment was periodically determined using a chromatograph (SHIMADZU GC-8A). Peaks areas were converted to the methanol concentration with a calibration curve. The methanol diffusion coefficient was calculated by following formula,[3] as stated elsewhere.[12,13]

$$C_{B(t)} = \frac{A}{V_B}\frac{DK}{L}C_A(t - t_0) \qquad (3)$$

where L, A, and V_B are the thickness of membrane, the effective area and the volume of receptor reservoir, respectively. C_A and C_B are the methanol concentration in the donor and receptor reservoirs, respectively. D, K, and t_0 are the methanol diffusivity, the partition coefficient and the time lag, respectively. The methanol permeability (P in $cm^2\ s^{-1}$) is defined as the product of diffusivity and partition coefficient, i.e., $P = DK$, and the concentration change of C_B with time is obtained from a linear slope (α), using Eq. (4).

$$P = DK = a \times \frac{V_B}{A} \times \frac{L}{C_A} \qquad (4)$$

RESULTS AND DISCUSSION

The preparation and characterization of Spaeks/Ppy composite membranes

The SPAEKS/Ppy composite membranes were prepared by the polymerization of pyrrole monomer in SPAEKS solutions. The pyrrole monomers could disperse uniformly in the SPAEKS solutions because of the interactions between the sulfonated acid groups in SPAEKS and the N groups in pyrrole monomers. After H_2O_2 was dripped into the solutions, Ppy was formed by way of *in situ* polymerization within the SPAEKS solutions. The SPAEKS/Ppy composite membranes were obtained through the solutions were cast onto a glass plates. The composite membranes are notated as SPAEKS/Ppy-1 with 5 wt % Ppy, SPAEKS/Ppy-2 with 10 wt % Ppy, and SPAEKS/Ppy-3 with 15 wt % Ppy. The SPAEKS/Ppy composite membranes were characterized by FTIR spectroscopy as shown in Figure 1. It displays the spectroscopy of pure SPAEKS membrane and SPAEKS/Ppy composite membranes. The C=C stretching of the benzene ring appears in the range of 1400–1600 cm^{-1}. The peaks at 1266 and 1656 cm^{-1} are induced by C—N and C=N stretching, respec-
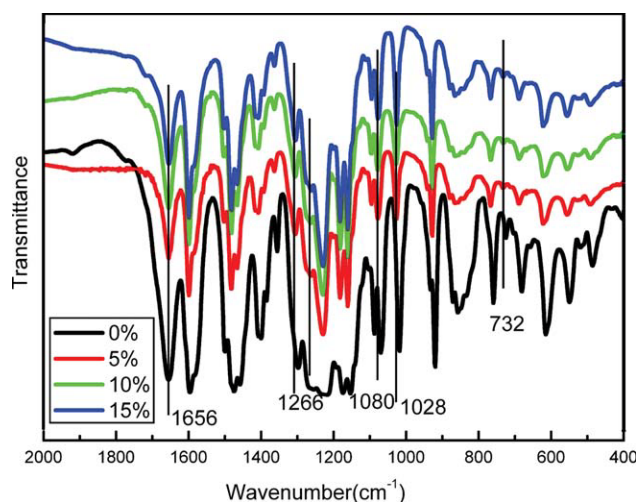

Figure 1 The FTIR spectra of SPAEKS membrane and SPAEKS/Ppy composite membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tively. The vibration plane angle of N—H is found at 732 cm^{-1}. Although the composite membranes are similar in band pattern, the intensity of the C—N and C=N absorption is different. With increasing content of Ppy, the intensity of the absorption increases slightly, this confirms the trend of the weight ratio of Ppy in SPAEKS membranes. Moreover, the absorption bands at 1019 and 1070 cm^{-1} corresponding to the stretching vibrations of the sulfonic groups for the pure SPAEKS were shifted to a higher wavenumbers (1028 and 1080 cm^{-1}). The shift is induced by the interaction between SPAEKS and Ppy. The result proved that the Ppy particles interact primarily with the sulfonic acid groups.[14]

The morphology of the SPAEKS/Ppy composite membranes

The distribution of Ppy particles in the SPAEKS membranes will directly determine their properties, such as water uptake, thermal stability, proton conductivity, and methanol permeability. In this article, the surface morphology of membrane was observed by a SEM instrument. The SEM pictures of SPAEKS/Ppy composite membranes were shown in Figure 2. Compared with neat polymer, the presence of typical polypyrrole particles was clearly observed as white spots.[15] It can be found that the Ppy particles were uniformly distributed in the SPAEKS matrix. Also, the density of the Ppy particles in the SPAEKS membranes increased with the content of pyrrole monomer increasing and seldom aggregated. This suggested the interaction between the sulfonic groups and N groups acts as a very important role in the distribution of
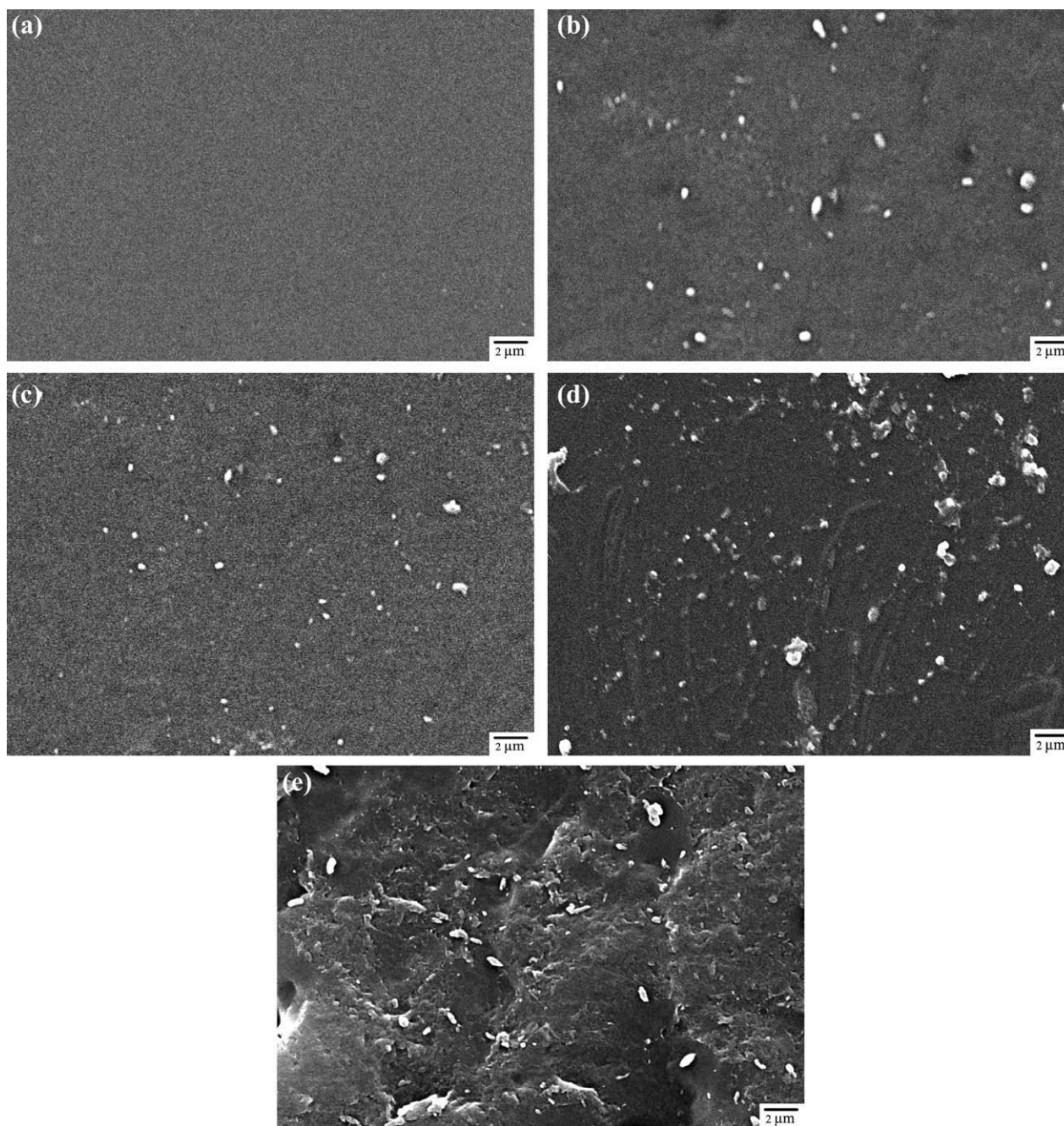
Figure 2 The SEM of SPAEKS and SPAEKS/Ppy composite membranes. (a) SPAEKS, (b) SPAEKS/Ppy-1, (c) SPAEKS/Ppy-2, (d) SPAEKS/Ppy-3, (e) cross-sectional morphology of SPAEKS/Ppy-2.

the Ppy particles in the SPAEKS matrix. It can be concluded from Figure 2(d) that the Ppy particles were not only dispersed on the surface but also through out the whole membrane. It is noteworthy that all the membranes have been immersed in water for about 48 h before the SEM test, which indicates that the Ppy particles can stably exist in the SPAEKS membranes under hydrated fully conditions. This also confirmed the advantages of the *in situ* polymerization method by means of interaction between the sulfonic groups of SPAEKS and N groups of pyrrole.

The thermal stability of membranes

TGA measurement was performed to evaluate the thermal stabilities of the membranes. Figure 3 shows the changes in the thermal stability in nitrogen as a result of the incorporation of polypyrrole particles into SPAEKS matrix. In each TGA curve, one can observe two distinct weight loss stages, of which the former one (250–300°C) was associated with the desulfonation process of SPAEKS membrane and SPAEKS/Ppy composite membranes. Before the first loss stage, each curve had a little weight loss before
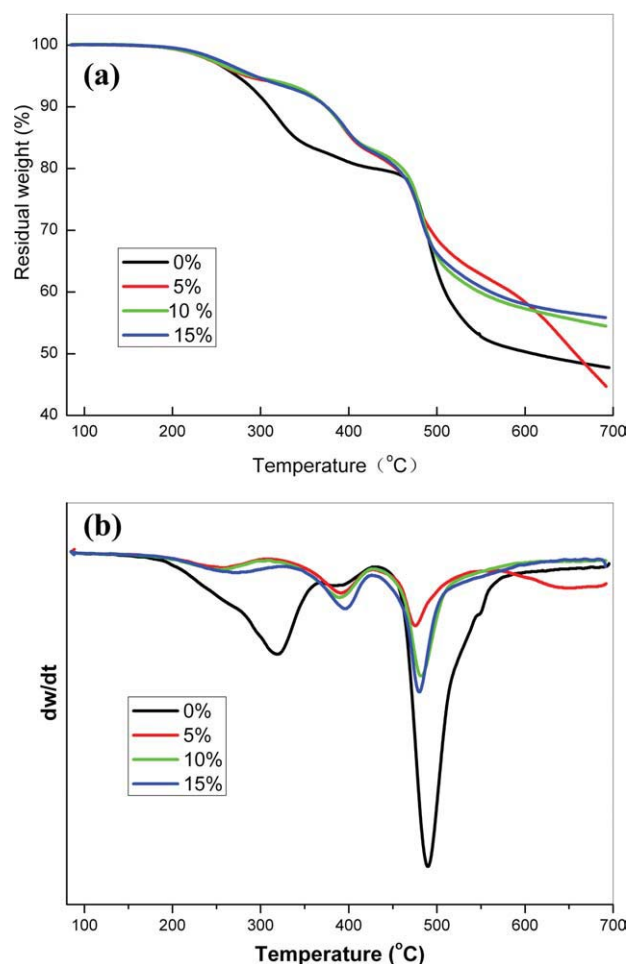
Figure 3 The TGA (a) and DTG(b) curves of SPAEKS membrane and SPAEKS/Ppy composite membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

desulfonation process, which was mainly attributed to the splitting-off of water. This can indicate that membrane had residual water despite drying each sample before the test, which proved that this series of composite membranes had good water-retention capacity. The second weight loss step at about 420°C was attributed to the decomposition of the main chain of the copolymers. These results indicated that all the membranes are thermally stable at about 300°C, which is good enough in thermal stability for usage in DMFCs as proton exchange membrane materials. In

addition, Figure 3 shows that the thermal degradation profile of each curve was very similar to one another, but the temperature corresponding to the onset for first weight loss (T_d) was different between the pure SPAEKS membrane and SPAEKS/Ppy composite membranes. Furthermore, the temperature of 5% weight loss ($T_{d5\%}$) gradually increased from 357°C of SPAEKS/Ppy-1 to 364°C of SPAEKS/Ppy-3 and was higher than 313°C of SPAEKS membrane. Therefore, the thermal stabilities of SPAEKS/Ppy composite membranes are superior to that of SPAEKS membrane due to the restriction of the cluster's mobility caused by the intermolecular interaction between SPAEKS and polypyrrole.[16–21]

Water uptake and water desorption of composite membranes

The water uptake is one of the essential parameters for both proton transporting and mechanical stability of proton exchange membranes. The proton transporting through the membrane requires a significant amount of water to coordinate with proton to maintain good proton conductivity. However, water uptake should be minimized to provide the membrane mechanical and dimensional stability. The water uptake of membrane was measured both at 25°C and 80°C, and the results are displayed in Table I. The SPAEKS/Ppy composite membranes show much lower water uptake than that of the pure SPAEKS membrane. Moreover, the water uptake of composite membranes decreases drastically with the weight content of Ppy increasing from 5 to 15%. This can be considered as the more incorporation of polypyrrole particles into the SPAEKS matrix, the more sulfonic groups were prevented from absorbing water molecules because of the strong interaction between the SPAEKS and Ppy.[22]

To test the water-retention capacity of membranes, TGA analyzer was used to record the water content of membrane changes with time at the temperature of 80°C. Before the measurement, all membranes were soaked in water. Figure 4 shows the water desorption isotherms curves of SPAEKS membrane and SPAEKS/Ppy composite membranes. The calculated results of water diffusion coefficient are shown

TABLE I
The Analytical Data of SPAEKS Membrane and SPAEKS/Ppy Composite Membranes

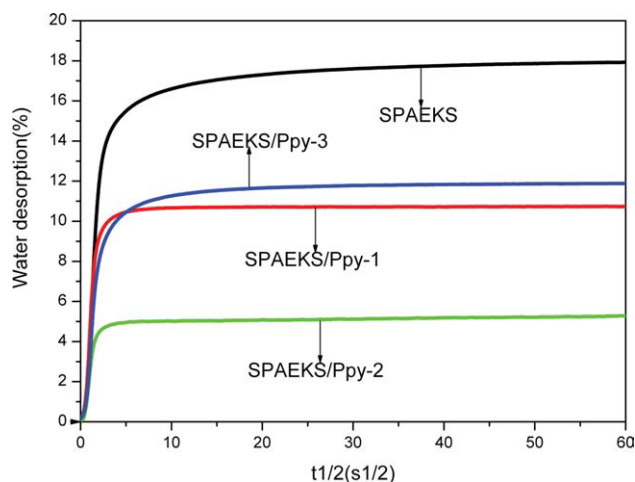| Samples	Water uptake (%)		Water diffusion Coefficient $\times 10^{-9}$ (cm²/s)	Methanol diffusion coefficient $\times 10^{-7}$ (cm²/s)	Proton conductivity $\times 10^{-2}$ (S/cm)	
	20°C	80°C			25°C	80°C
SPAEKS	27.90 ± 0.87	29.3 ± 0.92	9.89 ± 0.12	8.52 ± 0.13	5.8 ± 0.12	7.9 ± 0.14
SPAEKS/Ppy-1	24.52 ± 0.56	25.13 ± 0.61	8.72 ± 0.09	7.78 ± 0.11	5.2 ± 0.10	7.6 ± 0.11
SPAEKS/Ppy-2	21.62 ± 0.52	22.52 ± 0.55	5.86 ± 0.8	5.62 ± 0.09	4.7 ± 0.11	6.8 ± 0.13
SPAEKS/Ppy-3	17.86 ± 0.47	18.38 ± 0.53	2.39 ± 0.06	3.18 ± 0.10	3.9 ± 0.06	6.1 ± 0.08

Figure 4 Water desorption of SPAEKS membrane and SPAEKS/Ppy composite membranes at 80°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in Table I. From the results, the water diffusion coefficients of SPAEKS/Ppy composite membranes were lower than that of SPAEKS membrane. It indicated the water in the composite membranes evaporated more slowly than SPAEKS membranes. In another words, the SPAEKS/Ppy composite membrane had better water retention capability. It can be also found that the water diffusion coefficient of SPAEKS/Ppy composite membranes decreased with the increment of Ppy content. In conclusion, the water retention capabilities of the membranes at relative high temperatures are improved by the introduction of Ppy.

Proton conductivity and methanol permeability

High proton conductivity of the membrane is a basic requirement for the PEMFC. The proton conductivities of SPAEKS membrane and its composite membranes at different temperatures are displayed in Figure 5. These results show that the proton conductivities of SPAEKS/Ppy composite membranes were slightly lower than that of pure SPAEKS membrane and decreased with the content of Ppy increasing, which was similar to the relationship between the water uptake and content of Ppy. The reason of proton conductivity decreasing was attributing to the introduction of Ppy particles into the SPAEKS matrix. In case of SPAEKS membranes, the hydrophobic polymer matrix ensures the mechanical strength, whereas the hydrophilic sulfonic groups may aggregate into large hydrophilic clusters. These hydrophilic clusters could provide cation transport pathway or ionic transport channels.[23] The introduction of Ppy particles in SPAEKS membranes makes the proton transport channels becoming narrow due to the interaction between the sulfonic groups of SPAEKS and the N groups of

Ppy. But the new proton transport pathways from the N groups of Ppy to the sulfonic groups of SPAEKS were formed by the interaction between them, which increased the proton conductivity of membranes. In this experiment, the former factor probably the dominant influence on proton conductivity result. Therefore, the proton conductivity of the SPAEKS/Ppy composite membranes decreased slightly with increasing Ppy content.

For application in direct methanol fuel cells (DMFCs), the methanol permeability of the membrane must be taken into account. The membrane for DMFC is required to not only having high proton conductivity but also effectively separating methanol and oxygen. Diffusion or leakage of the methanol across the membrane leads to power loss and other undesirable consequences. Membranes with low methanol permeability allow high methanol feed concentration, thereby increasing the effective energy density of the fuel cell system. The high methanol permeability of the Nafion membrane as well as its high cost presents a major obstacle to its application in DMFCs. The methanol diffusion coefficients of SPAEKS membrane and its composite membranes are listed in Table I. Compared with the pure SPAEKS membrane, the methanol diffusion coefficients of SPAEKS/Ppy composite membranes gradually decreased from 7.78×10^{-7} to 3.18×10^{-7} cm^2/s with Ppy content increasing from 5 to 15 wt %. This tendency was consistent with the results of water uptake. The transport of methanol among membrane also requires successively transmitting channels.[24] The quantity and diameter of well-connected channels each other decreased in composite membranes due to the introduction of Ppy particles, which form the interaction between sulfonic groups
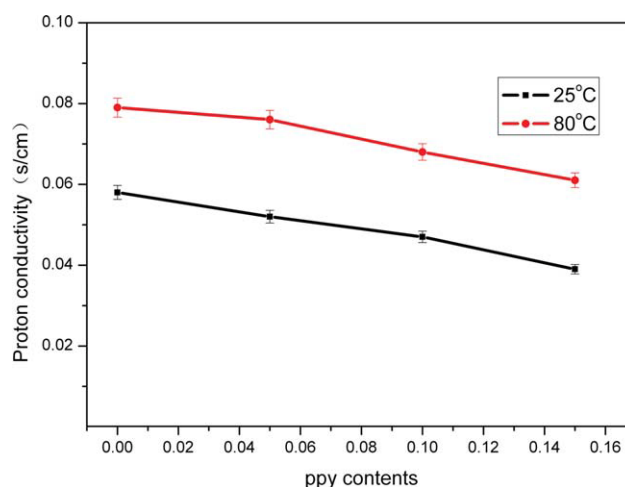

Figure 5 The proton conductivity of SPAEKS membrane and SPAEKS/Ppy composite membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and N groups. The interaction could restrict the movement of sulfonic groups, which hinders the sulfonic groups approaching each other. It is difficult that hydrophilic sulfonic groups form connected transporting channels among membranes. The content and the diameter of the connected channels have significant effects on the proton transport rate in membranes. The hydrophilic sulfonic groups form isolated ionic clusters in the continuous hydrophobic regions due to the interaction.[25] The diameter of the channels formed by ionic clusters may be also reduced upon the introduction of Ppy particles. Both factors resulted in the methanol permeability decreasing. All these results suggest that the SPEEK/Ppy membranes are prospective to be used as the candidate in DMFCs.

CONCLUSION

In this article, SPAEKS/Ppy composite membranes were prepared by an *in situ* polymerization method. Compared with pure SPAEKS membrane, the thermal stability, water retention, and methanol permeability of membranes were improved after the introduction of Ppy. Although the proton conductivities of SPAEKS/Ppy composite membranes were slightly lower than that of SPAEKS membrane and decreased with the increment of Ppy content, the proton conductivities of all the SPAEKS/Ppy composite membranes were higher than 0.038 S/cm or more, which are still well positioned to meet the application requirements of DMFCs. The SPAEKS/Ppy composite membranes show good potential for the usage in DMFCs.

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