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ORIGINAL RESEARCH

Properties improvement of SPEEK based proton exchange membranes by doping of ionic liquids and Y_2O_3

Jianbin Chen[a], Qiang Guo[a,*], Dan Li[a], Juying Tong[a,b], Xia Li[a]

[a]*School of Materials Science and Engineering, Shanghai University, Shanghai 201800, China*
[b]*School of Wenling, Zhejiang TV University, Wenling 317500, China*

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Abstract The membranes of sulfonated poly(etheretherketone) with 65% sulfonation degree were prepared by doping of Y_2O_3 and ionic liquids, such as 1-ethyl-3-methylimidazole tetrafluoroborate (EB) or 1-butyl-3-methylimidazole methanesulfonate (BS), respectively. And the properties, including conductivities, water uptake, thermal stability and mechanical properties, of pure SPEEK based proton exchange membrane and SPEEK based proton exchange membranes by doping of ionic liquids and Y_2O_3 have been studied in the present investigation. The experimental results showed that the conductivity of membranes increased with the temperature increased from 30 to 90 °C, except for that of pure SPEEK membrane increased with increasing temperature from 30 to 70 °C and decreased with increasing temperature from 70 to 90 °C. The conductivities of SPEEK/EB/Y_2O_3 and SPEEK/BS/Y_2O_3 composite membranes at 90 °C were 9.04×10^{-2} S cm^{-1} and 1.18×10^{-1} S cm^{-1} at 100% relative humidity (RH) and 8.04×10^{-2} S cm^{-1} and 1.02×10^{-1} S cm^{-1} at 50%RH, respectively. It has been also found that the water uptake and thermal stability of the membranes slightly improved by doping of ionic liquids and Y_2O_3. The tensile stress at break at room temperature was 2.61 MPa and 2.33 MPa, for SPEEK/EB/Y_2O_3 and SPEEK/BS/Y_2O_3, respectively. Therefore it may be considered that the modification with ionic liquids and

*Corresponding author. Tel.: +86 21 699 82791.
E-mail address: guoq@shu.edu.cn (Q. Guo).

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Y_2O_3 is a good potential method for improving the properties of SPEEK proton exchange membrane.

1. Introduction

In the last decade, the growing attentions have been paid to sulfonated poly (etheretherketone) (SPEEK) membrane due to its good chemical stability and mechanical properties [1–3]. However, the conductivity of pure SPEEK proton exchange membrane decreases at high temperature and low humidity. In a previous work of author's group, the SPEEK/Y_2O_3 composite membranes had been prepared. The characteristic peaks of Y_2O_3 disappeared but a typical amorphous diffraction peak appeared in the X-ray diffraction patterns, which proved the coordination between yttrium cation of Y_2O_3 and oxygen anion of sulfonic groups, resulting in the change of the original crystal form. However, the neutralization occurred between Y_2O_3 and sulfonic groups in composite membrane, which decreased their proton conductivities [4]. Ionic liquids, particularly its unique excellent physical and chemical properties, are being extensively studied for a variety of applications in chemical reaction, electrochemistry, catalytic chemistry and separation and purification. The high molecular polymer doped with ionic liquids would have good proton conduction at higher temperature and anhydrous condition [5]. However, the ionic liquids would be run off easily in composite membranes. In this paper, the composite membranes based on SPEEK were prepared by doping with ionic liquids and Y_2O_3. The conductivities at 100%RH and 50%RH as well as water uptake, thermal stability and mechanical properties of the membranes has been studied in this investigation.

2. Experimental

2.1. Preparation of membranes

Poly (etheretherketone) (PEEK) was obtained from Chemistry Department of Jilin University (Jilin, China) in the form of particle, and SPEEK was prepared as reported earlier [6,7]. After SPEEK with DS (Degree of Sulfonated) of 65% was triturated, it was dissolved in dimethylacetamide offered by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), to make 10 wt% solution. Then the mixture was doped with 1-ethyl-3-methylimidazole tetrafluoroborate (EB) or 1-butyl-3-methylimidazole methanesulfonate (BS) offered by Shanghai Chengjie Chemical Co., Ltd. (Shanghai, China) and Y_2O_3 with a particle size of 100 nm, offered by Shanghai Huaming Gaona Rare Earth New Materials Co., Ltd. (Shanghai, China), then stirred at room temperature for 4 h, followed by at 75 °C for 6 h. The composite membranes were obtained by casting their viscous solution onto a glass plate. The thickness of dried membranes was about 100 μm. Contents of membranes were described in Table 1.

2.2. Structure analysis of membranes

The structure of the membranes was analyzed by Fourier Transform Infrared (FTIR) spectra method, and the FTIR spectra of the membrane specimens was recorded with a AVATAR370 infrared spectrometer (Thermo Nicolet Instrument Co., USA), using the thin membrane specimens in the scanning range of 600–4000 cm^{-1}.

2.3. Proton conductivity measurement

The proton conductivity of membrane specimens in the traverse direction was measured in a measurement cell using AC Electrochemical Impedance Spectroscopy (EIS), which was composed of a Solartron Instruments 1287 electrochemical interface and a Solartron Instruments 1255B frequency response analyzer (Farnborough, UK), both of which were interfaced via GPIB to a computer [6–8]. The EIS recorded over a frequency range of 1–10^6 Hz. The amplitude of the sinusoidal modulation voltage was 10 mV, and the testing temperature ranged was from 30 °C to 90 °C and the relative humidity was 50% and 100%, respectively. Before the test, all membrane specimens were soaked in 1 mol L^{-1} hydrochloric acid solution for 4 h, and then rinsed for several times with de-ionized water. The resistance of the membranes was measured and the proton conductivity was calculated as described in detail in the references of 6, 7 and 8.

2.4. Tests of water uptake

The water uptake (S_w) of the membrane specimens was calculated by measuring the mass difference between the dry and hydrous membrane specimens [6–8]. The dried membrane specimens at 90 °C for 24 h were weighed (m_{dry}) and then immersed in deionized water for 24 h. Then the membranes were wiped with blotting paper to remove the surface water and quickly weighed (m_{wet}) again. The S_w was calculated using equation $S_w=(m_{wet}-m_{dry})/m_{dry}\times 100\%$, where m_{dry} was the mass of dry membrane, m_{wet} was the mass of membrane after immersion in deionized water.

2.5. Measurements of thermal and mechanical properties

The thermal stability of membranes was evaluated by recording thermo-gravimetric (TG) traces in nitrogen atmosphere

Table 1 Contents of composite membrane specimens.

Specimen	SPEEK (wt%)	Ionic liquids (wt%)		Y_2O_3 (wt%)
		EB	BS	
SPEEK	100	0	0	0
SPEEK/EB/Y_2O_3	94	5	0	1
SPEEK/BS/Y_2O_3	94	0	5	1
SPEEK/EB	95	5	0	0
SPEEK/BS	95	0	5	0

(Q500, TA Company, USA). The heating rate was 10 °C min^{-1}, the temperature ranged from 50 °C to 400 °C, and the specimen mass of 5±2 mg in the membrane form was used for recording TG traces. The mechanical property of hydrated membranes was measured with a tensile strength instrument DXLL-20000 (Shanghai, China) at room temperature.

3. Results and discussion

3.1. Structures analysis

Fig. 1 illustrates FTIR spectra of SPEEK/EB/Y_2O_3, SPEEK/BS/Y_2O_3, SPEEK/EB, SPEEK/BS and SPEEK specimens. The absorption peaks appeared at 1188 cm^{-1} and 1643 cm^{-1} corresponded to the groups of –Ar–O–Ar– and –Ar–C(=O)–Ar–, indicating that the structure of ether ketone appeared in specimens. The absorption peak of benzene ring at 1472 cm^{-1} was observed. The O=S=O band at 1224 cm^{-1} was the asymmetric stretching vibration peak, however, its symmetric stretching vibration peak at 1083 cm^{-1} disappeared in SPEEK/EB and SPEEK/BS, which may be influenced by hydrogen band of EB and BS themselves, EB and sulfonic groups or BS and sulfonic groups, respectively. The S=O stretching absorption peak at 1023 cm^{-1} was observed in specimens except for SPEEK/BS, which proved that the interaction occurred probably between BS and sulfonic groups. However, only a weak absorption at 1159 cm^{-1} was observed in the spectrum of SPEEK/BS/Y_2O_3. The peak at 1159 cm^{-1} disappeared in SPEEK/EB/Y_2O_3, due to the interaction between the sulfonic acid groups and the cations of the ionic liquids. The peak at 1595 cm^{-1} was denoted the stretching vibration of C=N in imidazole rings. Simultaneously, the broadband between 2900 cm^{-1} and 3400 cm^{-1} corresponding to the C–H stretching vibration of imidazole ring in specimens with containing EB and BS were observed, as shown in Fig. 1.

3.2. Proton conductivity of membranes

Fig. 2 shows the conductivities of SPEEK/BS/Y_2O_3, SPEEK/EB/Y_2O_3 composite membranes and pure SPEEK membrane at the RH of 100% and in the temperature range of 30 °C to 90 °C. It has been observed that the conductivity of the composite membranes increased with the temperature from 30 °C to 90 °C, while the conductivity of the pure SPEEK membrane increased with the temperature from 30 °C to 70 °C, decreased from 70 °C to 90 °C. Both SPEEK/BS/Y_2O_3 and SPEEK/EB/Y_2O_3 composite membranes had higher conductivities than pure SPEEK membrane, their values all exceeded 10^{-2} S cm^{-1}, which was the practical interest value in fuel cell [9]. The experimental results also showed that when temperature increased to 90 °C, the conductivity of maximizing was occurred in composite membranes, for example, SPEEK/BS/Y_2O_3 was 1.18×10^{-1} S cm^{-1} and SPEEK/EB/Y_2O_3 was 9.04×10^{-2} S cm^{-1}, respectively. However, the conductivity of pure SPEEK was only 1.06×10^{-2} S cm^{-1} at 90 °C, and its conductivity of maximizing was 1.83×10^{-2} S cm^{-1} at 70 °C.

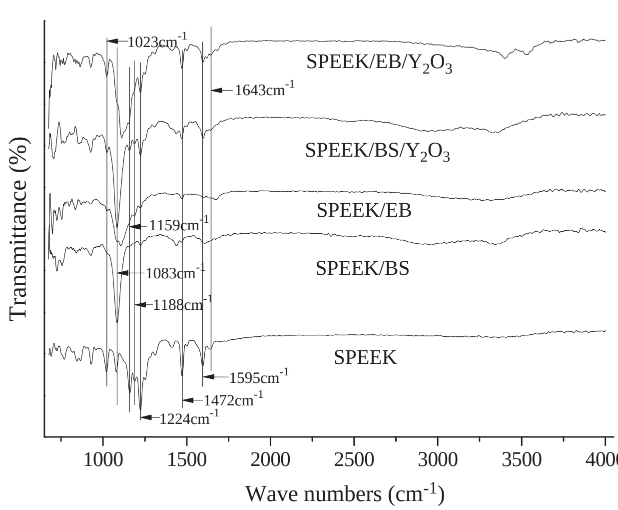

Fig. 1 FTIR spectra of specimens.

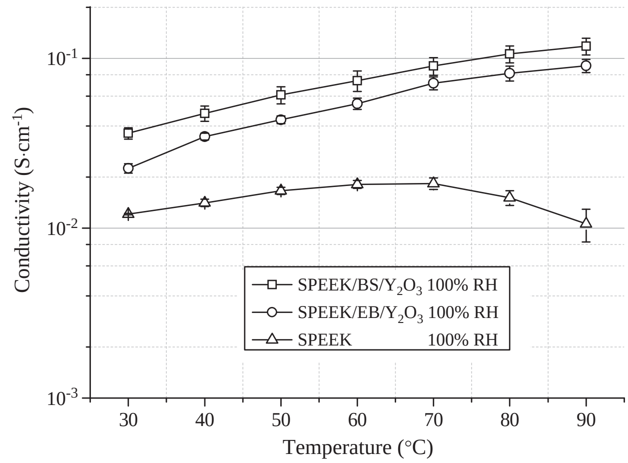

Fig. 2 Conductivity of specimens at 100%RH vs. temperature.

Fig. 3 shows the conductivities of SPEEK/BS/Y_2O_3, SPEEK/EB/Y_2O_3 composite membranes and pure SPEEK membrane at 50% RH from 30 °C to 90 °C. It can be seen that the conductivity of composite membrane increased with temperature from 30 °C to 90 °C, while the conductivity of pure SPEEK membrane increased with temperature from 30 °C to 60 °C, decreased from 60 °C to 90 °C. Both SPEEK/BS/Y_2O_3 and SPEEK/EB/Y_2O_3 composite membranes had higher conductivities than pure SPEEK membrane. And the maximum conductivity occurred in composite membranes at 90 °C, such as for SPEEK/BS/Y_2O_3 it was 1.02×10^{-1} S cm^{-1} and for SPEEK/EB/Y_2O_3 it was 8.04×10^{-2} S cm^{-1}. However, the conductivity of pure SPEEK was only 3.59×10^{-3} S cm^{-1} at 90 °C, its maximum conductivity was 5.35×10^{-3} S cm^{-1} at 60 °C.

There are two ways for proton transportation: one is hydrophilic sulfonic groups accompanied by the formation of H_3O^+ or $H_5O_2{}^+$ by the reaction of hydration in the hydrophilic regions, or anion of ionic liquids, and the other is hopping between the adjacent hydrophilic sulfonic groups by H^+ activity. At low temperature, the hydrophilic groups attracting the water molecules formed micro-aqueous regions after membrane hydration, and hence increasing the size of hydrophilic regions, shorting the 'effective distance' between sulfonic groups, and facilitating the proton transfer in two ways. At the same time, the ionic liquids participated with proton transportation. As a result, the composite membranes had higher conductivities at 100% RH or 50%RH, and the pure SPEEK membrane also had higher conductivity at 100%RH but lower one at 50%RH. With the temperature increased, the water molecules evaporated further, reducing hydrophilic regions in which proton transferred with H_3O^+ or $H_5O_2{}^+$ formation. On the other hand, the mobility of proton was enhanced, accelerating the hop in adjacent sulfonic groups. While the ionic liquids were enhanced, accelerating transportation of proton as ion-pair with anion of ionic liquids. Therefore, the composite membranes had higher conductivities at 50%RH and 100%RH, but the pure SPEEK had lower conductivities, especially at 50%RH, due to the important role of ionic liquids in proton transportation.

3.3. *Water uptake and mechanical property of membranes*

As shown in Table 2, the water uptake of membrane specimens increased with rising temperature. The water uptake of composite membranes were lower than that of pure SPEEK membrane, which demonstrated that the coordination or neutralization of acid–base occurred among sulfonic acid groups, ionic liquids and Y_2O_3, leading to the fewer amount of sulfonic groups. However, the proton conductivities of the composite membrane specimens were higher than that of pure SPEEK membrane specimen, indicating that the ionic liquids played an important role for proton transportation, and reduced the dependence on the water molecule. Otherwise, the SPEEK/EB/Y_2O_3 had lower water uptake, but still owned higher conductivity, which indicated the EB participating proton transportation.

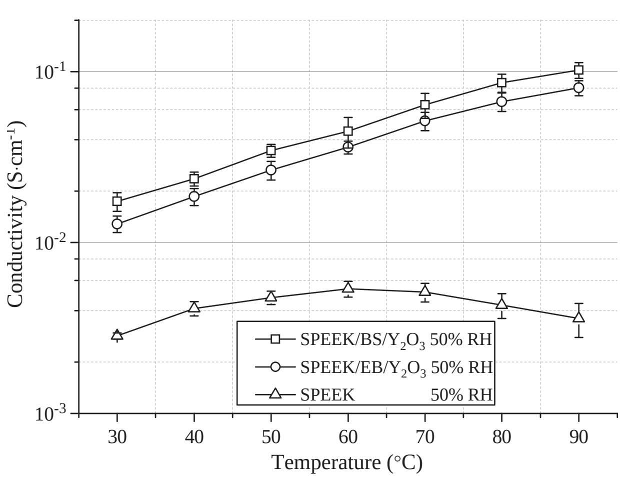

Fig. 3 Conductivity of specimens at 50%RH vs. temperature.

The mechanical properties of specimens were also shown in Table 2. It can be found that the SPEEK/EB/Y_2O_3 had higher tensile strength and elongation at break, which showed that the composite membrane had better strength and flexibility. The SPEEK/BS/Y_2O_3 had higher tensile strength and lower elongation at break, which may be attributed to the reaction of the molecule force between BS and sulfonic groups, and the coordination between Y_2O_3 and sulfonic groups. The strong electrostatic force of EB or BS and sulfonic acid groups restricted the stretch of backbone and hindered the strain during extension. This attractive result implied that the flexibility of composite membranes was greatly influenced by the added ionic liquids and Y_2O_3. Also, the steric hindrance caused by SPEEK/BS/Y_2O_3 specimen was smaller than that of SPEEK/EB/Y_2O_3 specimen, which made molecular chains shift easier, increasing the flexibility of membrane specimen. Furthermore, the strong interactions of EB and Y_2O_3 in specimens induced the interactions between molecular chains, resulting in the increase of tensile strength. These tensile strengths showed enough intensity for fuel cell application. The SPEEK membrane was lower tensile strength and higher elongation at break, indicating that the pure SPEEK membrane had higher flexibility, which is considered to be attributable to the reaction of hydrogen bonds.

3.4. *Thermal stability of membranes*

The results of the thermal stabilities behavior of pure SPEEK and composite membranes were shown in Fig. 4. A discrete two steps degradation profile was observed for the specimens. The first mass loss occurred near the temperature of about 100 °C, which was mainly attributed to the evaporation of water and solvent [10]. The second stage degradation occurred in temperature range of 250–350 °C [11–13]. It has been found that both the decomposition temperature of the SPEEK/EB/Y_2O_3 and SPEEK/BS/Y_2O_3 specimens was about 50 °C higher than that of the SPEEK specimen. Apparently, the interaction between sulfonic groups and EB or BS ionic liquids promoted the thermal stability of the composite membrane. The SPEEK/EB/Y_2O_3 and SPEEK/BS/Y_2O_3 specimens showed the promise for the use of proton exchange membrane.

4. Conclusions

(1) The composite membranes modified with EB or BS ionic liquids and Y_2O_3 showed higher conductivities than pure SPEEK membrane. The conductivities of SPEEK/EB/Y_2O_3

Table 2 Water uptake and mechanical properties of specimens.

Specimen	Water uptake (wt%)				Tensile strength (MPa)	Elongation at break (%)
	30 °C	50 °C	70 °C	90 °C		
SPEEK	41.30	43.91	48.44	65.62	1.94	90.09
SPEEK/EB/Y_2O_3	12.37	18.51	26.38	35.47	2.61	84.75
SPEEK/BS/Y_2O_3	22.38	25.45	40.01	55.19	2.33	15.86

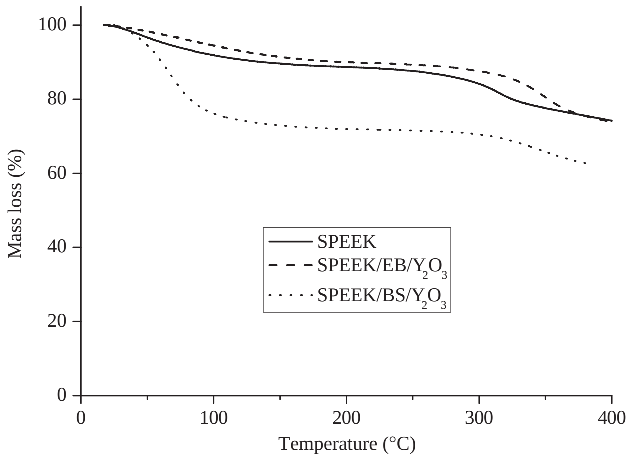

Fig. 4 TGA of membrane specimens.

and SPEEK/BS/Y_2O_3 composite membranes at 90 °C were 9.04×10^{-2} S cm^{-1} and 1.18×10^{-1} S cm^{-1} at 100%RH and 8.04×10^{-2} S cm^{-1} and 1.02×10^{-1} S cm^{-1} at 50%RH, respectively. The water uptake property was slightly improved when containing the ionic liquids and Y_2O_3. The water uptake of composite membrane specimens was lower than that of pure SPEEK membrane specimen.

(2) The composite membranes possessed higher tensile strength but lower elongation at break. The tensile strength of SPEEK/EB/Y_2O_3 specimen was the strongest among all the specimens, but the SPEEK specimen was the lowest tensile strength, while the elongation at break was the highest.

(3) The thermal stability of composite membranes modified with ionic liquids and Y_2O_3 slightly increased. Both the decomposition temperature of the SPEEK/EB/Y_2O_3 and SPEEK/BS/Y_2O_3 specimens was about 50 °C higher than that of the pure SPEEK specimen.

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