



Novel sulfonated poly(ether ether ketone) with pendant benzimidazole groups as a proton exchange membrane for direct methanol fuel cells

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ABSTRACT

A series of sulfonated poly(ether ether ketone)s bearing pendant carboxylic acid groups (C-SPEEKs) have been prepared and subsequently react with 1,2-diaminobenzene to obtain sulfonated poly(ether ether ketone)s with pendant benzimidazole groups (BI-SPEEKs). The expected structures of the sulfonated copolymers are confirmed by ^1H NMR. The resulting copolymers all show good thermal and mechanical properties. It should be noted that the introduction of benzimidazole groups into the copolymer improves its thermal and oxidative stability obviously. Meanwhile, compared to C-SPEEK, BI-SPEEK membranes show much lower water uptake and methanol permeability with the same sulfonation degree (DS). In order to study morphological changes of C-SPEEK and BI-SPEEK membranes, hydrophilic domains sizes from an atomic force microscopy (AFM) are investigated.

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1. Introduction

Today, proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) have been widely investigated because of their low emissions and high conversion efficiency. As a key component in this system, proton exchange membrane (PEM) functions as an electrolyte for transferring protons as well as providing a barrier to the gases or fuel cross-leaks between the electrodes [1,2]. Up to now, perfluorosulfonic acid membranes, such as Nafion[®], are the principal material used as the polymeric electrolyte in DMFC systems, because of their excellent chemical and mechanical stabilities and high proton conductivity [3,4]. However, some specific limitations exist for Nafion[®] membranes including very high cost, high methanol permeability, and loss of the preferable properties at high temperature ($t > 80^\circ\text{C}$). This stimulated many efforts in the development of alternative PEMs [5–8].

In recent years, many kinds of sulfonated aromatic polymers, such as sulfonated poly(ether ether ketone) (SPEEK), sulfonated polyimide (SPI) and sulfonated polysulfone (SPSF) have been widely investigated as candidate PEM materials [9–14]. Especially, acid-doped polybenzimidazole (PBI) has attracted a lot of attention due to its high proton conductivity at elevated temperature ($t > 150^\circ\text{C}$), which could be promising as a proton exchange membrane in DMFC operating at high temperature [15–18]. To avoid leaching out of

small inorganic acid molecules such as phosphoric acid at high temperature, chemical modification of PBI by introducing alkyl-sulfonate or arylsulfonate side chain onto reactive N–H sites was suggested [19–23]. Meanwhile, SPEEKs, owing to their excellent mechanical properties and stability in water, were studied as candidates for proton exchange membrane in DMFC. However, SPEEKs with high sulfonation degree (DS) are much swelling in water, which limits the end-use in fuel cell. One option is to blend highly sulfonated PEEKs with base polymer such as PBI [24,25]. However, swelling or phase separation of blended membrane at elevated temperature was observed in some cases resulting in dissociation of the membranes. Some groups had reported the acid–base composite membranes by blending SPEEK with basic small molecule containing benzimidazole or imidazole groups, and the resulting membranes exhibited good performance in DMFC with enhanced proton conduction while lowering the methanol crossover. However, this method cannot prevent the small molecules running out from the composite membranes under 100% humidity conditions [26,27].

To resolve this problem, in this paper, we synthesized novel sulfonated poly(ether ether ketone) copolymers containing benzimidazole groups on aliphatic side chain. Tethering benzimidazole groups directly onto the backbone of SPEEK avoided basic groups running out from the membranes in liquid water, meanwhile, incompatibility behavior among the different components of the blended membrane cannot occur. Another advantage of pendant benzimidazole group was the case of swaying, which could promote long-range proton motion in the polymer system. On the other hand, the interaction between sulfonic acid and benzimi-

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dazole groups could be responsible for the lower water uptake of BI-SPEEK in comparison with C-SPEEK and for the smaller size of the hydrophilic domains. Then, the properties of the membranes were studied in detail.

2. Experimental

2.1. Materials

4,4'-Difluorobenzophenone was purchased from Longjing Chemical Plant, China. Sodium 5,5'-carbony-bis(2-fluorobenzene-sulfonate) was synthesized according to a procedure described by Wang et al. [28]. 4,4'-Bis(4-hydroxyphenyl)valeric acid (DPA) and 1,2-diaminobenzene were obtained from Shanghai Chemical Works, China. Other reagents and solvents were obtained from commercial source and used as received.

2.2. Preparation of the sulfonated poly(ether ether ketone) copolymers with pendant carboxylic acid groups (C-SPEEKs)

C-SPEEK copolymers with various DS were prepared by varying the molar ratio of sodium 5,5'-carbony-bis(2-fluorobenzene-sulfonate) (monomer m) to 4,4'-difluorobenzophenone (monomer k). A typical synthesis procedure of C-SPAEEK-5 (DS = 1.0) was as follows: 0.025 mol (7.15 g) DPA, 0.0125 mol (5.275 g) monomer m, 0.0125 mol (2.725 g) monomer k and 7 g K_2CO_3 were added into a 250 mL three-neck flask equipped with a magnetic stirrer, a Dean-Stark trap, and a nitrogen gas inlet. Then 35 mL DMSO and 15 mL toluene were charged into the reaction flask under a nitrogen atmosphere. The mixture was heated at 140 °C for 3 h. After removal of toluene, the reaction temperature was increased to about 180 °C. When the solution viscosity had increased obviously, the mixture was cooled to 100 °C and poured into 500 mL HCl (0.01 M) solution. After being washed with hot deionized water for several times, the product was dried in vacuum at 80 °C for 24 h to give product with 96% yield.

2.3. Preparation of sulfonated poly(ether ether ketone) copolymers containing pendant benzimidazole groups (BI-SPEEKs)

The synthesis procedure for BI-SPEEK-5 was as follows: 1.5 g C-SPEEK-5 and 0.4 g 1,2-diaminobenzene were dissolved in 50 mL dimethylformamide (DMF) in a three-necked flask, followed by an addition of 1.0 g of lithium chloride and 10 mL of triphenylphosphite (TPP) into the flask. The solution was stirred at 100 °C for 3 h and then at 150 °C for 24 h under nitrogen atmosphere, and then the solution was poured into 500 mL ethanol to precipitate the copolymer. The obtained copolymer was washed with ethanol for three times, then filtered and dried at 80 °C overnight to give product with 95% yield.

2.4. Membrane preparation

C-SPEEK and BI-SPEEK membranes were prepared by casting their DMF solution (5–10%) onto the clean flat glass substrates and dried in vacuum at 50 °C for 24 h. The resulting membranes were removed from the glass plate and were acidified in 1.0 M HCl solutions overnight, the membranes in acid form were then rinsed with deionized water to remove any excess acid.

2.5. Copolymers characterization

1H NMR spectrometer was measured on a 500 MHz Bruker Avance 510 spectrometer at 298 K with deuterated dimethyl sulfoxide ($DMSO-d_6$) as the solvent and tetramethylsilane (TMS) as the standard. The thermal degradation processes were investigated

using Pyris 1TGA (Perkin-Elmer) thermogravimetric analyzer. The TGA measurements were carried out under a nitrogen atmosphere using a heating rate of 10 °C min^{-1} from 50 to 720 °C.

2.6. Characterization of the membranes

2.6.1. Water uptake and ion-exchange capacity of the membranes

The membranes were dried at 80 °C under vacuum for 12 h until constant weight as dry materials were obtained. They were immersed into deionized water at desired temperature for 24 h. Then the membranes were taken out, wiped with tissue paper, and quickly weighted on a microbalance. Water uptake (WU) of the membranes was calculated from:

$$WU (\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where W_d and W_s are the weight of dry and corresponding water-swollen membranes, respectively.

Ion exchange capacity (IEC) was determined through titration. The membranes in the H^+ form were immersed in a 1 M NaCl solution for 48 h to liberate the H^+ ions (the H^+ ions in the membrane were replaced by Na^+ ions). The H^+ ions in solution were then titrated with 0.01 M NaOH using phenolphthalein as an indicator. The IEC was calculated from:

$$IEC = \frac{\text{consumed NaOH (mL)} \times \text{molarity NaOH}}{\text{weight of dry membrane}} \quad (\text{meg g}^{-1}) \quad (2)$$

2.6.2. Mechanical properties

The mechanical properties of the membranes were measured by SHIMADU AG-I 1KN at the test speed of 2 mm min^{-1} , the size of the specie is 15 mm \times 4 mm. For each testing, three measurements at least were recorded and average value was calculated.

2.6.3. Oxidative stability

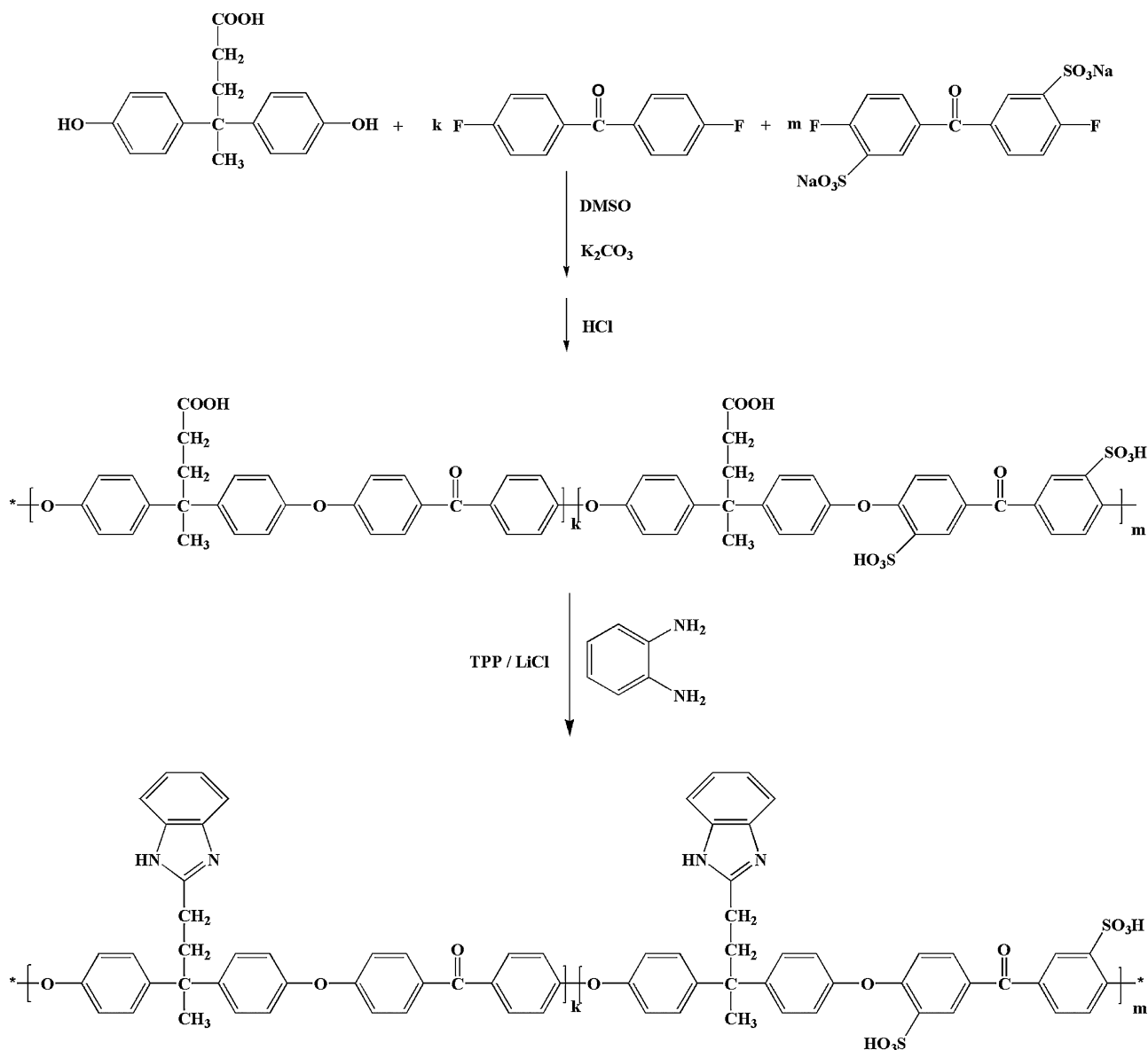
Oxidative stability of the membranes was tested by immersing the films into Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C. The oxidative stability was evaluated by recording the time when the membranes began to break.

2.6.4. Atomic force microscopy (AFM) analysis

AFM measurement was carried out with a commercial instrument (Digital Instrument, Nanoscope IIIa, Multimode) under ambient conditions at room temperature. The tapping mode image was measured at room temperature in air with the microfabricated rectangle glass cantilevers (Nanosensor).

2.6.5. Proton conductivity

The proton conductivity (σ) of each membrane was measured using an electrode system that contained a four-probe cell connected to an impedance/gain-phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287, Farnborough Hampshire, ONR, UK). The membranes were sandwiched between two pairs of gold-plate electrodes. The membranes and the electrodes were set in a Teflon cell and the distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water for measurement. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. All samples were equilibrated in water for at least 24 h before the conductivity measurements. At a given temperature, the samples were equilibrated for at least 30 min before any measurement. Repeated measurements were taken at that given temperature with 10 min interval until no more change in conductivity was observed. The proton conductivity of the membrane was calculated from the observed sample resistance



Scheme 1. The synthesis of C-SPEEK and BI-SPEEK copolymers.

from the relationship:

$$\sigma = \frac{L}{RS} \quad (3)$$

where σ is the proton conductivity (in S cm^{-1}), L is the distance between the electrodes used to measure the potential ($L = 1$ cm), R is the impedance of the membrane (in ohm), which was measured at the frequency that produced the minimum imaginary response, and S is the membrane section area (in cm^2).

2.6.6. Methanol permeability

The methanol permeability was determined using a diffusion cell described in the literature [29,30]. This cell consisted of two reservoirs, each with a capacity of approximately 100 mL, separated by a vertical membrane. Prior to testing, the membranes were immersed in deionized water for at least 12 h. Initially, reservoir V_A contained 10 M methanol–water solution, and reservoir V_B contained pure deionized water. The magnetic stirrers were used continuously during the measurement. Methanol concentrations in the water cell were determined by using a SHTMADU GC-8A

chromatograph. Methanol permeability was calculated in formula:

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0) \quad (4)$$

where A (in cm^2), L (in cm) and V_B (in mL) are the effective area, the thickness of the membranes and the volume of permeated reservoirs, respectively. C_A and C_B (in mol m^{-3}) are the methanol concentration in feed and in permeate, respectively. DK (in $\text{cm}^2 \text{ s}^{-1}$) denotes the methanol permeability.

3. Results and discussion

3.1. Copolymer synthesis

Condensation reaction between 1,2-diaminobenzene and carboxylic acid is universal method to synthesize benzimidazole unit [31,32]. As shown in Scheme 1, a series of C-SPEEKs with different DS were first synthesized by aromatic nucleophilic substitution reactions. Subsequently, sulfonated poly(ether ether ketone) copolymers with pendant benzimidazole group were synthesized by a reaction between carboxylic acid group and 1,2-

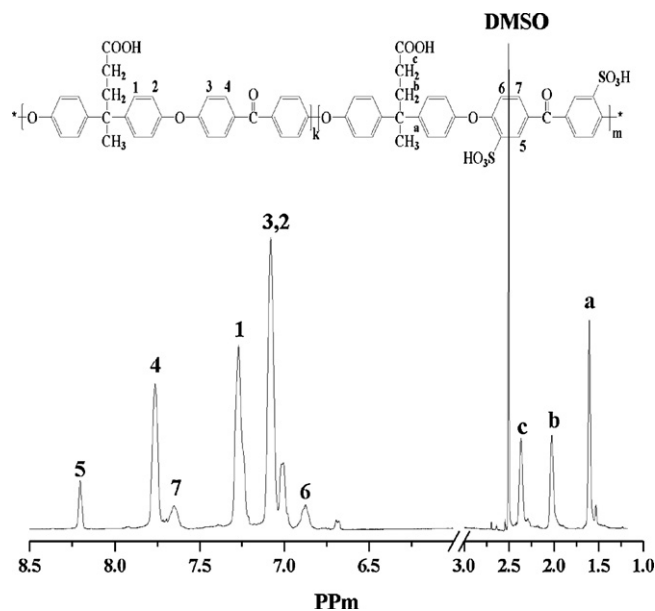


Fig. 1. ^1H NMR spectrum of C-SPEEK-3 in DMSO-d_6 .

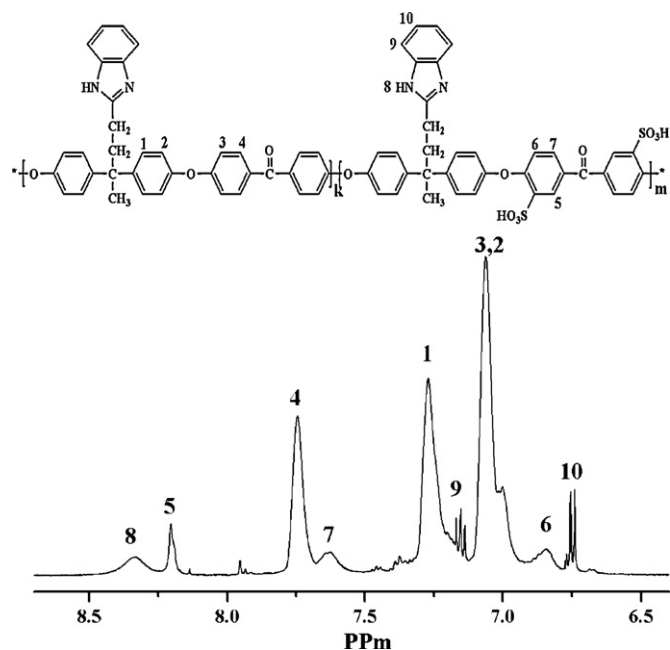


Fig. 2. ^1H NMR spectrum of BI-SPEEK-3 in DMSO-d_6 .

diaminobenzene using TPP as a dehydration agent. Lithium chloride was dispersant which enhanced the dissolution of the product in DMF. To avoid the occurrence of crosslinking, the reaction was first carried out at a lower temperature of 100°C for 3 h to form a single C–N bond between the carboxylic acid group and one amino group of 1,2-diaminobenzene, then the temperature was increased gradually to 150°C and remained at this temperature for 24 h to form C=N bond between the carboxylic carbon atom and the other amino group of 1,2-diaminobenzene.

Chemical structure of the copolymer was further confirmed by ^1H NMR. Figs. 1 and 2 show ^1H NMR spectra of C-SPEEK-3 and BI-SPEEK-3, respectively. As shown in Fig. 1, the signal at 8.18 ppm was assigned to the aromatic hydrogen atoms (H_5) at the ortho position to the electron-withdrawing $-\text{SO}_3\text{H}$ groups. The peaks at 2.36, 2.04 and 1.59 ppm were assigned to the hydrogen atoms of aliphatic side chain, respectively. The new peaks at 8.34, 7.18 and 6.72 ppm in Fig. 2 corresponded to the hydrogen atoms of benzimidazole groups, respectively. Thus the ^1H NMR spectrum indicated BI-SPEEK copolymers were synthesized successfully.

3.2. IEC and water uptake

IEC values for various C-SPEEKs and BI-SPEEKs were tested as listed in Table 1. As expected, these values increased with increasing DS. It should be noted that IEC values of BI-SPEEKs were much lower than that of C-SPEEKs with the same DS. Sulfonic acid group of SPEEK is strong enough to protonate the nitrogen

atom of benzimidazole. This gives rise mainly to an ionic interaction between protonated benzimidazole and deprotonated sulfonic group that can be further stabilized by the formation of hydrogen bonds between protonated benzimidazole and deprotonated sulfonic groups. As the result, the proton cannot be replaced by Na^+ due to the strong ionic interaction between sulfonic acid and benzimidazole groups of the copolymer. The same behaviour was observed by Rozier and Mercier groups [33,34].

Fig. 3 shows the water uptake of membranes at different temperature. As expected, the water uptake values of all membranes increased with increasing temperature and IEC. The water uptake observed for BI-SPEEK membranes were much lower than that of C-SPEEK with the same DS. For example, BI-SPEEK-4 showed lower water uptake (41.4%) than that of C-SPEEK-4 (169.2%) at 80°C . The difference of water uptake between BI-SPEEKs and C-SPEEKs can be attributed to their different molecular structure. The hydrophilic carboxylic acid groups on the pendent of the copolymer lead to the increasing of the water uptake of membranes [35]. Compared to C-SPEEK, BI-SPEEK copolymers contain basic benzimidazole groups, which preferentially interact with sulfonic acid groups and decrease the amount of free sulfonic acid group available to form hydrogen bond with water molecules. This result indicated that introducing basic benzimidazole group into the copolymer was an effective method for decreasing water uptake for high DS membranes.

Table 1

DS, IEC, water uptake, methanol permeability, proton conductivity and oxidation stability of the membranes.

Samples	DS	IEC (meq g^{-1})	WU (%)		DK ($\times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$)	σ (S cm^{-1})		Oxidative stability (h)
			25°C	80°C		25°C	80°C	
C-SPEEK-2	0.4	0.73	14.8	17.9	0.09	0.007	0.06	
C-SPEEK-3	0.6	1.13	17.3	61.6	0.38	0.035	0.12	17
C-SPEEK-4	0.8	1.38	50.1	169.2	0.86	0.073	0.16	1.5
C-SPEEK-5	1.0	1.67	76.4	506.9	1.48	0.088	0.13	1
BI-SPEEK-2	0.4	0.69	8.2	9.5	0.05	0.005	0.02	0.25
BI-SPEEK-3	0.6	0.83	11.9	12.6	0.07	0.006	0.03	40
BI-SPEEK-4	0.8	1.07	13.9	41.4	0.12	0.025	0.08	7
BI-SPEEK-5	1.0	1.14	23.6	256.3	0.49	0.045	0.14	4.5
Nafion 117	–	0.92	22	38	2.38	0.08	0.10	2.5

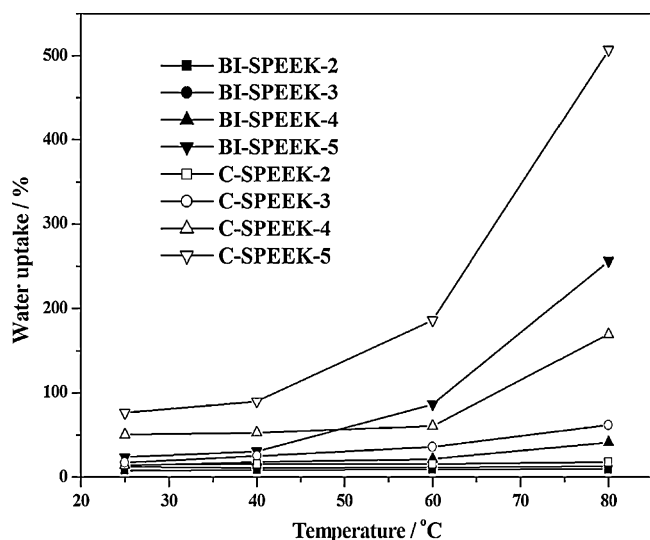


Fig. 3. Temperature dependence of water uptake values of various BI-SPEEK and C-SPEEK membranes.

3.3. Thermal and mechanical properties

The thermal stability of the C-SPEEKs and BI-SPEEKs was investigated by the thermogravimetric analysis (TGA). As shown in Fig. 4, all the SPEEK membranes exhibited three-step degradation pattern. The first weight loss occurred between 100 and 200 °C, which was attributed to the loss of moisture absorbed by the sulfonic acid groups. The second weight loss from 240 to 400 °C was closely associated with the thermal degradation of the sulfonic acid groups. The desulfonation temperature (320 °C) of BI-SPEEKs was higher than that (250 °C) of C-SPEEKs. As mentioned above, deprotonated sulfonic group can be stabilized by the formation of hydrogen bonds between protonated benzimidazole and deprotonated sulfonic groups, which might be the reason for increase in thermal stability in the second step. The last weight loss was observed around 450 °C, which was attributed to the degradation of main backbone.

Table 2 shows the mechanical properties of the SPEEK membranes. The C-SPEEK membranes had tensile modulus of 808.54–1293.74 MPa, elongations at break of 4.38–17.07, and tensile strength of 31.30–46.47 MPa. Compared to C-SPEEK membranes, BI-SPEEK membranes also showed excellent mechanical properties

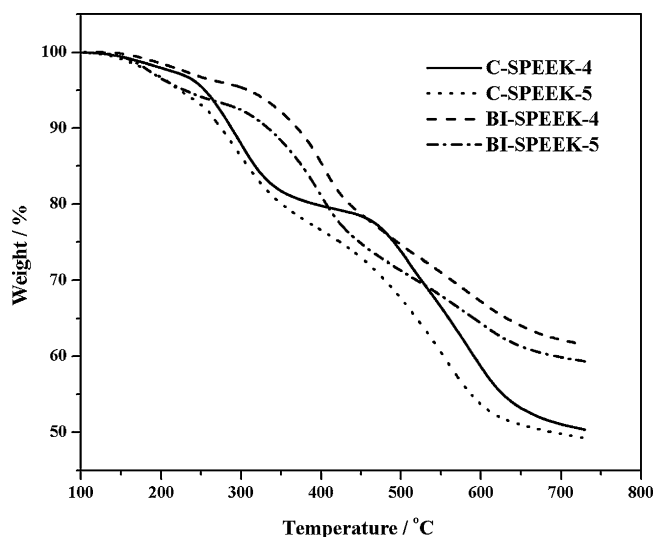


Fig. 4. TGA thermodiagram of C-SPEEK and BI-SPEEK copolymers.

Table 2

Mechanical properties of C-SPEEK and BI-SPEEK membranes.

Samples	Tensile modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)
C-SPEEK-2	1293.74	10.29	46.47
C-SPEEK-3	1196.79	4.38	41.76
C-SPEEK-4	808.54	6.06	31.30
C-SPEEK-5	1162.60	17.07	46.30
BI-SPEEK-2	1404.73	9.99	47.52
BI-SPEEK-3	1164.16	4.84	37.77
BI-SPEEK-4	1080.25	5.79	35.82
BI-SPEEK-5	1459.98	15.63	56.56

with tensile modulus of 1080.25–1459.98 MPa, elongations at break of 4.84–15.63 and tensile strength of 35.82–56.56 MPa. Comparison between C-SPEEK and BI-SPEEK membranes revealed that most BI-SPEEK membranes were mechanically stronger than C-SPEEK membranes. It is assumed that the interaction between sulfonic acid and benzimidazole groups restrict the molecular motion of the polymer chains resulting in stronger membranes.

3.4. Oxidative stability

The oxidative stabilities of the C-SPEEK and BI-SPEEK membranes were investigated by measuring the elapsed time, when a membrane began to dissolve after immersion into Fenton's reagent (3% H₂O₂ aqueous solution containing 2 ppm FeSO₄) at 80 °C. As listed in Table 1, BI-SPEEK membranes showed much more improved oxidative stabilities than C-SPEEK membranes. For example, BI-SPEEK-4 membrane endured for 4.5 h before beginning to dissolve. C-SPEEK-4 membrane only endured for 1 h, and then it began to dissolve. The introduction of hydrophobic benzimidazole groups decreases the water uptake of the membrane, while the basic benzimidazole groups can interact with sulfonic acid groups by hydrogen bond (Fig. 7), which stabilizes the sulfonate groups (SO₃⁻) when they dissociate.

3.5. Morphology analysis

Tapping mode phase images of the acid-form C-SPEEK-4 and BI-SPEEK-4 were recorded under ambient condition on a 500 nm × 500 nm size scale to investigate the microphase-separated structure (Fig. 5). The dark regions in the images were assigned to a soft structure, corresponding to the hydrophilic sulfonic acid groups containing water. The bright phases in the images were attributed to a hard structure, corresponding to hydrophobic polymer matrix. The hydrophilic domain sizes of C-SPEEK-4 were around 22 nm, while BI-SPEEK-4 made clusters of hydrophilic domains whose sizes were around 17 nm. These observations suggested that the interaction between benzimidazole groups and sulfonic acid groups decreased the free volume of the sulfonic acid groups, which is able to contain water.

3.6. Proton conductivity and methanol permeability

Proton conductivities of all hydrated membranes were measured in the temperature range of 25–80 °C. The conductivity data are tabulated in Table 1. As expected, the conductivities of all the membranes increased with increasing IEC and DS. BI-SPEEK membranes showed much lower conductivities than those of C-SPEEK membranes with the same DS. This can be attributed to the interactions between the sulfonic acid and benzimidazole groups. This kind of interaction decreases the amount of free sulfonic acid group available to release and transport protons. The decrease of proton conductivity was also attributed to the lower water uptake values of BI-SPEEK membranes.

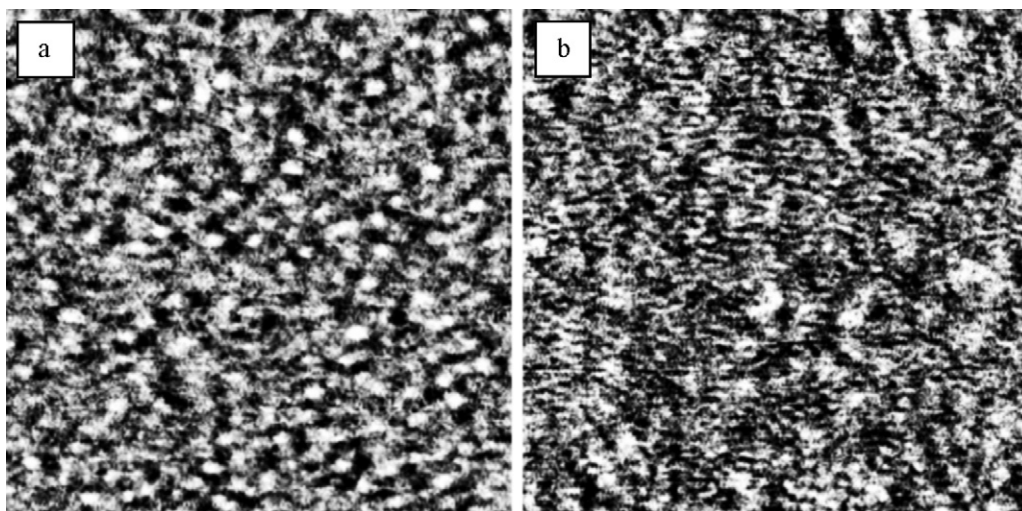


Fig. 5. AFM tapping phase images for acid-form C-SPEEK-4 and BI-SPEEK-4 membranes. Scan boxes are 500 nm × 500 nm, and phase scale is 2.0°.

Proton conduction mechanism of SPEEK with pendant benzimidazole groups under humidified conditions was attributed to both Grotthuss-type and vehicle-type mechanism. The vehicle-type mechanism could occur in the hydrophilic regions formed by the clustering of sulfonic acid groups, and the Grotthuss-type mechanism could occur in the regions where benzimidazole groups interact with sulfonic acid groups by hydrogen bond [36,37]. Fig. 6 shows the temperature dependence of the proton conductivity. All the membranes displayed increased proton conductivities with increasing temperature. As mentioned above, the proton conductivity of BI-SPEEK was determined by two proton conduction mechanisms. Under humidified conditions, the vehicle-type mechanism was predominant due to the availability of sulfonic acid groups, while the Grotthuss-type mechanism provided an enhancement (Fig. 7). However, benzimidazole group was much more basic than sulfonic acid group, which should hinder to a great extent proton hopping from protonated benzimidazole to deprotonated sulfonic acid groups and consequently the Grotthuss-type mechanism too.

Table 1 lists the methanol permeability of the C-SPEEK and BI-SPEEK membranes. The methanol permeability increased with increasing IEC and water uptake values. BI-SPEEKs showed much

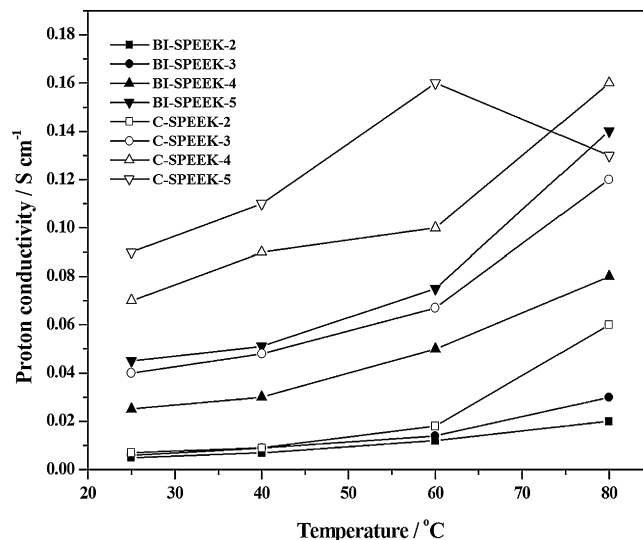


Fig. 6. Proton conductivity of BI-SPEEK membranes at different temperatures under fully hydrated conditions.

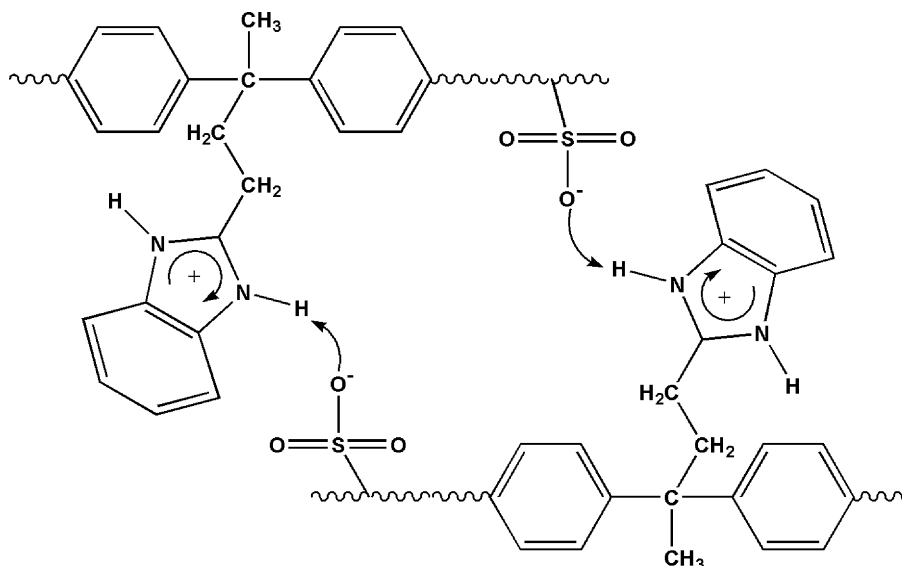


Fig. 7. Illustration of the assistance of the pendant benzimidazole groups in the Grotthuss-type proton conduction mechanism in the membranes.

lower methanol permeability than C-SPEEK with the same DS. This can also be interpreted by the formation of base–acid complex between sulfonic acid and benzimidazole groups. The formation of base–acid complex reduces vacant space that absorbs free water molecules and induces a much denser structure to act as a methanol barrier [38]. Moreover, BI-SPEEK-4 membrane, which had comparable water uptake values and proton conductivity to Nafion 117, showed one order of magnitude lower methanol permeability than Nafion 117.

4. Conclusion

A series of novel SPEEK copolymers with pendant benzimidazole groups have been prepared as proton conductive materials. The electrolyte properties of BI-SPEEKs were investigated and compared to C-SPEEKs. Because of the interaction between sulfonic acid and basic benzimidazole groups, thermal stability and oxidative stability of the copolymers were improved. Meanwhile, the water uptake values and methanol permeability of the BI-SPEEK membranes were much lower than those of C-SPEEK membranes with the same DS, due to the acid–base interaction. For example, the BI-SPEEK-4 film showed a conductivity of 0.08 S cm^{-1} at 80°C and methanol permeability of $1.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ compared with $2.38 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for Nafion 117. Combined with its good thermal stability and high mechanical properties, it shows potential application as PEM material in DMFC.

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