Sulfonated poly(ether ether ketone)/polybenzimidazole oligomer/epoxy resin composite membranes *in situ* polymerization for direct methanol fuel cell usages

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ABSTRACT

A diamine-terminated polybenzimidazole oligomer (o-PBI) has been synthesized for introducing the benzimidazole groups (BI) into sulfonated poly(ether ether ketone) (SPEEK) membranes. SPEEK/o-PBI/4,4′-diglycidyl(3,3′,5,5′-tetramethylbiphenyl) epoxy resin (TMBP) composite membranes *in situ* polymerization has been prepared for the purpose of improving the performance of SPEEK with high ion-exchange capacities (IEC) for the usage in the direct methanol fuel cells (DMFCs). The composite membranes with three-dimensional network structure are obtained through a cross-linking reaction between PBI oligomer and TMBP and the acid–base interaction between sulfonic acid groups and benzimidazole groups. Resulting membranes show a significantly increasing of all of the properties, such as high proton conductivity (0.14 S cm^{-1} at 80 °C), low methanol permeability (2.38 × 10^{-8} cm^2 s^{-1}), low water uptake (25.66% at 80 °C) and swelling ratio (4.11% at 80 °C), strong thermal and oxidative stability, and mechanical properties. Higher selectivity has been found for the composite membranes in comparison with SPEEK. Therefore, the SPEEK/o-PBI/TMBP composite membranes show a good potential in DMFCs usages.

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1. Introduction

Direct methanol fuel cells (DMFCs), which can convert chemical energy into electrical power directly, are promising and environmentally friendly energy production devices alternative to the fossil fuel combustion [1,2]. As the heart of DMFCs, proton exchange membrane (PEM) transfers protons from anode to cathode and separate the fuel and the oxidant [3,4]. Nowadays, the most common and promising PEMs materials are perfluorosulfonic acid polymers, such as Nafion (DuPont). However, some drawbacks of Nafion limit their further commercial application, such as expensive cost, strongly dependence on their hydration degree, high methanol permeability, and poor thermomechanical properties [5].

Recently, a lot of work has been focused on the fabrication of novel alternative PEMs based on sulfonated aromatic polymers, due to their well-known high thermal and chemical stabilities and excellent mechanical properties as well as low cost and easily functionalized [6–11]. However, PEMs based on these polymers only reach sufficient proton conductivity at high degree of sulfonation which usually lead to a high water uptake and water swelling, inadequate mechanical properties as well as high methanol permeability, which render the membranes unsuitable for the DMFCs [12,13]. To overcome these issues, several methods have been explored to improve the proton conductivity without sacrificing stability, such as introducing inorganic fillers [14–17], preparing acid–base composite membranes [18,19] and preparing cross-linked membranes [20,21].

The acid-based composite membranes based on sulfonated aromatic polymers and imidazoles or benzimidazoles have been studied recently [22,23]. These composite membranes are also referred to as ionic cross-linked membrane due to the acid–base interaction between sulfonic acid groups and benzimidazole groups. However, the basic groups may easily leach out of these the membranes in liquid water during the operation in fuel cells. In our previous work, we reported the introduction of benzimidazole groups into SPEEK by cross-linking, which used a benzimidazole trimer as the cross-linker. It also limited excess water uptake and methanol crossover and improved the stability and mechanical properties of the membranes [18].

In this study, we report a new acid-based composite membrane with *in situ* polymerization between PBI oligomer and TMBP in SPEEK membrane which formed a semi-interpenetrating polymer network [24]. The aim of this study is to investigate how the *in situ* method of introducing the PBI into the SPEEK could influence the

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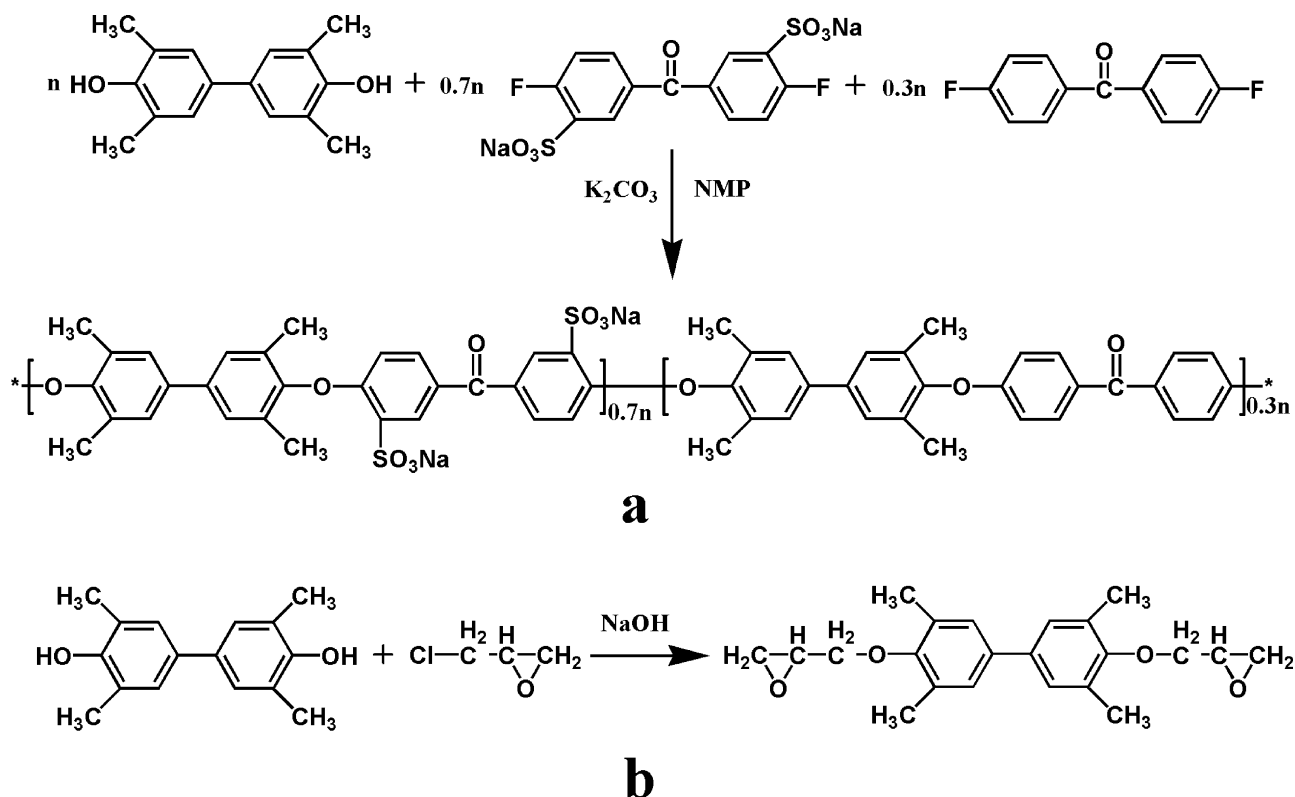
Scheme 1. The preparation and the chemical structure of SPEEK and TMBP.

performance of membranes. The three-dimensional network structure has been made through a cross-linking reaction between PBI oligomer and TMBP and the acid–base interaction between sulfonic acid groups and benzimidazole groups. Other properties were investigated, such as water uptake, mechanical performance. The properties of the resulting membranes much improved. And the *in situ* polymerization was shown efficient for the DMFCs membranes.

## 2. Experiment

2.1. Materials

Monomers 3,3′-diaminobenzidine (DAB) and diphenyl-*m*-phthalate (DPIP) were purchased from Sigma–Aldrich. All the other chemicals were obtained commercially and used without further purification.

2.2. Synthesis of SPEEK and TMBP

Sulfonated poly(ether ether ketone) (SPEEK) [25] with sulfonation degree (SD) of 1.4 and the 4,4′-diglycidyl(3,3′,5,5′-tetramethylbiphenyl) epoxy resin (TMBP) [26] with the epoxy equivalent of 177 were synthesized according to our previous report. Their preparation and chemical structure were shown in Scheme 1.

2.3. Synthesis of diamine-terminated polybenzimidazole oligomer

The synthetic procedure of the diamine-terminated PBI oligomer (o-PBI) is shown in Scheme 2. It was synthesized via the melt polymerization [27] and described as follows: DAB (11.44 g, 53.4 mmol) and DPIP (15.93 g, 50 mmol) were added to a three-neck resin reaction flask, which was equipped with a mechanical overhead stirrer and a nitrogen inlet and outlet. The reaction flask
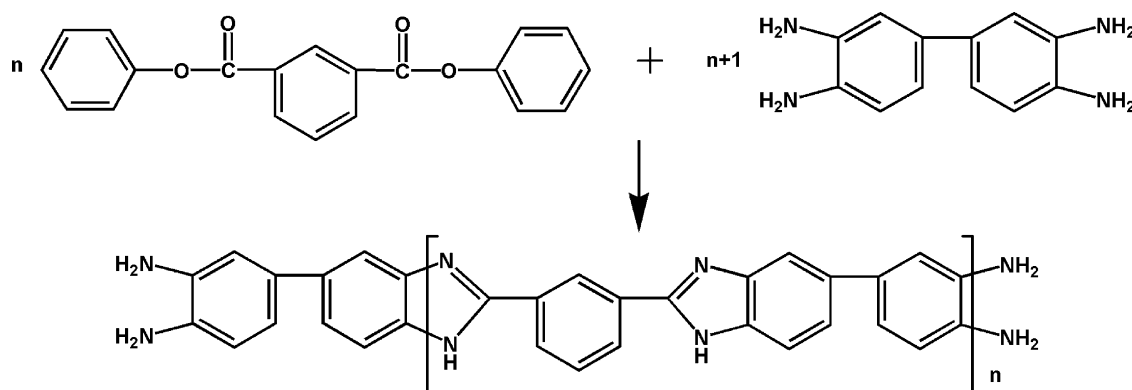
Scheme 2. The synthesis of the *o*-diamino-terminated polybenzimidazole oligomer.

was slowly heated in an oil bath in a nitrogen atmosphere to the melting point of the reaction mixture. Stirring was stopped when the reaction mixture was too hard to stir. The reaction temperature was held at 270 °C for 1–3 h. The reaction mixture was removed and pulverized to powder. And then the powder was reacted at 340 °C for 1–3 h and PBI oligomer was synthesized.

2.4. Composite membrane preparation

The SPEEK and the SPEEK/o-PBI/TMBP-X composite membranes (X is the content of all the o-PBI and TMBP in the composite membranes by weight percent) were prepared by solution casting and evaporation method. For the composite membranes, the o-PBI was first dissolved in 1-methyl-2-pyrrolidinone (NMP) by heating to prepare a solution. And then the SPEEK and TMBP was dissolved in the above solution to afford amass fraction of 10 g ml^{-1} solution (the requisite ratio of TMBP and o-PBI monomers was 4:1). Cast this final solution onto a glass plate followed by drying at 60 °C for 10 h and drying in a vacuum oven at 80 °C for 24 h, then heating at 120 °C for 4 h for thermal activation of the cross-linking reaction between TMBP and o-PBI. Each membrane (40–60 μm) was peeled off from the glass plate with deionized water. The membranes in acidic form were obtained by immersing into a 2 M HCl solution for 24 h, and then the membranes were washed with deionized water until the pH reached 6–7.

2.5. Characterization

The ^{1}H NMR spectra were collected on a Bruker 510 spectrometer (^{1}H, 500 MHz) at 25 °C with deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent and tetramethylsilane (TMS) as the standard. FT-IR spectra were recorded on a Nicolet Impact 410 Fourier transform infrared spectrometer using KBr disc and measuring in the range of 4000–400 cm^{-1}.

2.5.1. Thermal stability of the composite membranes

The thermogravimetric analysis (TGA) measurements of the composite membranes were determined by Perkin-Elmer TGA. Before testing, all the membrane samples were preheated to 120 °C and kept at this temperature for 15 min to remove any residual solvent or moisture. Then the samples were cooled to 100 °C and reheated to 800 °C with a temperature ramp of 10 °C min^{-1} under N$_2$ flow.

2.5.2. Ion-exchange capacity (IEC)

Titration technique was used to determine the IEC of the membranes. The membranes were equilibrated in a NaCl (2.0 M) aqueous solution for 48 h to exchange the protons with sodium ions. Then the amount of H$^+$ released from the membranes was determined by titrating with a standard NaOH solution (0.01 M) using phenolphthalein as the indicator. The titrated IEC (meq g^{-1}) of the membranes can be calculated from:

$$IEC_{titrated} = \frac{consumed\ NaOH(ml) \times molarity\ of\ NaOH}{weight\ of\ dried\ membrane} \quad (meq\ g^{-1}) \tag{1}$$

The theoretical IEC of SPEEK calculated from Ds was determined by:

$$IEC_{SPEEK} = \frac{1000D_S}{420.5 + 80\ D_S} \quad (meq\ g^{-1}) \tag{2}$$

where D_S is 1.4.

The theoretical IEC of composite membranes were calculated from the theoretical IEC of SPEEK, the available basic sites (ABS$_{BI}$)

per gram of the o-PBI, and the weight percentage of the two polymers in the composite according to [28]:

$$IEC_{calculated} = \%_{SPEEK}(IEC_{SPEEK}) - \%_{o-PBI}(ABS_{BI}) \quad (meq\ g^{-1}) \tag{3}$$

where ABS$_{BI}$ is given by:

$$ABS_{BI} = \frac{(2n + 8) \times 1000}{M_{o-PBI}} \quad (meq\ g^{-1}) \tag{4}$$

where n (15.6) is the average number of repeat unit of o-PBI, M$_{o-PBI}$ (5024 g mol^{-1}) is the molecular weights of o-PBI.

2.5.3. Mechanical properties of the composite membranes

Mechanical properties of the membranes were measured by SHMADZU AG-I 1KN at a speed of 2 mm min^{-1} in both the dry and wet state at room temperature. For measurement in the dry state, membranes were dried at 120 °C for 12 h in a vacuum before the test, and for measurement in the wet state, membranes were immersed in the deionized water for 24 h before the test. Membrane specimens of 15 mm × 4 mm were placed between the grips of the testing machine. Each sample was tested for at least four times to reach an average value.

2.5.4. Water uptake (WU) and swelling ratio

The water uptake (WU) and swelling ratio (SR) of the membranes were determined by measuring the weight and dimensional differences between the fully hydrated and dried membranes. The WU and SR of the membranes were calculated from:

$$Water\ uptake(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{5}$$

$$Swelling\ ratio(\%) = \frac{L_{wet} - L_{wet}}{L_{dry}} \times 100 \tag{6}$$

where W_{wet} and W_{dry} are the weights of wet and dry membranes, L_{wet} and L_{dry} are the length (or thickness) of wet and dry membranes, respectively.

2.5.5. Oxidative stability

The oxidative stability was investigated by soaking small pieces of membranes into Fenton's reagent (3 wt% H$_2$O$_2$ aqueous solution containing 2 ppm FeSO$_4$) at 80 °C. The oxidative stability was characterized by observing the expended time that the membranes started to become broken and disappeared in the solution and recoding the degradation of the membranes by weight loss after 1 h.

2.5.6. Proton conductivity

The proton conductivity was measured by a four-electrode ac impedance method from 0.1 Hz to 100 kHz, 10 mV ac perturbation and 0.0 V dc rest voltage at 25, 40, 60 and 80 °C using a Princeton Applied Research Model 2273A Potentiostat (Model 5210 frequency response detector, EG&GPARC, Princeton, NJ). The membranes were cut into 1 cm wide and 4 cm long pieces and were fixed in a measuring cell made of two outer gold wires (A and D) to feed current to the sample and two inner gold wires (B and C) to measure the voltage drop. The cell is shown in Fig. 1. All the membranes were mounted between two polytetrafluoroethylene (PTFE) plates. The humidity was kept at 100% during the measurement by immersing the cell in liquid water at desired temperature. The proton conductivity was calculated from:

$$\sigma = \frac{L}{R \times A} \tag{7}$$

where σ is the proton conductivity in S cm^{-1}, L is the distance between the two electrodes, R is resistance of the membrane, and A is the cross-sectional area of the membrane.

2.5.7. Methanol permeability

The methanol permeability was measured in an isothermal bath at 25 °C using a two-chamber diffusion cell method with a 10 M methanol solution. A detailed procedure was reported previously [6]. The concentration of the methanol in the water cell was determined by using a Shimadzu GC-8A chromatograph. Methanol permeability was calculated from:

$$C_B(t) = \frac{A}{V_B} \frac{D_K}{L} C_A(t - t_0) \qquad (8)$$

where C_A and C_B (mol l^{-1}) are the methanol concentrations methanol chamber and water chamber, respectively; A (cm^2) and L (cm) are the effective area and thickness of the membranes, respectively; V_B (cm^3) is the volume of the chamber; $(t - t_0)$ (s) is the test time; and D_K (cm^2 s^{-1}) is the methanol permeability.

3. Results and discussion

3.1. Synthesis and characterization of PBI oligomer

As shown in Scheme 2, the *o*-diamino-terminated polybenzimidazole oligomers (o-PBI) was synthesized via a two-steps melt polymerization. The monomer stoichiometry was offset to ensure the diamine end-group functionality and control the molecular weight (Mn). The structure and precise number-average molecular weight of o-PBI was determined from the ^{1}H NMR spectrum [29]. As shown in Fig. 1, the peaks ranging from 6.5 to 7.0 ppm and from 7.4 to 9.2 ppm were related to the protons on the *o*-diamino benzene moieties and the proton on the non-end-group aromatic groups. The peaks ranging from 13.0 to 13.3 ppm and from 4.4 to 4.6 ppm were assigned to the amine protons on benzimidazole moieties and the diamine protons, respectively. By comparing the intensity of the later two signals, we found that their ratio was approximately 3.9:1, and the average number of repeat unit was calculated to be 15.6. The molecular weight was calculated to be 5024 g mol^{-1}, which agreed quite well with the target Mn (5000 g mol^{-1}).

3.2. Composite membrane preparation and solubility test

The composite membranes were firstly obtained by using o-PBI as a curing agent for the TMBP epoxy resin. And *in situ* polymerization happened between o-PBI and TMBP in the SPEEK membrane. FTIR spectra were performed to confirm the structures
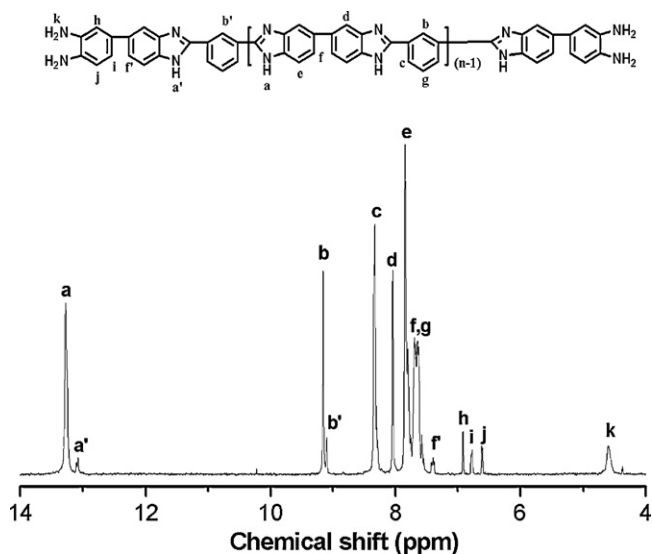

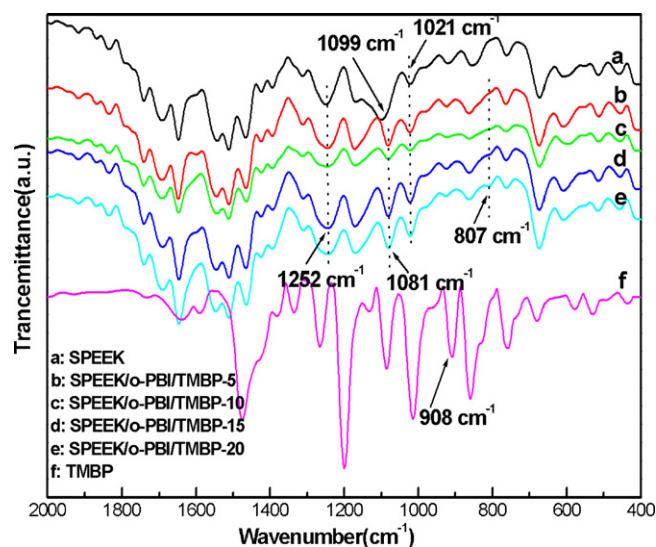**Fig. 1.** ^{1}H NMR spectra of PBI oligomer in DMSO-d_6.

Fig. 2. FT-IR spectra of SPEEK (a), SPEEK/o-PBI/TMBP-5, 10, 15, 20 (b–e), and TMBP (f).

of the SPEEK/o-PBI/TMBP composite membranes. As shown in Fig. 2, the typical absorption bands at 1021, 1081 and 1252 cm^{-1} were assigned to the asymmetric and symmetric O=S=O stretching vibrations. The absorption bands at 807 cm^{-1} was assigned to the absorption of the five-member heterocyclic ring of benzimidazole. The interaction between sulfonic acid and benzimidazole groups make these absorption bands to show a shift [30]. Also, the absorption bands at 908 cm^{-1} was related to the epoxy peak. The complete disappearance indicated that the epoxy ring opened up during the heating process and TMBP reacted with o-PBI completely.

Due to the cross-linking reaction and the acid–base interaction between sulfonic acid groups and benzimidazole groups, the three-dimensional network structure was obtained (Fig. 3). The solubility of the membranes was tested to confirm this result. Insoluble fraction was obtained from the ratio of the weight of the composite membranes after extraction from NMP to the initial weight. The pristine SPEEK membrane can be easily dissolved in common organic polar solvents, such as NMP, while the composite membranes cannot be dissolved in these solvents. As shown in Table 1, insoluble fraction increased with increasing the content of o-PBI and TMBP, which meant an increment of three-dimensional network structure density.

3.3. Ion exchange capacity (IEC), water uptake (WU) and swelling ratio (SR)

IEC values of the membranes were determined by titration method and calculation by subtracting the ABS$_{BI}$ per gram of o-PBI from the IEC$_{SPEEK}$ (formula (3)). Table 1 shows the IEC values. It should be noted that the IEC$_{titrated}$ matched closely with IEC$_{calculated}$ and these values decreased with increasing the o-PBI/TMBP content. This phenomenon further demonstrated the formation of the acid–base interaction between sulfonic acid and benzimidazole groups.

The water uptake is a very important property of PEM. The transport of proton in the form of H_3O^+ and $H_5O_2^+$ were achieved through hydrogen-bonded ionic channels and cationic mixtures. However, higher water uptake usually results in the excessive dimensional changes in membranes, which causes the loss of mechanical properties and the decline of methanol resistance. As expected, the water uptake and swelling ratio increased with the increasing temperature. And this tendency in the composite membranes is not as obvious as the pristine SPEEK. As shown in Fig. 4
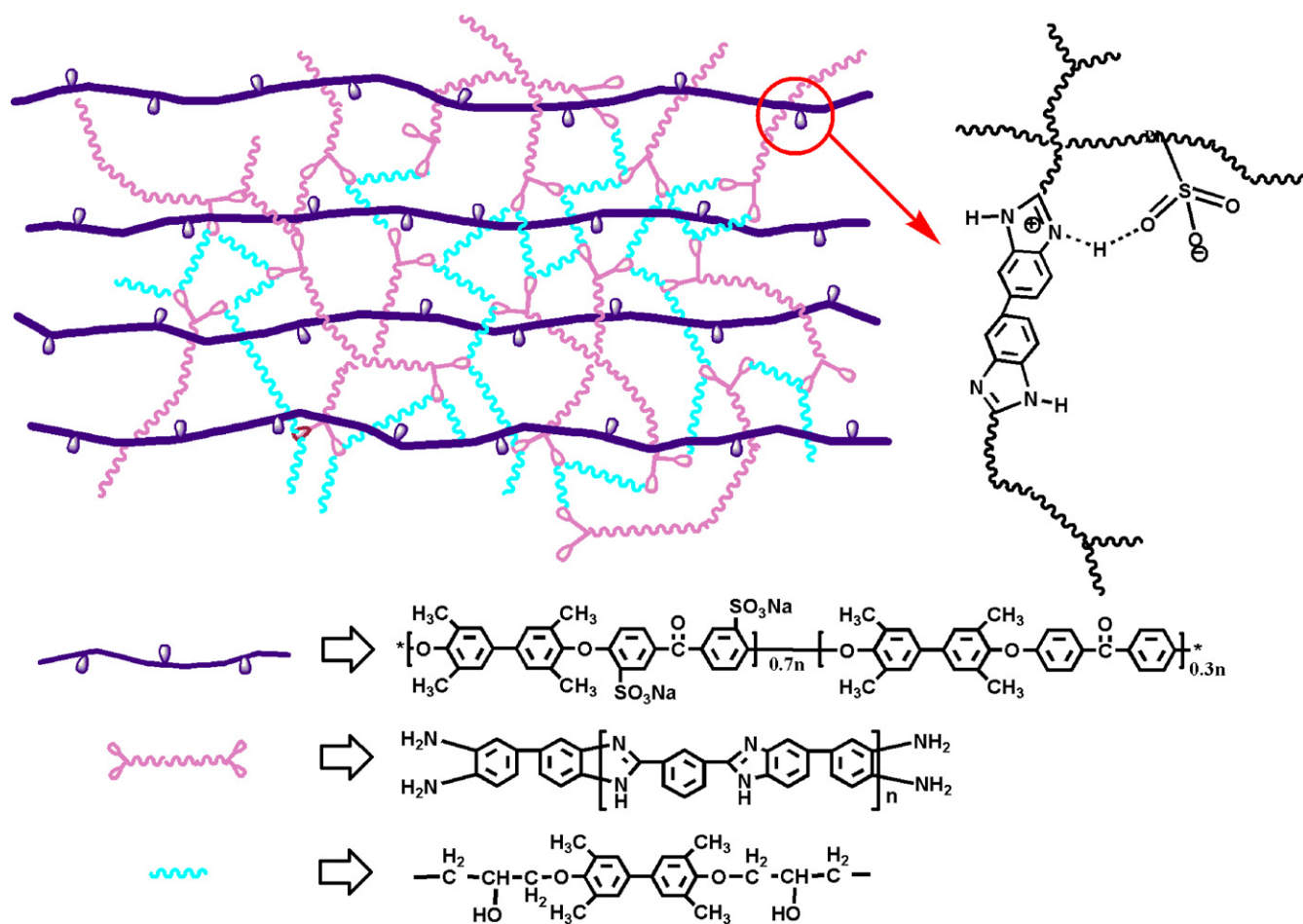
Fig. 3. Schematic representation of the composite membranes.

and Table 1, SPEEK membranes exhibited WU of 96.25% and SR of 26.14% at 80 °C, respectively. The WU and SR of SPEEK/o-PBI/TMBP-Xs showed a decreasing tendency with the increasing the content of o-PBI/TMBP. These results illustrate that the three-dimensional network structure of composite membranes holds the polymer chains together and restricts the hydrophilic domains and thus decreases the water uptake and dimensional change.

3.4. Thermal stability and oxidative stability

All the composite membranes showed significantly improved thermal stability compared with the pristine SPEEK investigated by TGA and derivative curves. As shown in Fig. 5, all the membranes exhibited a typical two-step degradation pattern. The initial

weight loss observing from 220 °C to 280 °C was attributed to the decomposition of the sulfonic acid group. And the second weight loss starting above 400 °C was assigned to the decomposition of the main polymer chain. Compared with the pristine SPEEK, these two weight loss regions of the composite membranes are higher, these weight loss regions show an increment with the content of the o-PBI/TMBP. These results indicated that the incorporation of the acid–base interaction between sulfonic acid groups and benzimidazole groups and a cross-linking structure between PBI oligomer and TMBP can improve the thermal stability of the membranes.

The oxidative stability of membranes was investigated by immersing the membranes in Fenton's reagent at 80 °C. The results were reported by the time that the membranes become brittle and disappeared in the solution and by the degradation of the

Table 1
Molar ratio of the benzimidazole and sulfonic acid groups (BI/SO$_3$H), insoluble fraction, ion-exchange capacities (IEC), water uptake (WU), swelling ratio, hydration number (λ) of the membranes.

Membranes	BI/SO$_3$H	Insoluble fraction (%)	IEC (meq g^{-1})		WU (wt%)		Swelling ratio (%)		λ	
			IEC[a]	IEC[b]	25 °C	80 °C	25 °C	80 °C	25 °C	80 °C
SPEEK	0	0	2.63	2.13	61.00	96.25	16.42	26.14	12.88	20.32
SPEEK/o-PBI/TMBP-5	0.10	27.99	2.19	1.93	39.18	56.54	14.18	16.34	2.86	4.52
SPEEK/o-PBI/TMBP-10	0.21	55.04	1.75	1.56	38.24	41.91	10.85	12.32	3.02	4.77
SPEEK/o-PBI/TMBP-15	0.34	75.33	1.32	1.15	25.18	27.62	6.52	7.67	3.20	5.05
SPEEK/o-PBI/TMBP-20	0.48	100	0.88	0.81	24.03	25.66	3.40	4.11	3.40	5.36
SPEEK/TMBP5 [32]	–	–	–	1.70	28.83	40.71	10.00	11.20	–	–

[a] The IEC values were calculated from Ds of SPEEK and composite ratio.
[b] The IEC values were measured by titration method.

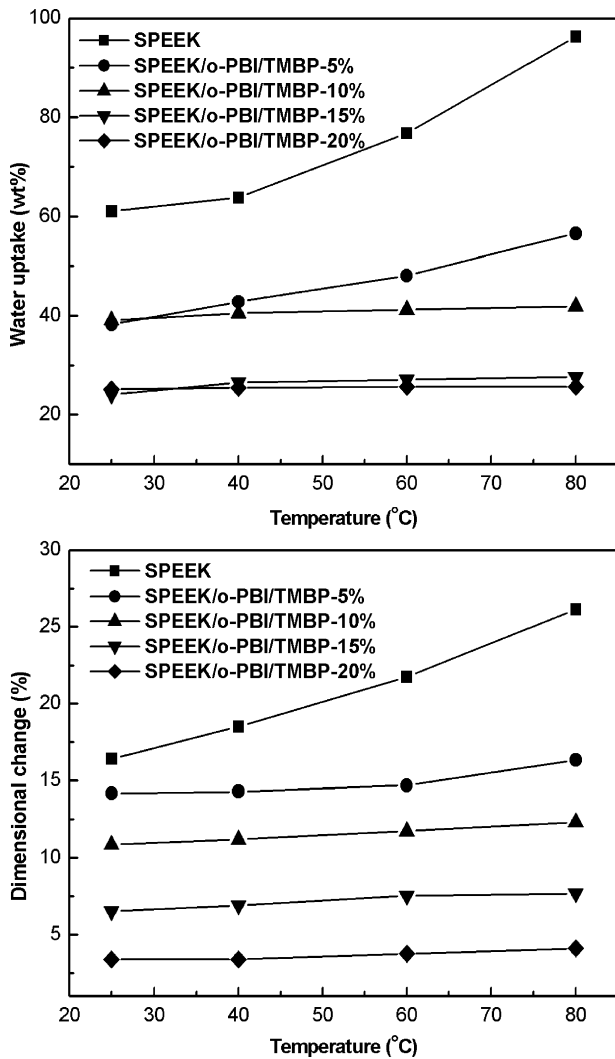**Fig. 5.** TGA and derivative curves of the membranes.

Fig. 4. Water uptake and swelling ratio of the membranes at different temperatures.

membranes by weight loss after 1 h. As shown in Table 2, the pristine SPEEK membrane completely disappeared in Fenton's reagent after 0.92 h, while the composite membranes did not break and maintained their original shape. Furthermore, the composite membrane showed only a degradation of 0.33–2.19 wt% after 1 h. As expected, the oxidative stability of composite membranes enhanced with increasing o-PBI/TMBP content. This result could be explained that the benzimidazole group can act as both donor and acceptor of proton (electron), which will trap the free radicals and slower free radical reaction of the degradation process [31].

3.5. Mechanical properties

The mechanical properties of the membranes both in the dry state and wet state are listed in Table 3. The mechanical properties of all membranes in the wet state were not as good as in the dry state. The Young's modulus and the tensile strength of the composite membranes were higher than that of the pristine SPEEK and the maximum load increase with the increment of o-PBI/TMBP in both the dry state and wet state. These results illustrate that the three-dimensional network structure restricted the molecular motion of the polymer chains and improved the mechanical properties of membranes. The same phenomenon was observed by Fu et

Table 2
Oxidative stability, proton conductivity and methanol permeability of the membranes.

Membranes	Oxidative time		Remaining weight[c] (%)	Proton conductivity (S cm^{-1})		Methanol permeability ($\times 10^{-8}$ cm^2 s^{-1})
	t_1 [a] (min)	t_2 [b] (h)		25 °C	80 °C	
SPEEK	34	0.92	0	0.0408	0.133	14.63
SPEEK/o-PBI/TMBP-5	58	4	97.81	0.0392	0.130	8.40
SPEEK/o-PBI/TMBP-10	64	>48	98.02	0.0394	0.134	6.22
SPEEK/o-PBI/TMBP-15	70	>48	99.12	0.0395	0.142	2.42
SPEEK/o-PBI/TMBP-20	73	>48	99.67	0.0410	0.130	2.38
SPEEK/TMBP5 [32]	–	–	–	0.036	0.080	114

[a] The expended time that the membranes started to become broken in the solution.
[b] The expended time that the membranes disappeared in the solution.
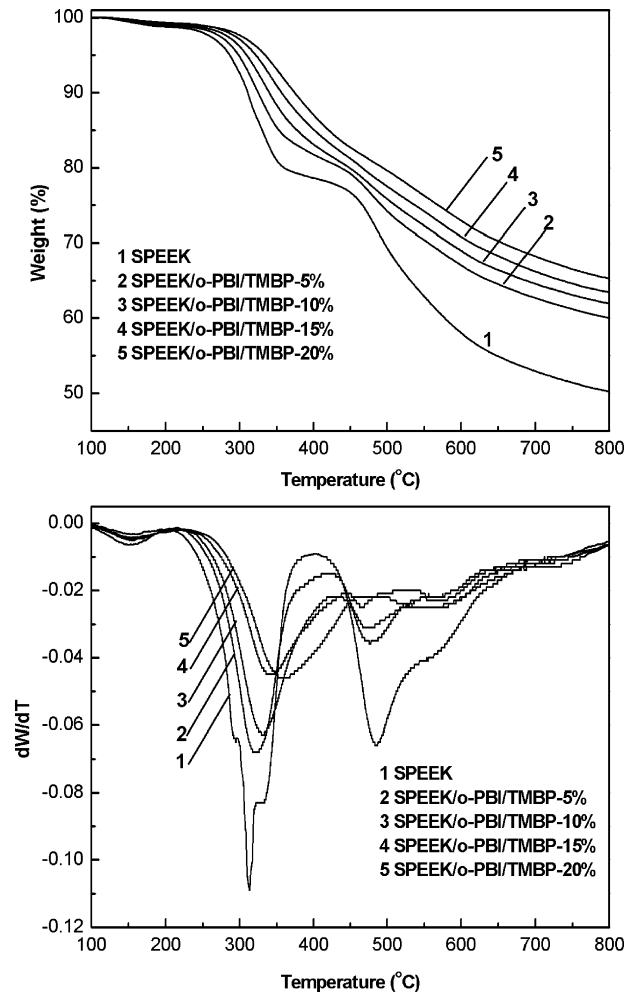[c] Remaining weight of the membranes under the same condition after 1 h.

Table 3
Mechanical properties of the membranes.

Membranes	Tensile strength (MPa)		Young's modulus (GPa)		Elongation at break (%)	
	Dry	Wet	Dry	Wet	Dry	Wet
SPEEK	39.70	14.92	1.04	0.26	24.95	14.62
SPEEK/o-PBI/TMBP-5	44.19	19.03	1.05	0.31	14.08	19.52
SPEEK/o-PBI/TMBP-10	48.14	19.42	1.26	0.51	16.02	11.50
SPEEK/o-PBI/TMBP-15	52.80	22.57	1.40	0.58	21.24	14.34
SPEEK/o-PBI/TMBP-20	60.12	27.08	1.67	0.79	15.73	8.71
SPEEK/TMBP5 [32]	44.55	–	1.04	–	9.56	–

al. [32]. However, compared with their membranes, the mechanical properties of membranes in this work were enhanced (Table 3).

3.6. Proton conductivity

The proton conductivity was measured by a four-electrode ac impedance method. The membrane samples were firstly immersed in deionized water for 30 days before the test, in order to thoroughly remove the free acid within the membranes. As shown in Fig. 6, the proton conductivities (σ) of the membranes are plotted against temperature. It can be seen that the proton conductivity of all the membranes increased with increasing temperature. Proton conductivity of the composite membranes (from $0.130\,S\,cm^{-1}$ to $0.142\,S\,cm^{-1}$) were similar with Nafion 117 ($0.146\,S\,cm^{-1}$) [33] at 80 °C. Among the SPEEK/o-PBI/TMBP-Xs, the SPEEK/o-PBI/TMBP-15 showed the highest proton conductivity, while the SPEEK/o-PBI/TMBP-20 exhibited the lowest proton conductivity. Fig. 7 exhibits the proton conductivity of SPEEK/o-PBI/TMBP-Xs plotted at a fixed condition (25, 40, 60 and 80 °C and 100% RH) as a function with increasing o-PBI/TMBP content. Combined with the results in Fig. 6, the proton conductivity of the SPEEK/o-PBI/TMBP-Xs increased at the beginning, and then decreased with increasing o-PBI/TMBP content, especially at elevated temperatures. The proton conductivity increases to the maximum value of $0.142\,S\,cm^{-1}$ of SPEEK/o-PBI/TMBP-15, and then decreases to a minimum value of $0.130\,S\,cm^{-1}$ of SPEEK/o-PBI/TMBP-20. These results demonstrated that the introduction of the optimum amount of o-PBI/TMBP could improve the proton conductivity. The optimum loading of o-PBI/TMBP is 15% for the maximum conductivity. This is the best ratio to enhance the concentration of donors and acceptors participating in the Grotthuss mechanism [21].

The proton conductivities of the membranes were plotted against λ (25 °C and 80 °C). As shown in Fig. 8, at the same
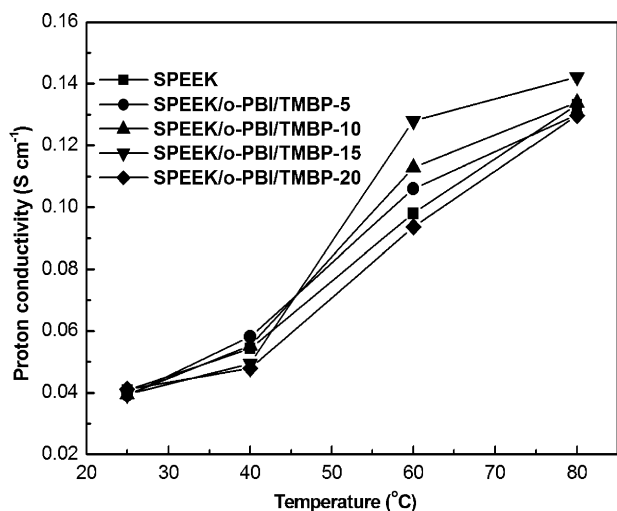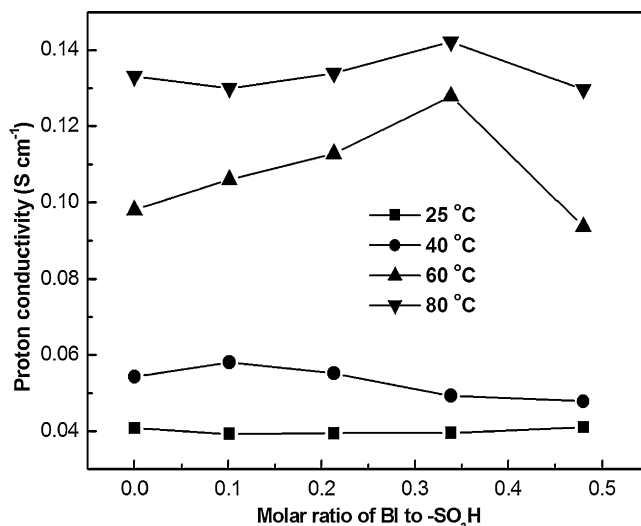
Fig. 7. Proton conductivities of SPEEK/o-PBI/TMBP-Xs versus loading of o-PBI/TMBP in the membranes at 25, 40, 60 and 80 °C under 100% RH.

temperature, the hydration number of the pristine SPEEK was higher than that of composite membranes. Although the proton conductivity of the SPEEK increased with the hydration number, this tendency is not obvious in the composite membranes. Notably, the proton conductivity of SPEEK/o-PBI/TMBP-15 was higher than that of the other composite membranes at the similar hydration number. This result indicated that the introduction of benzimidazole groups and o-PBI/TMBP cross-linked structure can reduce the dependence of proton conductivity on the water. In particular, compared with prior studies [32], SPEEK/o-PBI/
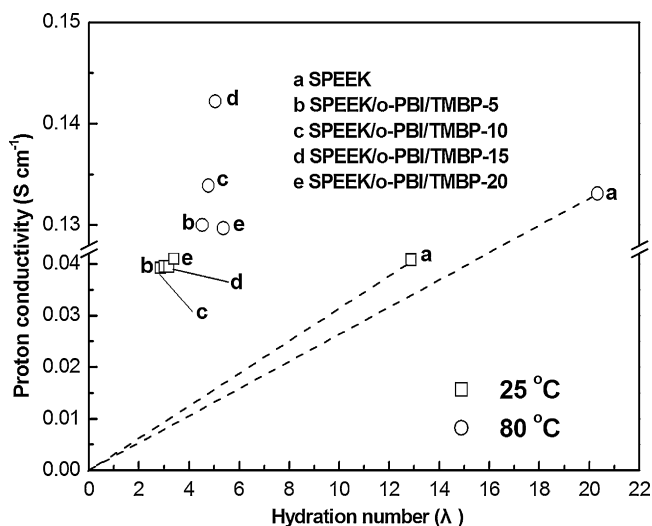
Fig. 6. Proton conductivity of the membranes as a function of temperatures.

Fig. 8. Dependence of proton conductivity of the membranes at 25 °C (□) and 80 °C (○) on the hydration number.
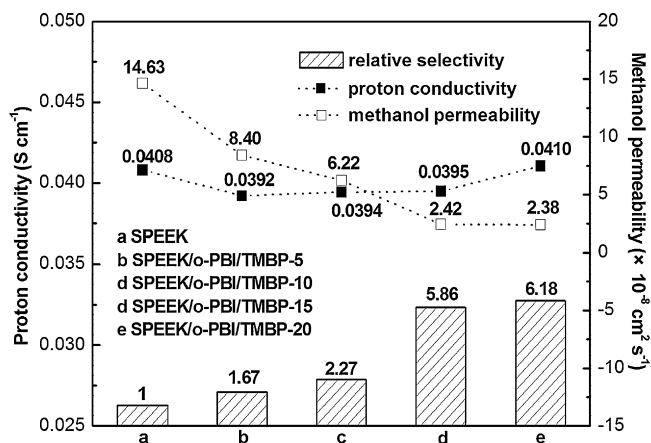
Fig. 9. Relative selectivity of the membranes.

TMBP-Xs as acid-based composite membranes showed enhanced proton conductivity (Table 2).

3.7. Methanol permeability

Membranes intended for DMFC must possess high proton conductivity, but also possess an effective barrier function to stop methanol crossover from anode to cathode. Nafion 117 has good proton conductivity but a low methanol barrier $(1.005 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}})$ [33]. The methanol permeabilities of SPEEK and SPEEK/o-PBI/TMBP-Xs are listed in Table 1. The methanol permeabilities of SPEEK/o-PBI/TMBP-Xs $(8.40 \times 10^{-8}$–$2.38 \times 10^{-8}\,\mathrm{cm^2\,s^{-1}})$ are one order of magnitude lower than the value for SPEEK $(1.463 \times 10^{-7}\,\mathrm{cm^2\,s^{-1}})$ and two orders of magnitude lower than the value for Nafion 117. As reported previously, proton conduction and methanol permeation take place through the same hydrophilic cluster channels [34,35]. In general, lower water content should decrease proton conductivity and methanol permeability. In this work, the methanol permeability is indeed decreasing. Fortunately, the introduction of optimum amount of benzimidazole increases the proton conductivity. Compared to pristine SPEEK, the decreasing methanol permeability also indicated that, the structures of SPEEK/o-PBI/TMBP-Xs were much denser due to the three-dimensional network structure.

3.8. Relative selectivity

The selectivity, which is the ratio of the proton conductivity to the methanol permeability, is a common metric to evaluate potential DMFC performance. The relative selectivity, which is the ratio of the selectivity of the composite membranes to the pristine SPEEK membrane, is also a useful parameter to predict the performance of the membranes. As shown in Fig. 9, significantly higher selectivity was observed for the composite membranes due to their higher proton conductivity and lower methanol permeability. The relative selectivities of the composite membranes (1.67–6.18) increased with increasing the o-PBI/TMBP content. This result suggests that the preparation of SPEEK/o-PBI/TMBP-Xs composite membranes with the three-dimensional network structure could be potentially used in DMFCs.

4. Conclusion

Composite membranes *in situ* polymerization based on SPEEK, o-PBI and TMBP were prepared and measured as PEMs. A

three-dimensional network structure in the composite membranes was obtained through a cross-linking reaction between PBI oligomer and TMBP and the acid–base interaction between sulfonic acid groups and benzimidazole groups. The successful completion of the cross-linking reaction between o-PBI and TMBP was shown by FTIR. As well as the formation of the three-dimensional network structure was proved by gel fraction test. The composite membranes exhibited drastically reduced water uptake, swelling ration, and methanol permeability compared with pristine SPEEK. Moreover, the thermal and oxidative stability, mechanical properties, and proton conductivity were significantly improved with increasing the content of o-PBI/TMBP. The relative selectivity results indicated that the SPEEK/o-PBI/TMBP-Xs composite membranes are potential candidates as membranes for DMFC applications.

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