Preparation and properties of sulfonated poly(ether ether ketone)s (SPEEK)/polypyrrole composite membranes for direct methanol fuel cells

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Abstract

Polypyrrole (Ppy) was successfully introduced into methyl substituted sulfonated poly(ether ether ketone) (SPEEK) membranes by polymerization in SPEEK solutions to improve their methanol resistance. Uniform polypyrrole (Ppy) distributed composite membranes were formed by this method by the interaction between SPEEK and Ppy. The properties of the composite membranes were characterized in detail. The composite membranes show very good proton conductive capability ($25\,^\circ$C: 0.05–$0.06\,\mathrm{s\,cm^{-1}}$) and good methanol resistance ($25\,^\circ$C: 5.3×10^{-7}–$1.1 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$).The methanol diffusion coefficients of composite membranes are much lower than that of pure SPEEK membranes ($1.5 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$). The composite membranes show very good potential usage in direct methanol fuel cells (DMFCs).
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Keywords: SPEEK; Ppy; DMFC; Proton exchange membranes

1. Introduction

The direct methanol fuel cell (DMFC) is a type of fuel cell, 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 [1,2]. Some applications for DMFCs also include distributed power for both stationary and dynamic applications where they could replace batteries. Each application shares a common goal of high fuel efficiency, non-polluting by-products and economical proton exchange membranes. The proton exchange membrane material is a key component of the PEMFC for transferring protons from the anode to the cathode as well as providing a barrier to fuel crossover between the electrodes. The membranes traditionally used in a proton exchange membrane fuel cell (PEMFC) are perfluorosulfonic polymers, such as Nafion®. Although they show superior performance in fuel cells, their high cost and high methanol crossover make them impractical for large-scale production [3,4]. Therefore, alternative membrane materials such as sulfonated poly(aryl ether ketone)s (SPAEK) [5], sulfonated poly(aryl ether sulfone)s (SPAES) [6] and sulfonated poly(imide) (SPI) [7], etc. are being widely studied. In our previous work, SPAEK was developed for proton exchange membranes [8–10]. Although it showed relatively good properties for fuel cells, the brittleness of the membranes at elevated temperatures and the relatively high methanol permeability in the membranes with high sulfonation have limited their usage. For the DMFC, a high methanol permeability rate across the proton exchange membranes poses a critical problem in reducing the practical use of a DMFC. There have been many attempts to reduce the methanol permeability through the proton exchange membranes, which are: (1) modify the membranes' surface to block methanol transport, (2) control the size of the transport channels of protons, (3) explore new types of membrane materials, etc. Recently developed acid–base composite membranes were widely used to solve this problem. Especially the blend of sulfonated polymers with polymers

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containing amine groups was confirmed to be an efficient strategy to improve the mechanical and methanol crossover properties. In our previous work, polyaniline (PANI) was introduced into sulfonated poly(ether ether ketone ketone) (SPEEKK) membranes to solve this problem. Although the membranes showed good properties, the poor solubility of PANI has limited further research [11]. Polypyrrole (Ppy) nano-structured particles have received considerable attention as they have many potential applications in catalysis, chromatography and controlled release of drugs and in pigment applications. The Ppy/sulfonated polymers composite membranes were widely investigated due to the special interaction between the sulfonated acid groups and amine groups [12–16]. The interaction can lead to the following results [12,13]:

(1) The interaction will lead to the compatibility of the blending polymers. This will lead toreduction of swelling, improvement of mechanical properties and a further decrease in the methanol crossover of membranes.
(2) Mixing of acidic and basic molecules generally form a protonically conductive pathway. Blending with amine polymers will lead to the formation of proton transport channels from the protonated-amine groups to the sulfonated groups, when the membranes are hydrated.

Nafion/Ppy membranes prepared by Xu et al. showed some prospect for DMFC use [14]. They showed that the introduction of Ppy particles into Nafion membranes could efficiently decrease methanol permeability [14]. Later Pickup and co-workers did the similar work [15]. During the preparation of the composite membranes (the Ppy was introduced into Nafion by situ polymerization in Nafion membranes), the content of Ppy in the membranes cannot be efficiently controlled, due to the limitation of the monomer (pyrrole monomer) uptake by the membranes.

Although much work on the Ppy composite membranes was carried out, poor solubility of Ppy is still a great difficulty to overcome in the preparation of the composite membranes. In this paper, we will report on a new method to form uniformly distributed SPEEK/Ppy composite membranes to improve the methanol resistance of the membranes. In this method, we first make the pyrrole monomer uniformly dispersed in the SPEEK solutions by making use of the interaction between them. Further we obtain uniform Ppy distributed composite membranes by polymerization in the SPEEK solutions. This can efficiently control the Ppy content in SPEEK membranes. The purpose of introducing the Ppy particles into SPEEK membranes is to improve the methanol resistance of the SPEEK membranes with high sulfonation. The properties of the membranes is studied in detail.

2. Experimental

2.1. Materials and reagents

SPEEK polymers were prepared by direct aromatic nucleophilic substitution step polymerization. The detailed synthesis procedure and characterization of these copolymers were reported previously [8–10]. The ion exchange capacity (IEC) of SPEEK used in this paper is: 1.92 meq g^{-1}. The structure of SPEEK is shown in Scheme 1, which contains four methyl groups for each SPEEK unit.

2.2. The preparation of the composite membranes

The composite membranes were prepared by the polymerization of pyrrole monomer in SPEEK solutions. Firstly, a fixed weight ratio of pyrrole monomer and SPEEK polymers were dissolved in DMF solutions, stirred about 1 h, then 30 wt.% H$_2$O$_2$ (equal to the amount of the pyrrole monomer) was slowly added, stirred for another 4 h, the whole process was carried out at room temperature. The resulting solutions were then cast onto glass plates, dried at 80 °C for about 24 h, to obtain 50–100 μm thick membranes.

2.3. The characterization of membranes

TGA measurements were performed on NETZSCH STA449C under N$_2$ at a heating rate of 10 °C min^{-1}. FTIR and UV spectra were obtained by a Bruker Vector-22 FTIR spectrometer and a SHIMADZU-UV2501. All the measurements were carried out on the membranes.

The surface morphology of the composite membranes was observed by SEM (SHIMADZU SSX-550). The membranes were gold-coated prior to SEM measurements.

The water uptake (S_w) of the membranes was calculated by setting the weight difference between the dry and swollen membranes. The dried membranes were weighed (mass$_{dry}$) and then soaked in water until the weight remained constant. Then they were wiped with blotting paper. The weight (mass$_{wet}$) of the wet membranes was quickly weighed again. The water uptake of membranes (S_w) was calculated with formula (1):

$$S_w = \frac{mass_{wet} - mass_{dry}}{mass_{dry}} \times 100\% \tag{1}$$

The number of water molecules per sulfonic site (λ) can be determined by formula (2):

$$\lambda = \frac{mass_{wet} - mass_{dry}/M_{H_2O}}{IEC \cdot mass_{dry}} \tag{2}$$
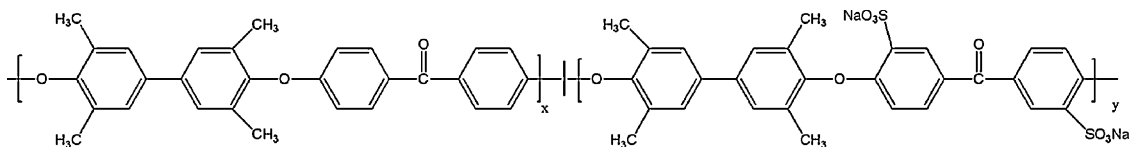
Scheme 1. The structure of SPEEK.

The ion exchange capacity (IEC) of the membranes was determined by titration at room temperature. The membranes in the acidic forms (H$^+$) were converted to the sodium forms by immersing the membranes in 1 M NaCl solutions for 24 h to exchange the H$^+$ ions for Na$^+$ ions. The exchanged H$^+$ ions within the solutions were titrated with 0.01N NaOH solutions.

The water desorption measurement was made by a Pyris 1TGA (Perkin-Elmer) at 80 °C and at constant pressure. The Pyris 1TGA was used to determine the weight changes of the samples with time.

The methanol diffusion coefficient was determined by using a cell basically consisting of two half-cells separated by the membrane, which was fixed between two rubber rings.

Methanol 1 M 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 a SHIMADU GC-8A chromatograph. Peak areas were converted into methanol concentration with a calibration curve. The methanol diffusion coefficient was calculated according to ref. [17]. The measurement of proton conductivity of the membranes was carried out by using a Philips 1260 impedance/gain-phase analyzer over a frequency range of 10 Hz–1 MHz. Conductivity measurement of fully hydrated membranes was carried out with the cell immersed in liquid water. The proton conductivity was determined with the test cell similar to the one employed by Zawodzinski et al. [18].

Cell performance was evaluated by using a DMFC unit cell, and the catalysts used at the anode and the cathode were Pt-Ru/C and Pt/C, respectively. The catalyst loadings at the anode and the cathode based on the catalyst weight were 2.5 mg cm^{-2}. Two molar methanol at the cathode, was supplied by a Masterflex liquid micro-pump at a rate of 0.082 L min^{-1}, while the cathode was fed with dry O$_2$ at a rate of 2 L min^{-1} via a flow meter. The cell temperature was kept at 70 °C.
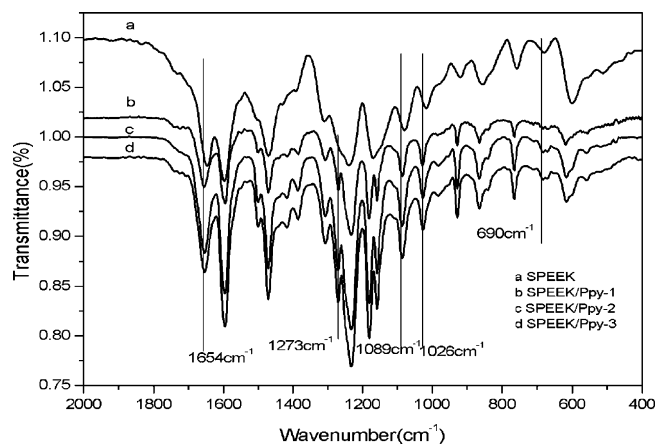

Fig. 1. The FTIR of composite membranes.

3. Results and discussion

3.1. Membrane preparation and characterization

The SPEEK/Ppy composite membranes were prepared by polymerization in SPEEK solutions (Scheme 2). Due to the interaction between the sulfonated acid groups in SPEEK and the amine groups in pyrrole monomers, the pyrrole monomers dispersed uniformly in the SPEEK solutions. After the oxidants were added to the solutions, Ppy was formed uniformly within the SPEEK solutions. The solutions were cast onto a glass plates to obtain the SPEEK/Ppy composite membranes. In this paper, the membranes obtained with different weight ratios of the pyrrole monomer to SPEEK (5, 10 and 15%), are named SPEEK/Ppy-1, SPEEK/Ppy-2 and SPEEK/Ppy-3, respectively. FTIR and UV spectra were performed on the composite membranes to confirm the expected structures of the composite membranes (Fig. 1). The C=C stretching of the benzene ring
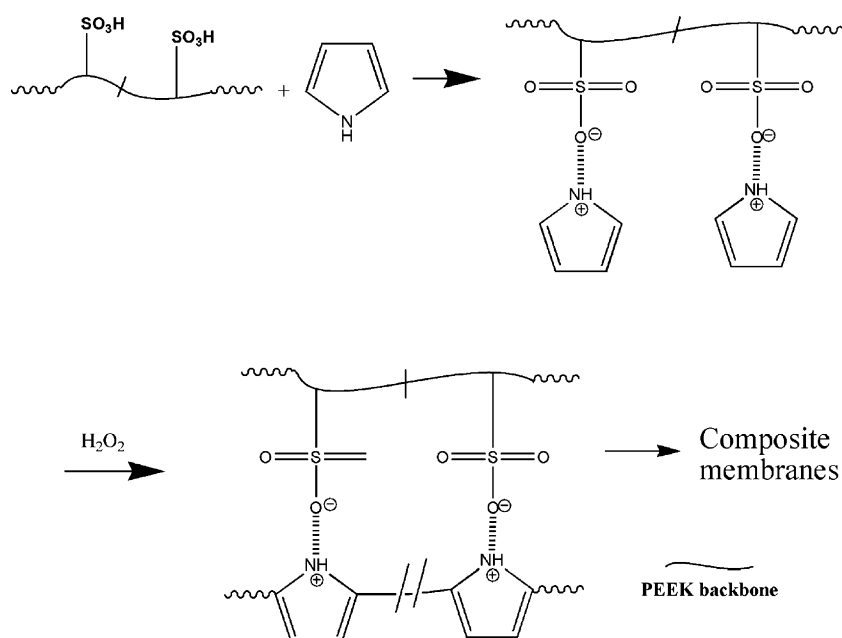
Scheme 2. The preparation of SPEEK/Ppy composite membranes.

appears at 1500–1400 cm^{-1}. The peaks at 1270 and 1654 cm^{-1} are induced by C−N and C=N stretching, respectively. As shown in SPEEK, there are no related stretchings with C−N and C=N groups. 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, which confirms the trend of the weight ratio of Ppy in SPEEK membranes. The absorption bands at 1089 and 1026 cm^{-1} in the composite membranes can be assigned to asymmetric and symmetric O=S=O stretching vibrations of the sulfonated groups. However, the related vibrations for the sulfonated groups in SPEEK are shown at 1080 and 1014 cm^{-1}. The absorption of the sulfonated groups in the SPEEK/Ppy composite membranes showed a blue shift compared to SPEEK. The blue shift is induced by the interaction between SPEEK and Ppy.

The UV–vis spectra of the SPEEKK/Ppy composite membranes are shown in Fig. 2. All the membranes show absorption peaks at 250–280, 360 and 500 nm. The absorptions at 250–280 and 360 nm correspond to the stretching of the benzene and pyrrole rings. The intense absorption at 500 nm may be due to the antibipolaron to bipolaron band transition of Ppy [19]. The FTIR and UV results show that we have successfully introduced the Ppy particles into SPEEK membranes.
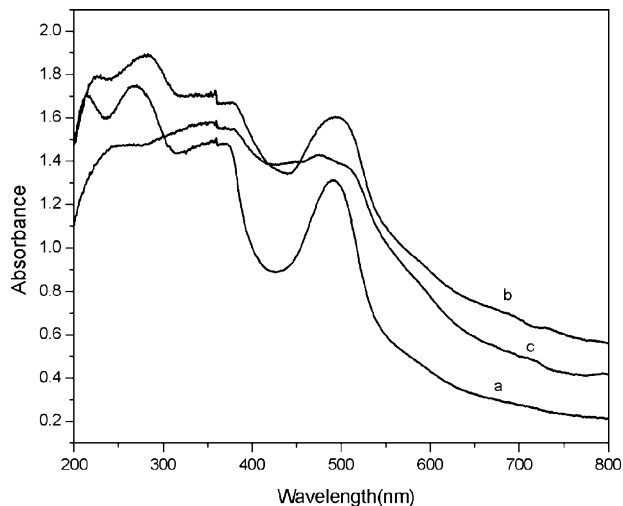

Fig. 2. The UV spectra of the SPEEKK/Ppy composite membranes. (a) SPEEK/Ppy-1, (b) SPEEK/Ppy-2 and (c) SPEEK/Ppy-3.

3.2. The morphology of the composite membranes

The distribution of the Ppy particles in the SPEEK membranes has a great influence on their transport properties.
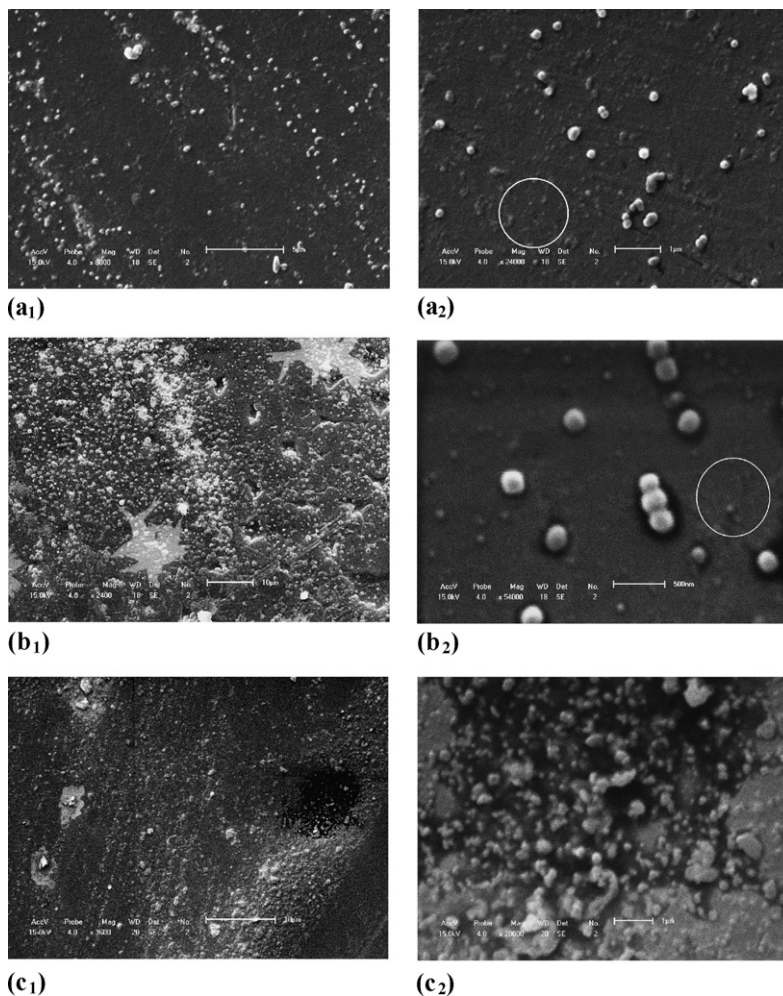

(a₁) (a₂) (b₁) (b₂) (c₁) (c₂)

Fig. 3. The SEM of composite membranes. (a) SPEEK/Ppy-1, (b) SPEEK/Ppy-2 and (c) SPEEK/Ppy-3.

Scanning electron microscopy (SEM) was performed to study the morphology of the composite membranes. As shown in Fig. 3, the nano-Ppy particles were dispersed in the SPEEK membranes very uniformly. The morphology of the Ppy particles is indicated to be nano-spheres. With the weight ratio of the pyrrole monomer increasing, the intensity of the Ppy particles in the SPEEK matrix increases. When the weight ratio of the pyrrole monomer is kept at 5 and 10% the Ppy particles were well distributed in theSPEEK matrix and seldom aggregated, however, the Ppy particles partially aggregated when the ratio reached 15%. The Ppy particles prepared by us distribute more uniformly in the SPEEK membranes than the ones prepared by the normal method. The interaction between the sulfonic acid groups and amine groups plays a very important role in the dispersion of the Ppy particles in the SPEEK matrix. As reported by Lee [20,21], this phenomenon might lead increase of the electrical conductivity and mechanical strength by inducing electrostatic interactions between Ppy and SPEEK. As shown in Fig. 3, the SPEEK matrix may be a continuous phase and the Ppy is the dispersed phase, the network of Ppy conducting granular aggregates in the SPEEK matrix is well formed [21,22]. In addition, we expect from the spheres that are on the surface that the regions that circles marked in Fig. 3(a_2 and b_2) show many Ppy spheres are embedded in the membranes. Note that all the membranes have been immersed in water for about 48 h before the SEM test, which indicates that the Ppy particles are stable in the SPEEK membranes under full hydrated conditions.

3.3. The thermal stability of membranes

Fig. 4 shows the TG curves of SPEEK and its composite membranes. All the curves show very similar profiles. They all contain two weight loss steps. The first one at about 250–300 °C is attributed to the splitting-off of the sulfonic acid groups of SPEEK. The second weight loss step at about 450 °C corresponds to the decomposition of the main polymer chain [5]. The membranes are all stable at about 300 °C, which is good enough for proton exchange membranes. Although the membranes show similar profiles of TG curves, the temperatures corresponding to the onset of thermal degradation and the slope of mass loss are different. Compared to the SPEEK membranes, the composite membranes have relatively high onset temperatures. In addition, SPEEK lost about 45 wt.% at 600 °C after thermal decomposition, while the SPEEK/Ppy composite membranes lost only about 30% at the same temperature. TGA results pro-
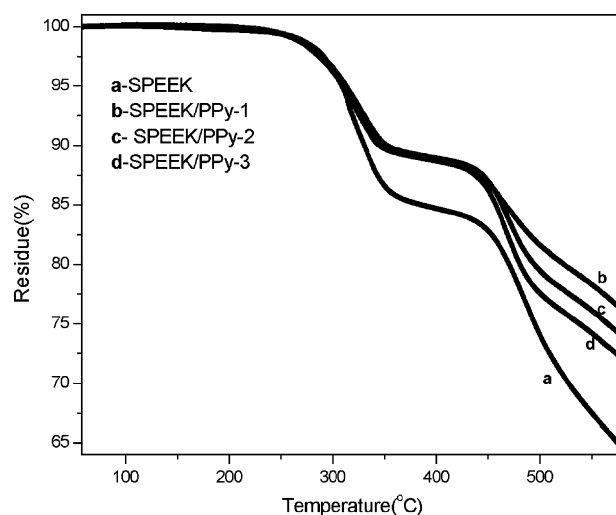

Fig. 4. The TGA curves of SPEEK and its composite membranes.

vide information about the changes in the thermal stability as a result of the incorporation of the Ppy particles into the clusters of SPEEK. The restriction of the cluster's mobility caused by the intermolecular interaction between SPEEK and Ppy seems to contribute the thermal stability of the composite membranes [17,26].

3.4. Water uptake, water desorption and IEC of composite membranes

Water uptake and IEC of SPEEK and its composite membranes are shown in Table 1. The water uptake of SPEEK/Ppy decreases drastically after the addition of Ppy particles into SPEEK. The water uptake of SPEEK is 44%, whereas, SPEEK/Ppy composite membranes show the water uptake of 31.1, 30.8 and 30.4%, respectively, with the weight content of Ppy increasing from 5 to 15%. Moreover, the IEC of the composite membranes shows a similar trend. This can be considered as the incorporation of nano-sized polypyrrole particles into the SPEEK matrix, resulting into the restricted mobility of the ionic clusters [17]. The interaction between the SPEEK and Ppy makes the structure of membranes more compact and partially sulfonated groups cannot participate in the proton exchange process. However, the number of water molecules per sulfonic site in Table 1 increases with the Ppy content increasing in composite membranes [26]. The interaction between the SPEEK

Table 1
The analytical data of SPEEK and its composite membranes

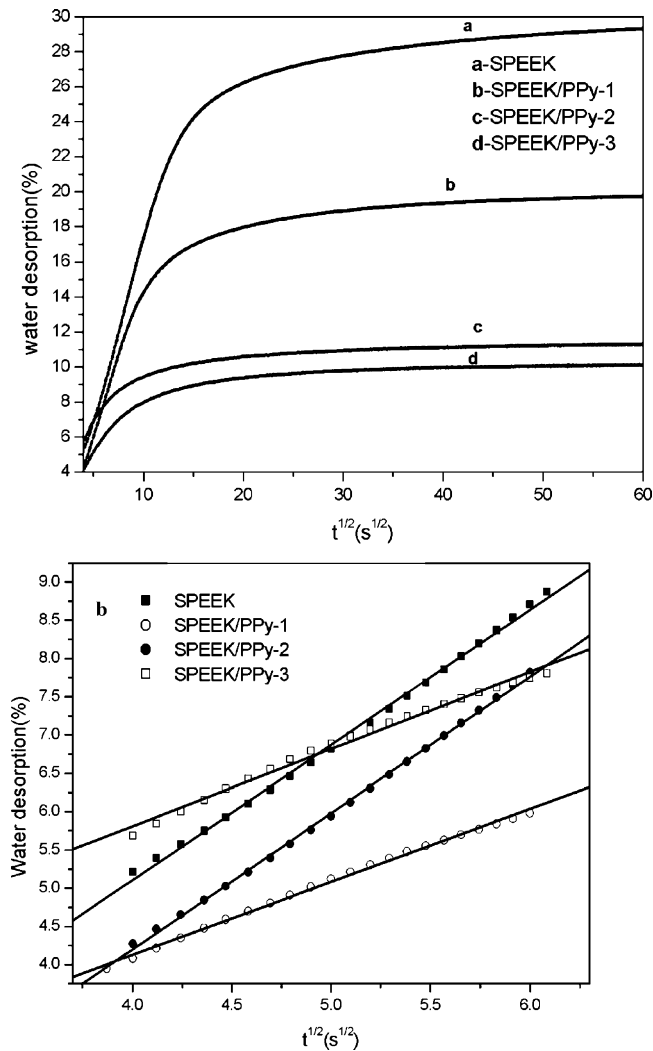|	SPEEK	SPEEK/Ppy-1	SPEEK/Ppy-2	SPEEK/Ppy-3
Water uptake (%)	44	31.1	30.8	30.4
IEC (meq)	1.92	1.19	1.15	1.11
λ (H_2O/SO_3^-)	12.7	14.5	14.8	15.2
Water diffusion coefficient($\times 10^{-9}\,m^2\,s^{-1}$)	5.4	2.23	0.67	0.32
Methanol diffusion coefficient($\times 10^{-7}\,cm^2\,s^{-1}$)	15.7	11.5	7.47	5.31
Conductivity (s cm^{-1}) at 25 °C	0.07	0.056	0.049	0.051
Conductivity (s cm^{-1}) at 80 °C	0.11	0.11	0.093	0.077

Fig. 5. The water desorption of SPEEK and its composite membranes.

and Ppy prevents partially sulfonated groups from absorbing water molecules. Water desorption isotherms of SPEEKK and its composite membranes are shown in Fig. 5. The relationship between the water desorption and time may follow Fick diffusion laws [23]. The desorption isotherm in Fig. 5a shows that water in composite membranes evaporates more slowly than SPEEKK membranes, which may result from the interaction between the SPEEK and Ppy. The line between the M_t/M_∞ and $t^{1/2}$ of SPEEKK is shown in Fig. 5b. The water diffusion of SPEEK and its composite membranes calculated from the slope of the line is 5.4×10^{-9}, 2.23×10^{-9}, 6.7×10^{-10} and 3.1×10^{-10} m^2 s^{-1}, respectively. From the results, the velocity of water volatilization decreases with increasing content of Ppy particles. In another words, the water retention of the composite membranes at relative high temperatures is improved by the introduction of the Ppy particles.

3.5. Methanol permeability and proton conductivity

Methanol permeability and proton conductivity are the two transport properties which determine the cell performance in a DMFC. A good performance needs high proton conductivity and low methanol permeability. The methanol permeability of SPEEK and its composite membranes is shown in Table 1. The methanol permeability of the composite membranes decreases dramatically compared to the SPEEK membranes. With the content of Ppy increasing, the methanol permeability decreases. The pure SPEEK membrane shows the methanol diffusion coefficient of 1.57×10^{-6} cm^2 s^{-1} at room temperature, whereas, the composite membranes, which contain 5, 10 and 15 wt.% of Ppy particles show the coefficient of 1.15×10^{-6}, 7.47×10^{-7} and 5.31×10^{-7} cm^2 s^{-1}, respectively. Usually the transport phenomenon through the membrane is influenced by kinetic and equilibrium factors. Porous membranes can be affected by kinetic factors rather than equilibrium factors. The transport properties of porous membranes are mainly influenced by bulk water in the pores [24]. SPEEK membranes, which are non-porous membranes, however, have different transport properties due to the compact and smooth surface without pores. In the same manner, the composite membranes also have dense structures due to the compatibility between the SPEEK matrix and Ppy. The interaction between the SPEEK and Ppy makes for more compact structures of the composite membranes, which will lead to low methanol permeability of membranes. The proton conductivity of SPEEK and its composite membranes at different temperatures is shown in Fig. 6. The proton conductivity of all the membranes was higher than 10^{-2} s cm^{-1}, which is the lowest value for practical interest in fuel cells. With the content of Ppy increasing, the proton conductivity of the membranes shows a contrary tendency. The decreasing of the proton conductivity is mainly influenced by the introduction of nano-sized Ppy particles into the SPEEK matrix. Traditionally proton exchange membranes usually contain two dominant regions: hydrophilic and hydrophobic ones. The hydrophobic domains formed by non-sulfonated polymer segments provide the hydrated PEMs with mechanical strength whereas the hydrophilic domains contain sulfonated groups which ensure proton conductivity. The
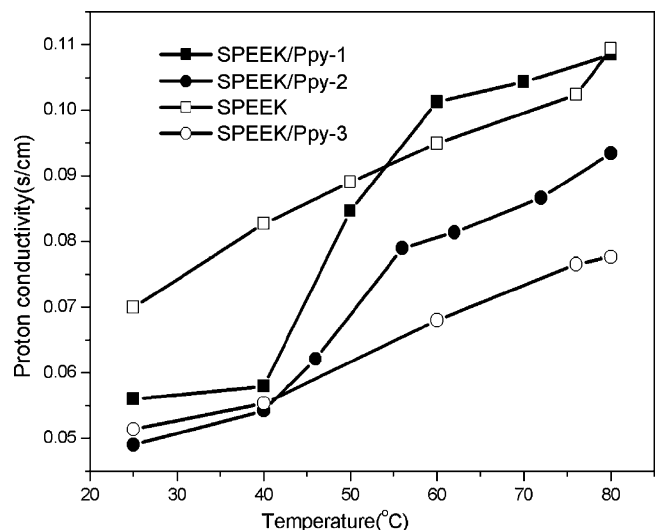

Fig. 6. The proton conductivity of SPEEK and its composite membranes at different temperatures.
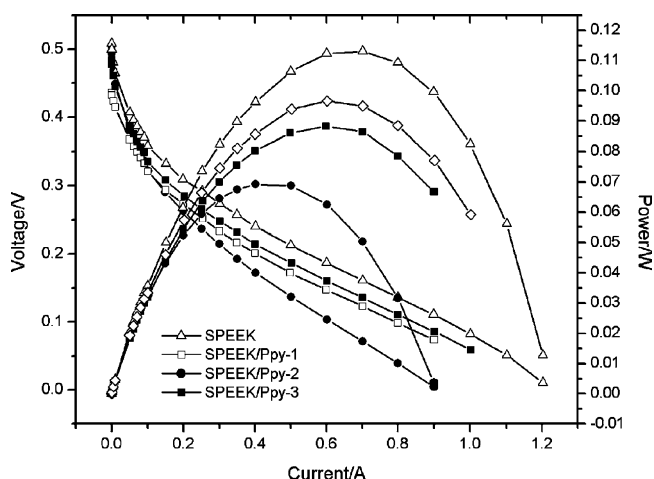
Fig. 7. Polarization curves of SPEEK and its composite membranes.

existence of the two regions may lead to a microphase-separated structure, which will determine the proton conductivity of the membranes [4]. The introduction of Ppy particles in SPEEK membranes will lead to more dense structures of membranes due to the interaction between them [26]. Compared to SPEEK membranes, the composite membranes show a less phase-separated structure. The mobility of the ionic clusters in the composite membranes will be more restricted, which will lead to a low proton conductive ability of the composite membranes. It is interesting to find that a SPEEK/Ppy-1 membrane shows similar even higher proton conductivity when the temperature exceeds 60 °C. This phenomenon may be explained by the interaction between the SPEEK and Ppy as well. The interaction can lead to effective proton-conducting pathways and a further increase in the membrane proton conductivity under fully hydrated conditions [25]. So in this system, there are two factors that influence the proton conductivity of the composite membranes. On the one hand, the introduction of the Ppy makes for a more compact membrane which will lead to decreased results and on the other hand, the interaction between the sulfonated acid groups and amine groups can form transport channels from the protonated-amine groups to the sulfonated groups, which will result in increased proton conductivity (Scheme 2). The two factors will determine the overall proton conductivity of the composite membranes.

3.6. Fuel cell performance of composite membranes

Fig. 7 shows the polarization curves of the SPEEK and its composite membranes. All the membranes show very good performance in DMFC cells. The cell performance of the SPEEKK membrane was a little better than its composite membranes. Among the composite membranes SPEEK/Ppy-3 showed the best performance. However, in the case of SPEEK/Ppy-1, the methanol permeability was higher than those of other composite membranes despite the comparable proton conductivity to SPEEK. As a result of that, SPEEK/Ppy-1 had the lowest cell performance. Because the polypyrrole particles in

the internal space acted as a resistance resulting in significant decrease in the proton conduction through the membrane. It is interesting to note that after the fuel cell performance experiment, SPEEK membranes show much more serious swelling than the composite membranes, despite the fact that they have a little better performance. We believe that the composite membranes will show a much longer life than SPEEK membranes.

4. Conclusion

SPEEK/Ppy composite membranes were expected to decrease the methanol permeability of SPEEK membranes with a high IEC. In this paper, we first introduced the Ppy particles into SPEEK solutions, then prepared SPEEK/Ppy composite membranes by solution casting. The results show a powerful way to obtain uniformly distributed SPEEK/Ppy membranes, which can control the content of Ppy very efficiently. The composite membranes show good proton conductivity, low methanol permeability and have good thermal stability. The composite membranes have good potential for use in DMFCs.

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