Carboxyl-terminated benzimidazole-assisted cross-linked sulfonated poly(ether ether ketone)s for highly conductive PEM with low water uptake and methanol permeability

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A carboxyl-terminated benzimidazole trimer was synthesized as a crosslinker by controlling the ratio of 3,3′-diaminobenzidine and isophthalic acid. Composite membranes were obtained by mixing the benzimidazole trimer and sulfonated poly(ether ether ketone) (SPEEK) together. Cross-linked membranes were obtained by heating the composite membranes at 160 °C. All of the properties of the cross-linked membranes were significantly increased, including proton conductivity, methanol permeability and water uptake due to the more compact structure compared to the non-cross-linked membranes. The cross-linked SPEEK-BI7 and cross-linked SPEEK-BI11 had excellent proton conductivities (0.22 and 0.19 S cm^{-1}) at 80 °C, which were higher than that of Nafion 117 (0.125 S cm^{-1}). Transmission electron microscopy (TEM) analysis revealed a clear microphase separated structure of cross-linked membranes. Other properties, such as thermal and mechanical stability, required for use as a proton exchange membrane (PEM) have been investigated. The cross-linked membranes showed improved properties over membranes without crosslinking.

Introduction

Direct methanol fuel cells (DMFCs)[1–3] have attracted much attention due to their high energy efficiency, low emission, compact cell design and other benefits. Proton exchange membranes (PEM), a key component in DMFC, transports protons from anode to cathode and at the same time separates the fuel and the oxidant.[4,5] Perfluorosulfonic acid membranes, such as Nafion are commercialized membranes used in DMFCs due to their good physical, chemical stability and high proton conductivity.[6,7] However, many disadvantages, such as limited operation temperature ($T < 80$ °C), poor thermal properties, high cost and high methanol permeability, limit their usage.[7–10] Sulfonated aromatic polymers[11–15] have recently been developed by several groups as high performance and low cost alternative materials. But there must be certain acidic groups in order to achieve sufficient proton conductivity. Unfortunately, a high degree of sulfonation induces high methanol permeability and excessive water swelling.[16–18]

Polybenzimidazole is a kind of high-performance polymer that exhibits good mechanical and thermal properties.[19–21] On the other hand, benzimidazole rings possess both donor and acceptor hydrogen bonding sites due to its amphoteric nature. A lot of work has focused on introducing benzimidazole groups into sulfonated aromatic polymers for the above purpose by different means. Introducing acid-based composite membranes of sulfonated aromatic polymers and benzimidazole or imidazole were considered as promising strategies to reduce water uptake and improve dimensional stability.[22,23] Though these resulting membranes exhibited enhanced proton conduction and lower methanol crossover, this method may result in the leaching out of small molecules during usage in fuel cells. Li *et al.*[24–26] reported that the synthesis of sulfonated aromatic polymers bearing benzimidazole pendant groups, and the incorporation of benzimidazole groups by these methods, can improve thermal and mechanical stability, WU, and methanol permeability. However, these membranes showed lower proton conductivity than that of the foregone simple SPEEKs.

In this study, we propose a new strategy to introduce benzimidazole groups into SPEEK by crosslinking. A novel benzimidazole trimer has been synthesized as the crosslinker for the first time. Cross-linked membranes were obtained by the heating method.[27–29] We prepared composite membranes and cross-linked membranes with a majority partner, SPEEK with a high degree of sulfonation (D_s), and a minority partner, benzimidazole trimer. The majority partner guaranteed good proton conductivity of the membranes and the minority partner improved the mechanical properties and dimensional change, meanwhile, the appropriate ratio of benzimidazole groups as proton donors and acceptors should help to enhance proton conductivity. The introduction of benzimidazole groups into SPEEK avoided basic groups leaching out from the membranes in liquid water, as well as incompatibility behavior among the different components of the blended membranes. The cross-linked membranes were investigated as PEMs used in DMFCs. All of the properties, such as proton conductivity, water swelling, methanol permeability and mechanical property, were studied in detail. And the results showed that this method of crosslinking is suitable for further research of PEMs.

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Experimental section

Materials

Monomers 3,3′-diaminobenzidine (DAB), isophthalic acid, poly(phosphoric acid) (PPA) and poly(ether ether ketone) (PEEK) were purchased from commercial vendors and used without further purification unless specified.

Synthesis

Benzimidazole trimer was synthesized in PPA. A typical coupling reaction was performed as follows: 2.6784 g (12.5 mmol) of DAB and 4.1533 g (25 mmol) of isophthalic acid were mixed with 137 g of PPA in a three-neck 250 ml flask equipped with a nitrogen inlet/outlet and a mechanical stirrer. The mixture was heated at 220 °C for 24 h. The resulting dark brown solution was coagulated in deionized water and stirred for 24 h. The trimer was filtered, and washed with deionized water several times until the water was neutralized. It was dried at 120 °C *in vacuo* for at least 24 h. Chemical structures are shown in Fig. 1. Representative ^{1}H NMR spectra of the benzimidazole trimer using deuterated dimethyl sulfoxide (DMSO-d$_6$) solutions are also shown in Fig. 1. As can be seen, the peaks of 13.25 ppm and 7.5–9.0 ppm were assigned to the amine protons on the benzimidazole moieties and the proton on the aromatic groups, respectively. By comparing the intensity of these signals we found their ratio approximately was 1 : 1, this substantiated the successful synthesis of benzimidazole trimer. FTIR (neat, cm^{-1}): 3396 (N–H stretching), 1686 (C=O), 1630 (C=N), 1585, 1447 (aromatic), 1361 (C–N stretching), 1300–1000 (C–O stretching).

Post-sulfonation PEEK with a degree of sulfonation ($D_s = 0.76$) was synthesized in concentrated sulfuric acid at 70 °C for 4.5 h.[30]

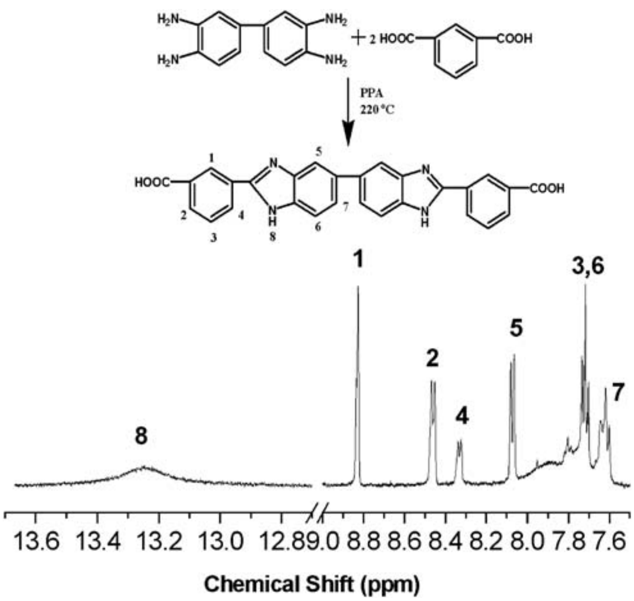


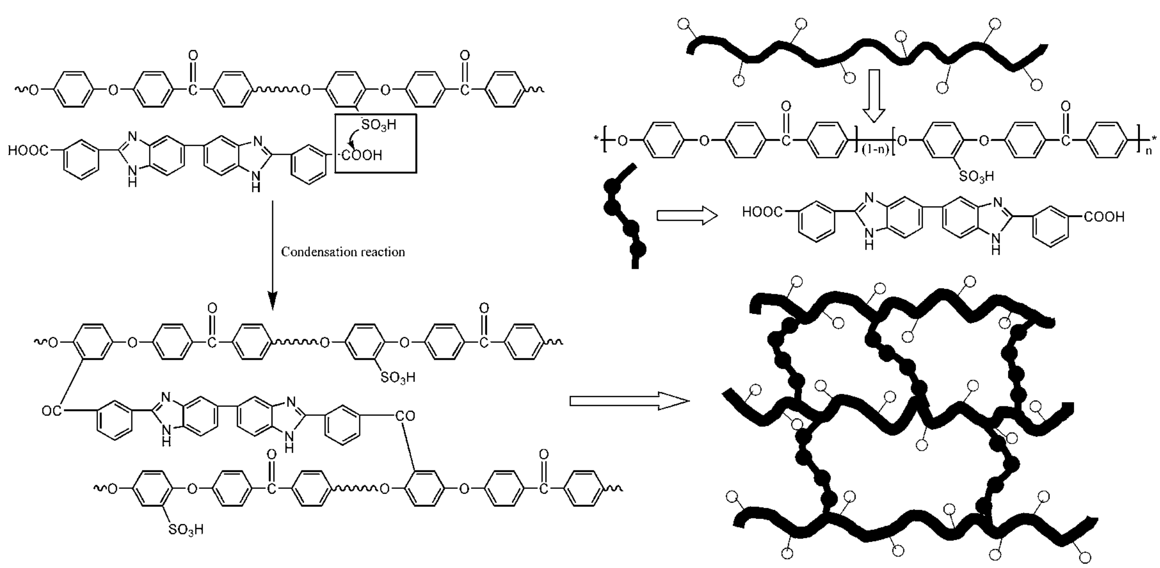
Fig. 1 Synthesis of benzimidazole trimer and ^{1}H NMR spectra of benzimidazole trimer (in DMSO-d$_6$).

Membrane preparation and crosslinking treatment

The benzimidazole trimer was first dissolved in DMSO by heating to afford a mass fraction of 6–10%, and then the SPEEK was dissolved in the above solution. This final solution was cast onto a clean glass plate followed by heating at 60 °C for 12 h, and then 100 °C for 6 h to remove the solvent. The cross-linked membranes were prepared through Friedel–Crafts reaction by heating the membranes at 160 °C for 10 h in a vacuum oven.[27–29] The cross-linked membranes were peeled off from the substrate with deionzed water. All the membranes had a thickness around 30–40 μm. The crosslinking reaction and the simulated stereo configuration are shown in Scheme 1.

Characterization and measurements

The ^{1}H NMR spectra were collected by an AVANCE 500 at 25 °C with deuterated dimethyl sulfoxide (DMSO-d$_6$) as the solvent and tetramethylsilane (TMS) as the standard. Thermal



Scheme 1 Crosslinking reaction and the simulated stereo configuration of cross-linked membranes

stability of the crosslinking membranes was determined by a Perkin-Elmer TGA. A temperature ramp of 10 °C min^{-1} was applied under nitrogen flow. The mechanical properties of the membranes were measured by a SHIMADZU AG-I 1KN at a speed of 2 mm min^{-1}, the size of the membranes was 1 mm × 4 mm. Each sample was tested at least four times to reach an average value.

Water uptake and dimensional change of the membranes were determined by measuring the weight and dimensional differences between the fully hydrated membranes and dried membranes.[31,32] A titration technique was used to determine the IEC of the membranes.[31,32] Proton conductivities of membranes were measured by the four-point probe method over a frequency range of 10–10^7 Hz at 25, 40, 60 and 80 °C using a Princeton Applied Research Model 2273A Potentiostat (Model 5210 frequency response detector, EG&GPARC, Princeton, NJ).[31,32] 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.[31,32] TEM images were determined by a JEM-2000EX. Before the test, the SPEEK was first converted into the Ag^+ form by immersing the SPEEK in a $AgNO_3$ solution for 48 h. The composite membrane samples were prepared by casting the composite solutions onto copper grids; cross-linked membranes samples were obtained by heating the copper grids for TEM use.

Results and discussion

Ion-exchange capacities and solubility

The IEC values of the membranes were determined by titrating the membranes in aqueous NaCl solution with standard sodium hydroxide solution. Table 1 shows the IEC values. It should be noted that the IEC values of composite membranes (SPEEK-BIs) and cross-linked membranes (cross-linked SPEEK-BIs) are much lower than that of the SPEEK, in addition the IEC values of cross-linked SPEEK-BIs are lower than those of SPEEK-BIs at the same loading ratio of benzimidazole trimer. These results implied the formation of an acid–base interaction between sulfonic acid and benzimidazole groups, and the diminishment of carboxyl after crosslinking. Table 1 also shows the solubility of the membranes. The SPEEK and SPEEK-BIs membranes can easily be dissolved in common organic polar solvents such as DMSO, while the cross-linked membranes cannot be dissolved in the same solvents.

Thermal stability

The thermal properties of the SPEEK, SPEEK-BIs and cross-linked SPEEK-BIs polymers were investigated by TGA. Fig. 2 shows the TGA and derivative curves (example for SPEEK, SPEEK-BI15 and cross-linked SPEEK-BI15). The figure shows that the plain SPEEK exhibited a typical two-step degradation pattern. The first weight loss region between 250 and 400 °C is believed to be associated with the elimination of sulfonic acid groups, and the second weight loss step starting at about 450 °C corresponded to the decomposition of the main polymer chain. The desulfonation temperatures of SPEEK-BIs and cross-linked SPEEK-BIs are higher than those of SPEEK. The SPEEK-BIs

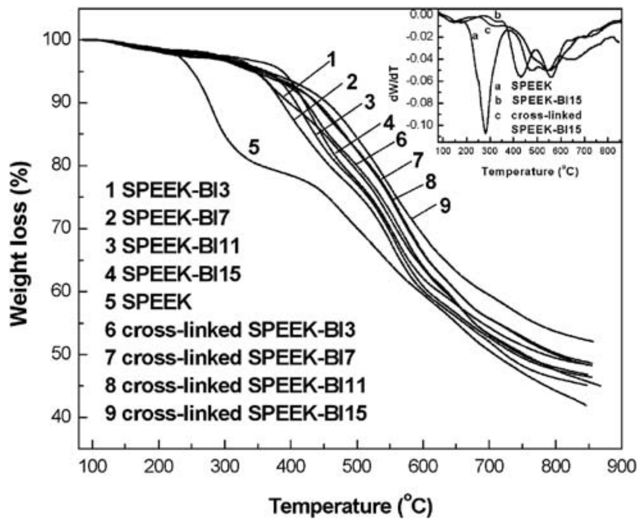


Fig. 2 TGA and derivative curves of membranes under N_2 atmosphere.

Table 1 Ion-exchange capacities (IEC), water uptake (WU), dimensional change, solubility, proton conductivity and methanol permeability of membranes

Membrane	Wt% BI in polymer	IEC[a] (meq g^{-1})	WU (wt %) 25 °C	WU (wt %) 80 °C	Dimensional change (%) 25 °C	Dimensional change (%) 80 °C	Solubility in DMSO	Proton conductivity/ mS cm^{-1} 25 °C	Proton conductivity/ mS cm^{-1} 80 °C	Methanol permeability/ × 10^{-7} cm^2 s^{-1}
SPEEK-BI3	3%	197	33.3	157.4	2.0	44.0	Yes	0.011	0.15	14.65
SPEEK-BI7	7%	1.72	25.3	34.3	1.7	8.7	Yes	0.013	0.14	7.83
SPEEK-BI11	11%	1.40	22.8	27.9	1.7	4.0	Yes	0.015	0.16	3.68
SPEEK-BI15	15%	1.27	18.3	21.7	2.0	2.7	Yes	0.015	0.13	2.48
SPEEK	0	2.31 and 2.18[b]	40.4	soluble	8.3	soluble	Yes	0.025	0.11[d]	19.18
Cross-linked SPEEK-BI3	3%	1.87	21.4	24.4	3.3	6.0	No	0.021	0.17	2.38
Cross-linked SPEEK-BI7	7%	1.63	21.1	24.4	2.3	5.0	No	0.030	0.22	1.67
Cross-linked SPEEK-BI11	11%	1.29	19.0	21.8	0.7	3.3	No	0.027	0.19	1.57
Cross-linked SPEEK-BI15	15%	1.23	16.3	20.9	0	1.7	No	0.022	0.18	1.05
Nafion 117[33]	—	0.90	19.0[c]	28.6	—	—	—	0.0571[c]	0.125	15.5

[a] Ion exchange capacity (IEC) was determined by the titration (except [b]). [b] IEC was determined by ^1H NMR. [c] Property of Nafion 117 was at 30 °C.[33] [d] Measured at 60 °C due to solubility at 80 °C.

also exhibited a typical two-step degradation pattern. However, visible decomposition did not appear for cross-linked SPEEK-BIs before 400 °C, which only exhibited a one-step degradation pattern (between about 450 to 700 °C). These results indicated that the incorporation of benzimidazole groups and crosslinking bonds can improve the thermal stability of the polymer.

Water uptake and dimensional change

Water uptake plays the most important role in proton conductivity in membranes because H_2O molecules act as a transportation medium of protons. However, high WU leads to large dimensional changes in membranes which causes low mechanical properties. So it is necessary that there are suitable water molecules around the sulfonic acid groups.

Fig. 3 and Table 1 show the WU and dimensional change of the membranes. It is obvious that the WU and dimensional change of SPEEK-BIs and cross-linked SPEEK-BIs show a decreasing tendency with the introduction of benzimidazole trimer. SPEEK is soluble in 80 °C water, but SPEEK-BI3 and the cross-linked SPEEK-BI3 are insoluble with a dimensional change of 44.0% and 6.0%, respectively. The shape of SPEEK-BIs and cross-linked SPEEK-BIs was maintained, and cross-linked SPEEK-BI membranes had a lower dimensional change than that of SPEEK-BIs. The dimensional changes of all the cross-linked membranes were lower than that of the Nafion 117,[33] while they had almost the same WU. This result illustrates that loading of benzimidazole trimer and crosslinking improved dimensional stability of the membranes, and suggests that there are acid–base interactions between sulfonic acid groups and amine groups. At the same time, crosslinking bonds between the SPEEK and benzimidazole trimer help to hold the polymer chains together in order to restrict the hydrophilic domains and thus decrease dimensional change.

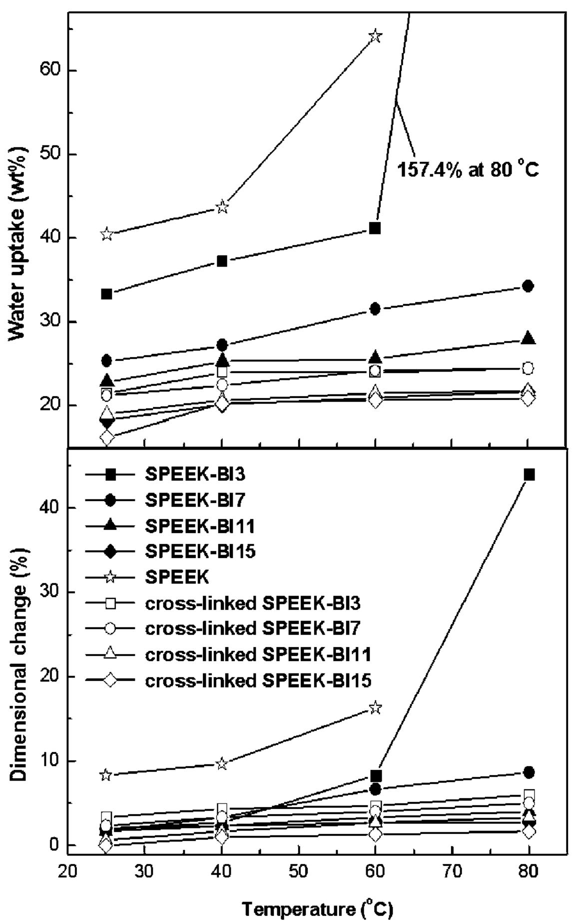


Fig. 3 Water uptake and dimensional change of the membranes.

Mechanical property

The mechanical properties of cross-linked membranes have been compared to SPEEK, Nafion 117[33,34] and composite membranes without crosslinking in both the dry and wet state. As shown in Table 2, the mechanical properties of all membranes in the wet state are not as good as those of membranes in the dry state. The SPEEK-BI and cross-linked SPEEK-BI membranes show higher tensile strength and Young's modulus, and the lower elongation than that of SPEEK and Nafion 117[33,34] in both the dry and wet state. In the wet state, the mechanical properties of cross-linked SPEEK-BIs are better than those of SPEEK-BIs. Fig. 4 shows how the Young's modulus varied with different loading ratios of the benzimidazole trimer in membranes in the wet state. The Young's modulus of SPEEK-BIs and cross-linked SPEEK-BIs increase with the increment of benzimidazole trimer ratio. Meanwhile, Young's modulus of cross-linked SPEEK-BIs are even higher than that of SPEEK-BIs at same loading ratio. In the dry state, the SPEEK-BIs and cross-linked SPEEK-BI membranes exhibit similar mechanical properties. These results show that the introduction of benzimidazole trimer and cross-linking improved mechanical properties of the SPEEK, especially in the wet state. It also suggests that the mechanical properties of membranes can been related to their water uptake and swelling.

Proton conductivity and methanol permeability

The proton conductivities, as a function of temperature for the membranes with different loading ratios of benzimidazole trimer, are summarized in Fig. 5. For all membranes, proton conductivity increases with increasing temperature. The proton conductivity of the membranes before crosslinking is lower than that of SPEEK due to the interaction between the sulfonic acid groups and amine groups. After crosslinking, all the membranes have good proton conductivities, and higher than that of the SPEEK, because the cross-linked SPEEK-BI membranes can tolerate much higher ionic contents without excessive swelling, which makes the membranes possess highly concentrated, isotropically connected ionic domains.[35–37] What needs to be emphasized is that the cross-linked SPEEK-BI7 and cross-linked SPEEK-BI11 have excellent proton conductivities (0.22 and 0.19 S cm^{-1}) at 80 °C, which are higher than that of the Nafion 117 (0.125 S cm^{-1}).[33]

Fig. 6 shows how the proton conductivity of cross-linked SPEEK-BIs at a fixed condition (80 °C and 100% RH) varied with different loading ratios of the benzimidazole trimer. As the figure shows, with the increasing of loading ratio, the proton conductivity of the membranes increases to a maximum conductivity of 0.22 S cm^{-1} at a benzimidazole trimer loading

Table 2 Mechanical property of membranes

	Tensile strength (MPa)		Young's modulus (GPa)		Elongation at break (%)	
Membranes	dry	wet	dry	wet	dry	wet
SPEEK-BI3	69.54	23.98	1.70	0.37	29.99	16.11
SPEEK-BI7	71.48	26.72	1.80	0.51	15.02	15.47
SPEEK-BI11	78.03	31.83	2.02	0.72	14.48	11.89
SPEEK-BI15	72.30	39.81	1.96	0.91	11.17	11.93
SPEEK	62.31	20.18	1.22	0.30	32.17	23.90
cross-linked SPEEK-BI3	69.80	34.42	1.69	0.69	10.74	12.17
cross-linked SPEEK-BI7	70.58	38.44	1.96	0.73	18.86	10.54
cross-linked SPEEK-BI11	75.39	47.59	1.92	0.86	25.92	17.31
cross-linked SPEEK-BI15	71.71	45.23	1.75	1.00	19.08	13.97
Nafion 117[33,34]	38.0	28.4	0.18	0.10	301.5	329.2

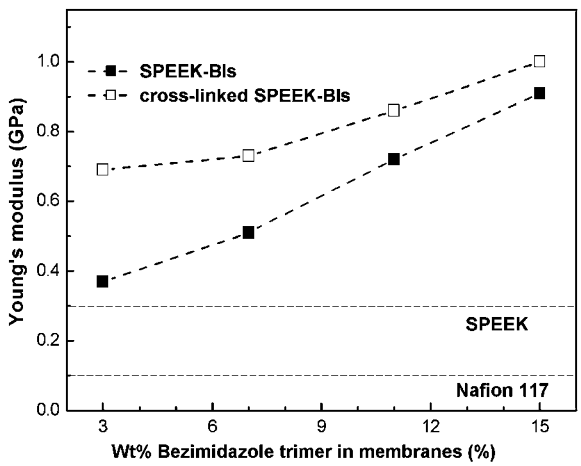


Fig. 4 Young's modulus of SPEEK-BIs and cross-linked SPEEK-BIs dependence on loading of benzimidazole trimer in membranes at room temperature in the wet state.

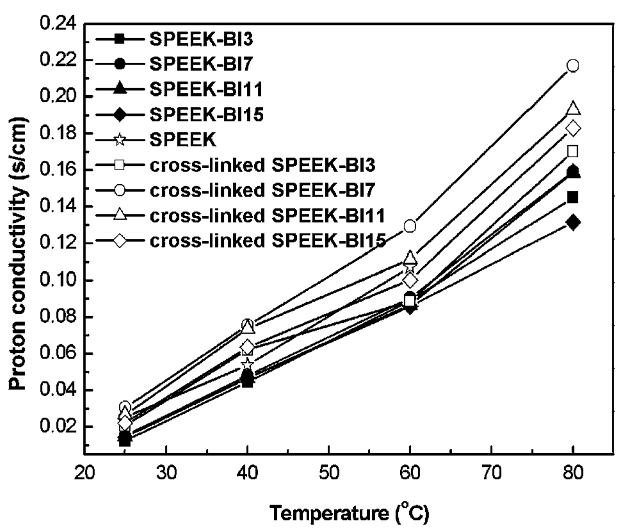


Fig. 5 Proton conductivity of the membranes.

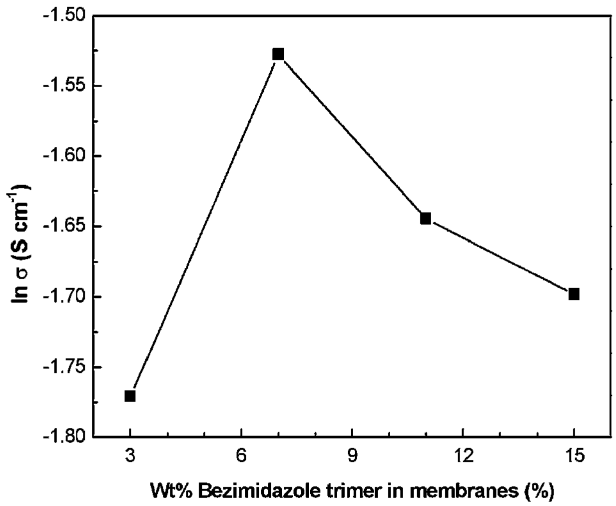


Fig. 6 Proton conductivities of cross-linked SPEEK-BIs dependence on loading of benzimidazole trimer in membranes at 80 °C under 100% RH condition.

ratio of 7%, and then decreases with loading ratio of the benzimidazole trimer. The proper loading ratio of benzimidazole should be chosen to enhance the concentration of donors and acceptors participating in the Grotthuss mechanism. The optimum ratio is 7%, where the conductivity is maximum. The proton conductivity of the composite based on sulfonated poly(phentylene oxide) and benzimidazole studied by Liu *et al.*[23] showed 8.93×10^{-4} S cm^{-1} at optimum doping ratio.

In Fig. 7 the relative water uptake as a function of relative proton conductivities of various membranes to Nafion 117[33] at 80 °C is shown. We can see that the proton conductivities of all the cross-linked membranes and SPEEK-BI(7,11,15) are higher than that of Nafion 117,[33] while they have similar WU data which are caused by lower dimensional change. This lower dimensional change makes membranes possess a higher effective concentration of sulfonic acid groups within the membranes which is useful for enhancement of proton conductivity.[35]

Membranes intended for DMFC must possess an effective barrier function to stop methanol crossover from anode to cathode. The methanol permeabilities of the SPEEK, SPEEK-BIs and cross-linked SPEEK-BIs with 10% methanol concentration at 25 °C are listed in Table 1. The methanol permeabilities of both SPEEK-BIs (2.48–14.65×10^{-7} cm^2 s^{-1}) and cross-linked SPEEK-BIs (1.05–2.38×10^{-7} cm^2 s^{-1}) decrease varied with different loading ratio of benzimidazole trimer and both are

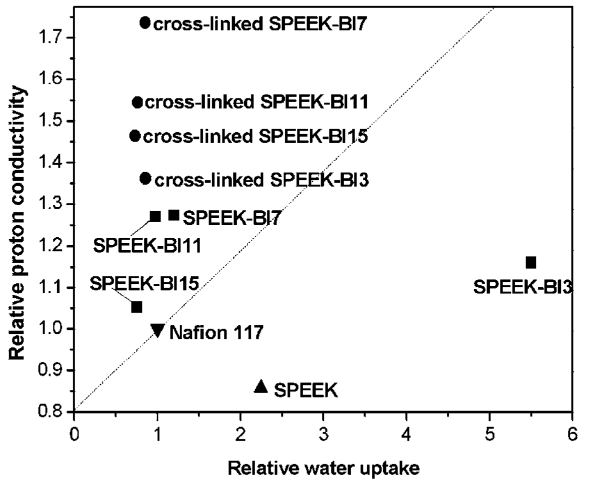


Fig. 7 Relative proton conductivities as a function of relative water uptake at 80 °C.

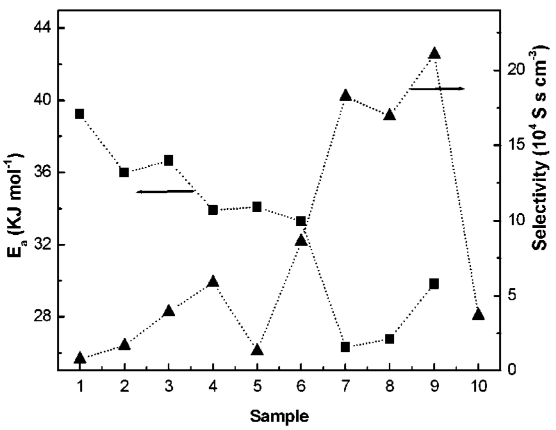


Fig. 8 Activation energy of proton conductivity (E_a) and selectivity of the membranes (property of Nafion 117 was measured at 30 °C) (sample 1–10: SPEEK-BI(3,7,11,15), cross-linked SPEEK-BI(3,7,11,15), Nafion 117).

lower than that of SPEEK (19.18 × 10^{-7} cm^2 s^{-1}) and Nafion 117 (15.5 × 10^{-7} cm^2 s^{-1}).[33] Meanwhile, methanol permeabilities of membranes after crosslinking are lower than that of membranes before crosslinking due to the more compact structure. Selectivity, which is the ratio of the proton conductivity to the methanol permeability, is also a useful parameter to predict potential DMFC performance. As shown in Fig. 8, the selectivities of the cross-linked SPEEK-BIs (8.62–21.05 × 10^4 S s cm^{-3}) are higher than that of Nafion 117 (3.68 × 10^4 S s cm^{-3}).[33] There is also information about activation energy of proton conductivity (E_a) in Fig. 8, which is obtained from the Arrhenius relation of proton conductivity as a function of temperature.[38] E_a of cross-linked SPEEK-BI7 is the lowest, which shows it has potential for use in DMFCs.

Microstructure of the composite membrane and cross-linked membranes

The microstructure of the composite membrane and cross-linked membrane were investigated by TEM. The dark areas represent hydrophilic domain and bright areas represent the hydrophobic domain. Fig. 9 shows the morphologies of SPEEK-BI7 and cross-linked SPEEK-BI7 membranes. In the TEM figure of SPEEK-BI7 membrane, the black clusters are randomly dispersed throughout the composite membrane matrix and phase separation is not apparent, which indicated the lack of connectivity of the ionic phase in the membrane. In contrast, cross-linked SPEEK-BI7 membrane possesses well-segregated morphologies of ionic-rich and lamellar structures, which substantiated the good connectivity of the ionic phase in membrane to give ionic channels for good conductivity. This kind of hydrophilic/hydrophobic microphase separation morphology is also quite similar to WU and proton conductivities.

Conclusions

Cross-linked sulfonated poly(ether ether ketone)s (SPEEKs) have been synthesized, based on a novel crosslinker, benzimidazole trimer. The cross reticulation structures of SPEEK-BIs were obtained after crosslinking by heating the composite membranes which were composed of benzimidazole trimer and SPEEK. The sulfonic acid groups and amine groups had an acid–base interaction, and crosslinking bonds of the SPEEK and benzimidazoel trimer helped to make membranes more compact. Compared with SPEEK, all of the properties of the cross-linked membranes were significantly improved, such as proton

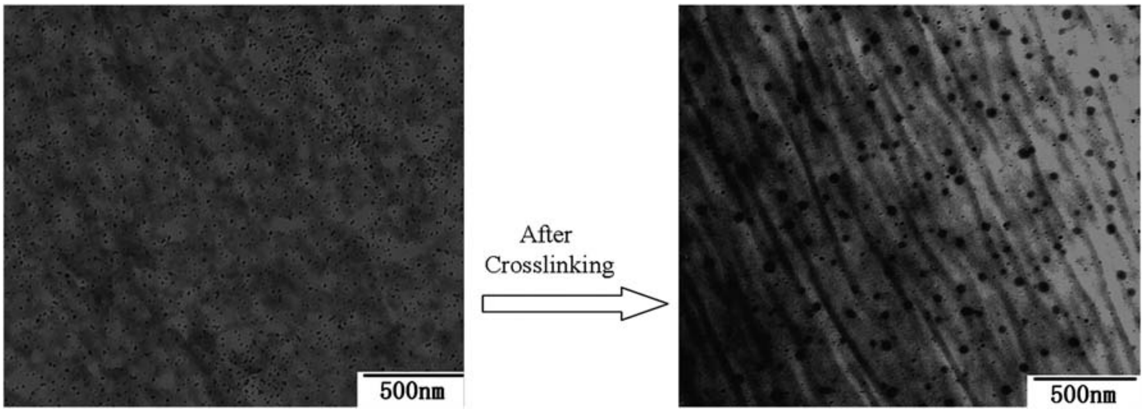


Fig. 9 TEM micrographs of SPEEK-BI7 and cross-linked SPEEK-BI7 membranes.

conductivity, methanol permeability and water uptake, which indicated that the cross-linked membranes had more compact structures. The proton conductivity of cross-linked SPEEK-BI7 was 0.22 S cm^{-1}, which was higher than that of SPEEK (0.11 S cm^{-1} at 60 °C) and also higher than that of Nafion 117[33] (0.125 S cm^{-1} at 80 °C), while water uptake was lower. After crosslinking, all the membranes showed better thermal, mechanical and dimensional change stability than those of SPEEK membranes. All the results indicated that the cross-linked membranes are potential candidates as membranes for DMFC. Also, the heating crosslinking method in this work is an efficient way to improve properties of the membranes.

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