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High-performance proton exchange membranes for direct methanol fuel cells based on SPEEK/polybenzoxazine crosslinked structure

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Abstract

Sulfonated poly(etheretherketone)/polybenzoxazine (SPEEK/PBa) crosslinked blends were prepared as a proton exchange membrane (PEM) for direct methanol fuel cells (DMFCs) application. SPEEK catalyzed the ring-opening polymerization of Benzoxazine (Ba) monomers and then reacted with PBa to form a crosslinked membrane with greatly improved mechanical integrity. Extraction testing, Fourier-transform infrared, and X-ray photoelectron spectroscopy results indicate that the crosslinking reaction took place at $150^{o}C$ between the SPEEK and PBa. The crosslinked SPEEK/PBa structure gives a better dimensional stability, thermal stability, and mechanical integrity than SPEEK membrane alone. The proton conductivity of the SPEEK/PBa-15% membrane is 4.25×10^{-3} S/cm at $30^{o}C$, and reaches 2.46×10^{-2} S/cm at $80^{o}C$. The methanol diffusion coefficient of the SPEEK/PBa-15% is reduced by 93% when compared to Nafion-117 membrane under the same

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testing conditions. The maximum selectivity at $80^{\circ}C$ is 4.45×10^3 S s cm^{-3} for SPEEK/PBa-15%, which is nearly 1.3 times higher than that of a Nafion-117 membrane. The observed excellent properties of SPEEK/PBa membranes are attributed to the uniformly crosslinked structure of SPEEK/PBa and the rigid backbone of PBa.

Keywords: Proton exchange membrane, Sulfonated poly(etheretherketone), Polybenzoxazine, Crosslinked structure

Introduction

Direct methanol fuel cells (DMFCs) have been considered ideal fuel cell systems for portable devices, such as cell phones and laptops, and for transportation fuel needs due to their convenient fuel supply, quick start time, and instant refueling [1-3]. Proton exchange membrane (PEM), which is one of the most important components of a DMFC system, needs to possess several key attributes to ensure good DMFC performance, including excellent dimensional stability, good mechanical and thermal properties, high proton conductivity, manufacturability, and low cost [4,5]. Perfluorinated sulfonic acid membranes, in particular the Nafion® series from DuPont, are the most widely used commercial PEM because of their excellent chemical and electrochemical stability together with a high proton conductivity in hydrated state. However, their drawbacks, such as high cost, severe drop in Young's modulus, and dimensional instability under hot-wet conditions, limit their applications in DMFCs [6]. Therefore, many attempts have been made to develop new PEM materials based on sulfonated aromatic polymers [7-10].

Sulfonated poly(etheretherketone) (SPEEK) is an excellent option among PEM materials due to its excellent thermal stability, good mechanical properties, and low cost. Generally, a high degree of sulfonation (DS) of SPEEK is required to achieve sufficient proton conductivity. However, high DS

will decrease dimensional stability, methanol diffusion, and mechanical properties of the membrane. Crosslinking has been demonstrated to be an efficient and simple approach to restrict methanol diffusion, enhance mechanical properties, and improve dimensional stability of SPEEK [11-13]. Rhodena *et al.* [14] reported that crosslinking of high DS SPEEK with 1,4-benzenedimethanol could form a hydrophobic polymer backbone, which increased mechanical strength of the membrane for hydrogen PEM fuel cells. Similar findings were shown by Lee *et al.* [15] and Zhu *et al.* [16]. Lately, Choudhary *et al.* [17] observed a much better hydrolytic stability of SPEEK/poly(ethylene glycol) crosslinked membrane compared to SPEEK membranes.

Polybenzoxazines (PBa) have gained substantial interest because of their excellent thermal and hydrophobic properties, along with attractive mechanical, chemical, and electrical properties [18, 19]. Therefore, PBa hold great promises in applications, such as composites, coatings, adhesives, and microelectronic encapsulants [20]. Herein, we have prepared a novel PEM material based on blends of sulfonated poly(etheretherketone) (SPEEK) with crosslinked polybenzoxazine (SPEEK/PBa). The morphology and crosslinking structure of the blend were investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). Properties of proton exchange membranes including membrane morphology, swelling behavior, thermal stability, mechanical strength, methanol permeability, proton conductivity, and selectivity were investigated in detail. The superior properties of SPEEK/PBa for DMFC applications are discussed.

Experimental

Materials

PEEK (Industrial grade, 1000P) was provided by EVONIK (Germany). Concentrated sulfonic acid (Chemical pure, CP, 95%-98%) was obtained from Changzheng Chemical Reagent Co. (Chengdu,

China). Dimethyl-d6 sulfoxide (DMSO-d6, chromatographically pure) was purchased from Sigma-Aldrich (St. Louis, USA). Dimethyl formamide (DMF, CP), dimethylacetamide (DMAc), acetone (CP), bisphenol A (AR), aniline (AR) and paraformaldehyde (AR) were all purchased from Kelong Chemical Reagent Co. (Chengdu, China) and were used as-received.

Sulfonation of PEEK

The sulfonation of PEEK was conducted by using concentrated H_2SO_4 (95%-98%), which is similar to the procedure reported elsewhere [21,22]. Five grams of PEEK were dissolved in 100g of concentrated H_2SO_4. The solution was stirred at 70°C for 6h. The acidic solution was transferred drop-wise into 500mL of distilled water cooled in an ice water bath, forming precipitation of the SPEEK polymer. The SPEEK polymer was washed with distilled water until neutrality was reached and then dried at 90°C for 12 h, followed with vacuum dry at 100°C for 8h. The structure of SPEEK is shown in Scheme 1. The degree of sulfonation (DS) of the obtained SPEEK was calculated to be 64.0% by ^{1}H NMR spectroscopy [23].
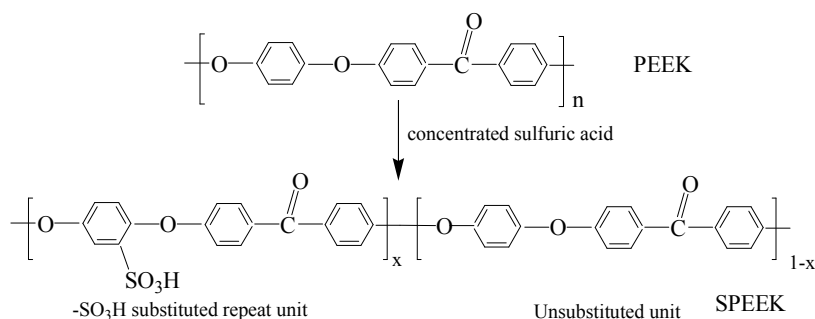
Scheme 1. Sulfonation reaction and chemical structure of SPEEK.

Preparation of Benzoxazine monomer

Benzoxazine was prepared by bisphenol A, aniline, and paraformaldehyde using a solution method similar to the reported procedure [24]. Bisphenol A (1 mol), paraformaldehyde (4.4 mol), and 200 ml toluene were heated at 65°C with mechanical stirring. Aniline (2 mol) was then added drop-wise into

the mixture. The reaction was conducted at 100°C for 2h, and distilled for another 2h at 110-120°C to remove toluene. The solid product was yellow at room temperature.

^{1}H NMR (DMSO-d$_6$, ppm: δ, frequency: 300MHz) of Ba showed δ=1.53 (s, C-CH$_3$), δ=4.61 (s, C-CH$_2$-N-), δ=5.40 (s, N-CH$_2$-O-), δ=6.60-7.25 (14H, Ar). FTIR spectra (KBr) of Ba exhibited: 3034 cm^{-1} (C-H stretching vibration in aromatic), 2875 cm^{-1} and 2965 cm^{-1} (asymmetric and anti-symmetry C-H in –CH$_3$), 1499 cm^{-1} and 1598 cm^{-1} (substituted benzene ring stretching), 1233 cm^{-1} (Ar-O-C symmetric stretching), 1154 cm^{-1} (C-N-C asymmetric stretching), 942 cm^{-1} (C-H out-of-plane in –CH$_3$), 752 and 891 cm^{-1} (C-H out-of-plane bend vibration in tri-substituted benzene), 693 cm^{-1} (C-H out-of-plane bend vibration in mono-substituted benzene). According to Differential Scanning Calorimetry (DSC) (TA Q20, USA) results, Ba monomers started to polymerize at 233°C and reached the peak reaction temperature at 254°C (Fig. 1SI).
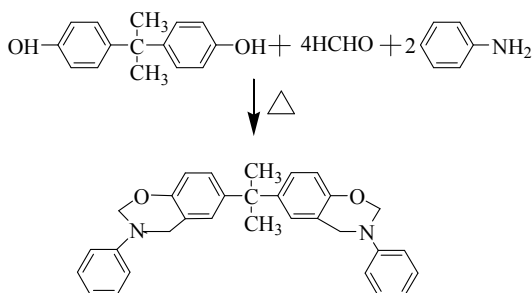
Scheme 2. Chemical structure of Benzoxazine monomer.

Preparation of crosslinked membrane

Solutions of the SPEEK and Ba in DMAc were cast onto a glass mold and dried in an air-circulating oven at 90°C for 12h, followed by vacuum dry at 100°C for 24h. The obtained membranes were then heated at 150°C for 3h. The crosslinked membranes containing 5, 10, 15, 20, and 25 wt.% of PBa were prepared and denoted as SPEEK/PBa-5%, SPEEK/PBa-10%, SPEEK/PBa-15%, SPEEK/PBa-20% and SPEEK/PBa-25%, respectively.

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Characterization

FTIR (Nicolet 6700) and XPS (Kratos XSAM 800; photon energy (Al Ka) =1,486.6 eV; P=12 kW×1 mA.) were utilized to characterize the chemical structure of SPEEK/PBa membranes. Energy dispersive spectroscopy (EDS) study on the tensile fracture surface of SPEEK/PBa-15% membrane was performed through a JEOL JSM-5009LV field emission scanning electron microscope (FE-SEM) at an accelerating voltage of 5 kV. Prior to SEM imaging, the fracture surface was sputtered with a thin layer of Au-Pt to provide conductive surfaces. TEM was performed using a JEOL 2010 high-resolution transmission electron microscope operating at an accelerating voltage of 200 kV. To stain the sulfonic acid (R-SO$_3$H) group in the membrane, the membrane was immersed in 1N of lead acetate [Pb(CH$_3$COO)$_2$] solution for 48h to form [Pb(R-SO$_3$)$_2$)] and then rinsed with deionized water. A Reichert-Jung Ultracut-E microtone was utilized to prepare thin sections with 70-100 nm in thickness for TEM imaging.

The tensile properties of the dry and wet membranes were characterized using a WDW-1000 universal testing machine (Zhejiang, China) at a crosshead speed of 50 mm/min. The wet membranes were obtained by immersing the dry membranes in deionized water at 30°C for 12h. Thermo-gravimetric analysis (TGA) of pristine SPEEK and SPEEK/PBa crosslinked membranes were performed by using a NETZSCH 209 F1 (Selb, Germany) instrument from room temperature to 700°C at a heating rate of 20 ^{o}C/min with nitrogen flushed at 60 ml/min.

The degree of Ba homopolymerization and further crosslinking between SPEEK and PBa was determined by acetone and DMF extraction (reflux 48 h) conducted with Soxhlet extractors. The homopolymerization degree of Ba (HPD) was calculated using equation (1):

$$HPD(\%) = \frac{M_0 - (M_1 - M_2)}{M_0} \times 100\% \quad (1)$$

The degree of crosslinking (DCL) of SPEEK/PBa membrane was calculated by equation (2):

$$DCL(\%) = \frac{M_3 - M_0}{M} \times 100\% \qquad (2)$$

where M_0 is the total mass of Ba contained in SPEEK/Ba membrane; M_1 is the mass of crosslinked SPEEK/PBa membrane before acetone extraction; M_2 is the mass of crosslinked SPEEK/PBa membrane after acetone extraction; M_3 is the mass of insoluble materials of crosslinked SPEEK/PBa membrane in DMF extraction; M is the original mass of crosslinked SPEEK/PBa membrane before DMF extraction. M_0, M_1, M_2, M_3, and M were obtained when the samples dried to a constant weight under vacuum.

Water uptake, swelling behavior, and methanol permeability

Water resistance of the membranes was evaluated by water uptake experiments. The prepared membranes were immersed in deionized water at $30^{\circ}C$ for 12 h or $80^{\circ}C$ for 1 h. The water uptake and swelling ratio of membranes in water were calculated using equations (3) and (4) respectively:

$$U_w = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100\% \qquad (3)$$

$$S_v = \frac{V_{wet} - V_{dry}}{V_{dry}} \times 100\% \qquad (4)$$

where M_{dry} is the mass of dry membrane, M_{wet} is the mass of membrane after immersion in deionized water, V_{dry} is the volume of the dry membrane, and V_{wet} is the volume of the membrane after immersion in deionized water. The experiments were carried out in triplicate to account for experimental error. The swelling ratio of the membranes in methanol-water solution was measured and calculated using a similar method. The prepared membranes were immersed in 2 M methanol-water solution at $30^{\circ}C$ for 1 h. Then, the swelling ratio was calculated by equation (4).

The methanol permeability of the proton exchange membranes was determined by using a sealed two-compartment stainless steel cell. Compartment A was filled with 2 M methanol-water solution

while compartment B was filled with deionized water. The membrane was placed in between these two compartments. The sample solution from compartment B was taken at a time interval (Δt) of 8h at 30 or 80°C. The methanol concentration in each solution was analyzed by gas chromatography (GC) using Restek Rtx-5 column. The methanol permeability (*P*) was calculated using equation (5):

$$C_{B(t)} = \frac{A.P}{V_B \cdot L} C_A \Delta t \qquad (5)$$

Where C_A and $C_{B(t)}$ are the methanol concentration in compartment A and B (M), respectively, Δt is the permeation time (s), A is the exposed area of the membrane (cm^2), L is the membrane thickness (cm), and V_B is the solution volume in compartment A or B (300 cm^3).

Ion exchange capacity (IEC) and proton conductivity

The ion exchange capacity (IEC) of the membranes was evaluated *via* a typical titration method. The pre-weighted membrane was immersed in 1.0 M NaCl solution for 48 h to liberate the H$^+$ by exchanging with Na$^+$. The dissociated H$^+$ was then titrated with 0.01 M NaOH solution using phenolphthalein as the end point indicator. The IEC value was calculated by equation (6):

$$IEC = \frac{V_{NaOH} \times C_{NaOH}}{M_{dry}} \times 1000 \quad (\text{mmol}\cdot\text{g}^{-1}) \qquad (6)$$

where V_{NaOH} and C_{NaOH} are the volume and molar concentration of NaOH solution consumed in the titration, respectively. M_{dry} is the weight of the dry membrane.

The in-plane proton conductivity of the membranes was measured in two-point-probe conductivity cells by the AC Electrochemical Impedance Spectroscopy (EIS) method. The EIS was recorded with a frequency response analyzer (FRA, Compactstat, IVIUM Tech.) over a frequency range of 1-10^5 Hz with oscillating voltage of 20 mV. All the membranes were immersed in deionized water for 12 h prior to measurement. The in-plane conductivity of the membrane was calculated by equation (7):

$$\sigma = \frac{L}{A \cdot R} (S \cdot cm^{-1}) \qquad (7)$$

where L is the distance between the probes, A (cm^2) is the cross-sectional area of the testing membrane, and R (Ω) is the membrane resistance obtained from the FRA.

Results and discussion

Crosslinked structure and reaction mechanism

The solvent extraction results on the SPEEK/PBa membranes are listed in Table 1. Benzoxazine monomer is dissolved in both acetone and DMF. PBa is insoluble in either. SPEEK is soluble in DMF but insoluble in acetone. SPEEK/PBa membranes are found to be insoluble in acetone but partially soluble in DMF, suggesting some degree of crosslinking between PBa and SPEEK is present. The partially crosslinked membranes do not show any weight loss after acetone extraction, indicating the complete curing of Ba monomer in the membrane. Also, the mass of insoluble materials after DMF extraction from the SPEEK membrane is found to be higher than that of PBa-containing membrane, which further indicates that some crosslinking reaction between PBa and SPEEK has taken place. The mass of insoluble materials after DMF extraction is increased with increasing Ba content in the membrane. In other words, the degree of crosslinking of SPEEK/PBa membrane is increased with increasing Ba content.

Table 1 Characteristic of SPEEK/PBa membranes.

Samples	Solubility [a]		DCL (%) [b]	HPD (%)[c]
	Acetone	DMF		
SPEEK	●	○	----	----
Ba	○	○	----	----
PBa	●	●	-----	----
Further crosslinking content	●	●	-----	-----
SPEEK/PBa-5%	●	◎	1.1	100
SPEEK/PBa-10%	●	◎	2.3	100
SPEEK/PBa-15%	●	◎	4.0	100
SPEEK/PBa-20%	●	◎	8.7	100
SPEEK/PBa-25%	●	◎	11.8	100

[a] "●": insoluble, "◎": partially soluble, "○": soluble.

[b] DCL, the degree of crosslinking between SPEEK and PBa; Soxhlet extraction for 48h with DMF.

[c] HPD, degree of homopolymerzation of Ba; Soxhlet extraction for 48h with acetone.

The crosslinking reaction was further confirmed by FTIR (Fig. 1). Obviously, the characteristic symmetric and asymmetric absorption bands at 1225 cm^{-1} and 1156 cm^{-1} for Ar-O-C have disappeared after completion of the curing cycle. Meanwhile, the absorption at 1084 cm^{-1} assigned to asymmetric O=S=O vibration becomes weaker, which might be associated with the chemical reaction between SPEEK and Ba. The peak at 3440 cm^{-1} mainly attributed to –OH in –SO$_3$H shifts to 3452 cm^{-1} and became broad. This change is likely due to high density of hydrogen bonding formed between –SO$_3$H in SPEEK and –OH in polymerized Ba.
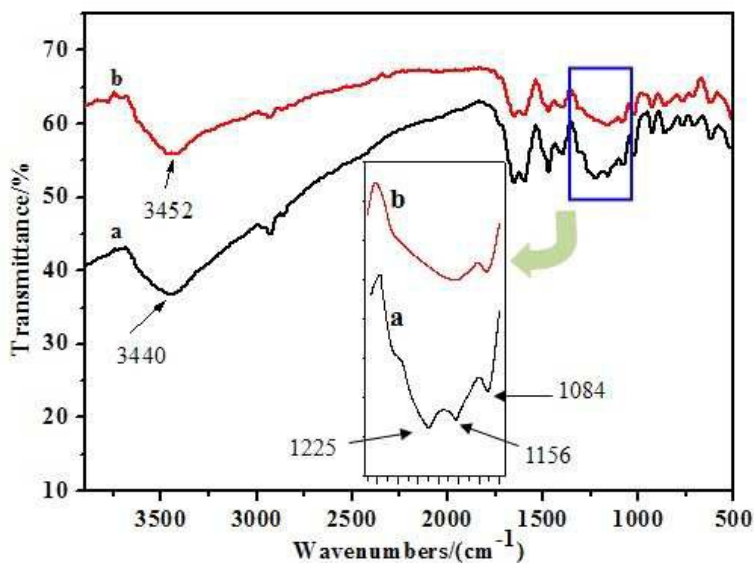
Fig. 1 FTIR spectra of (a) SPEEK/PBa-15% before crosslinking and (b) SPEEK/PBa-15% after

crosslinking.

XPS was used to determine the chemical state of elements in SPEEK/PBa matrix before and

after crosslinking reaction. The C1s, N1s, O1s, and S2p XPS spectra of SPEEK/PBa membranes are

shown in Fig. 2. The C1s spectrum is fitted smoothly into three-component peaks for SPEEK/PBa

membrane before crosslinking. The peaks at 284.61 eV, 285.72 eV and 287.01 eV are associated with

C-$\underline{C}$-C, C-$\underline{C}$-N/C-$\underline{C}$-S, and O-$\underline{C}$-N, respectively [25,26]. The peak at 287.01 eV has disappeared

completely after the crosslinking process, indicating the successful ring opening curing of Ba

monomer in SPEEK matrix. There is no obvious change for the energy spectra of nitrogen, implying

the stable chemical state for N. A similar phenomenon is also observed in the spectrum of O1s (Fig.4

(c)). There is only a 0.02eV shift for Ar-C($\underline{O}$)-Ar and Ar-$\underline{O}$-Ar. However, the peak at 531.61 eV for

Ar-$\underline{O}$-H and $-S(O_2)$-$\underline{O}$-H has moved to 531.76 eV, which could be caused by the chemical reaction of

$-SO_3H$. Interestingly, a new XPS peak of sulfur appears at 169.90 eV, assigned to the formation of

neutral substituent [27], supporting the evidence of reaction between $-SO_3H$ and PBa in SPEEK
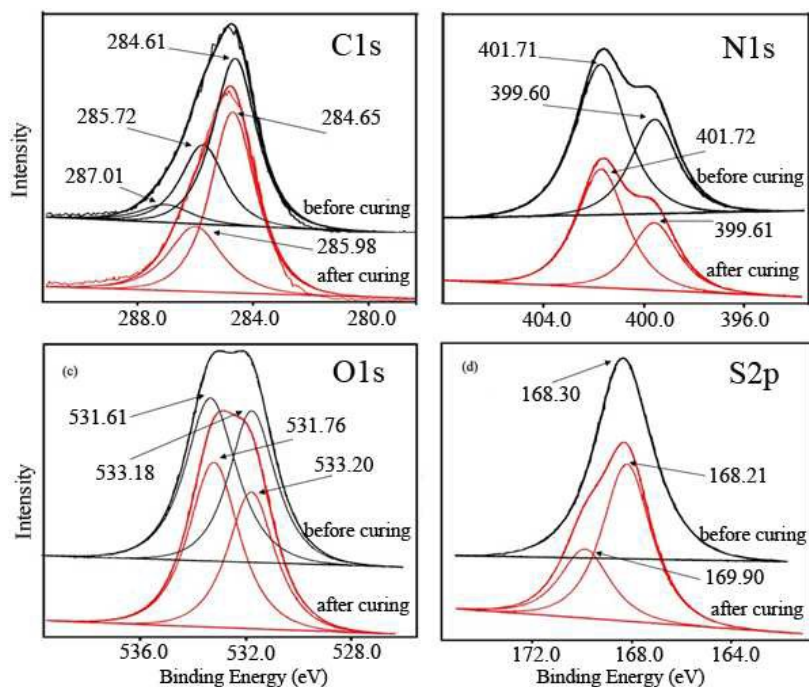
matrix.

Fig. 2 XPS spectra of SPEEK/PBa-15% before and after crosslinking. (a) C1s, (b) N1s, (c) O1s and (d) S2p.

The Ba monomer itself started to polymerize at 233°C and reached the peak reaction temperature at 254°C as determined by DSC (Fig. 1SI). However, the SPEEK/PBa membrane was cured completely at 150 ^{o}C based on the extraction test (Fig. 2SI). Apparently, $-SO_3H$ serves to catalyze the ring-opening polymerization of Ba monomers. Combined with FTIR and XPS results, we propose a catalyzed crosslinking reaction mechanism for SPEEK/PBa membrane. The promotion of ring-opening polymerization of Ba is attributed to the formation of amine stabilizing intermediates catalyzed by SPEEK (Scheme 3, Reaction (a)). The ring-opening of Ba formed the corresponding reversible intermediates of aminomethyl and iminium cations, respectively (Scheme 3, Reaction (b)) [28]. These intermediates react with Ba monomers to give more concentrated intermediates to promote faster polymerization. Furthermore, the molecular chains propagate to form the Mannich bridge structure in ortho-position of *p*-phenol during the ring-opening polymerization of Ba (Scheme 3,

Reaction (c)). According to XPS results, there are two types of electronic states of sulfur, indicating that –SO$_3$H group in SPEEK has subsequently reacted with –OH in PBa (Scheme 3, Reaction (d)). It will favor the formation of a compact crosslinking network.
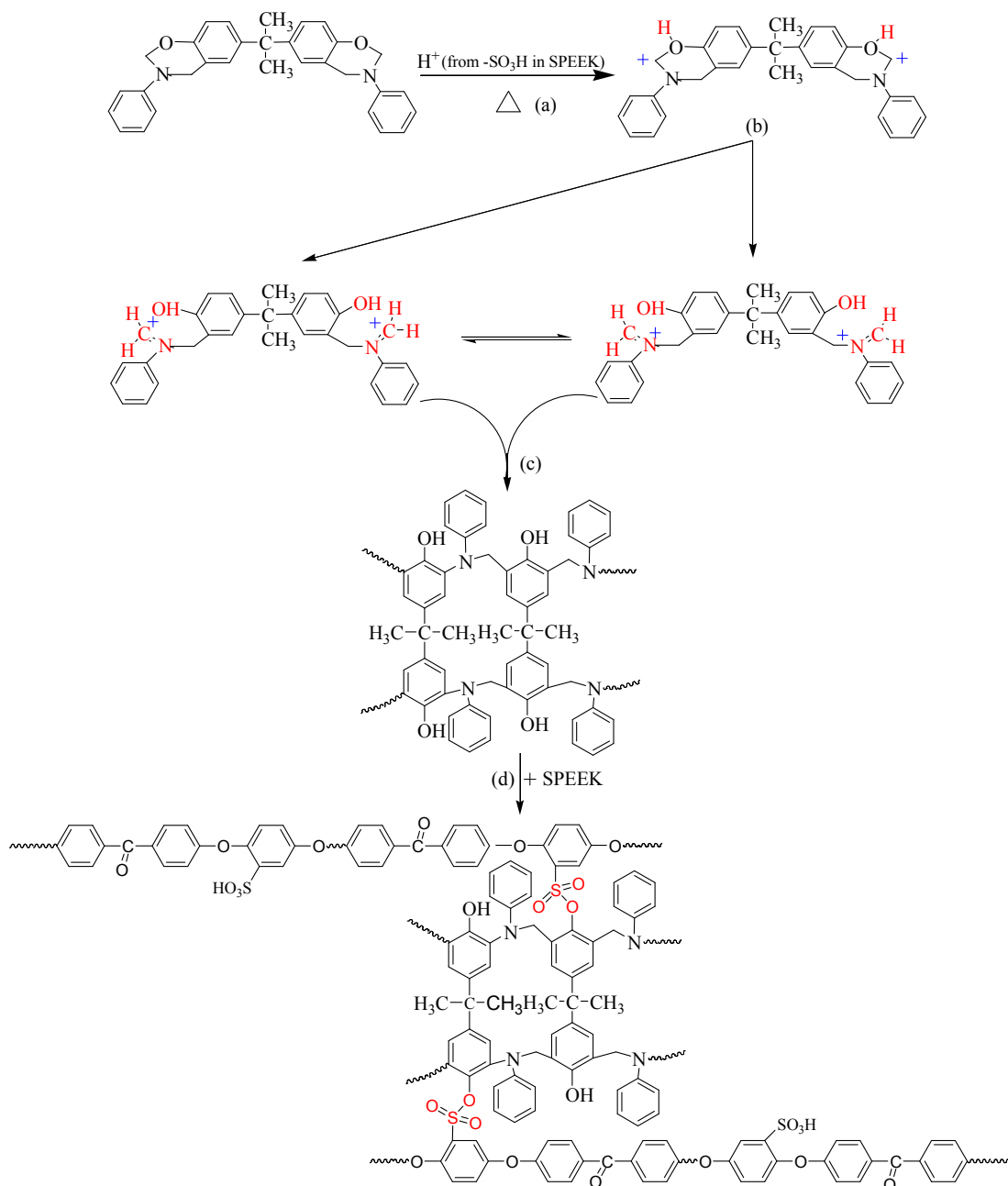
Scheme 3 Possible mechanism scheme for the crosslinking reaction.

Thermal analysis

The TGA curves of SPEEK and SPEEK/PBa membranes are shown in Fig. 3. Obviously, the thermal decomposition behavior of SPEEK is distinguished in three regions. The first one occurs between 190 and 255°C, corresponding to a maximum mass loss rate at 213°C. The weight loss of this region is mainly due to the evaporation of bound water locked by hydrogen bonding. The second thermal degradation with a maximum mass loss rate (T$_{max}$) at 356°C is related to the desulfonation reaction of –SO$_3$H groups. The final mass loss starts approximately at 427°C with T$_{max}$ at 531°C and is attributed to the decomposition of the main chain of SPEEK [29]. All SPEEK/PBa membranes show similar thermal degradation curves with two stages of decomposition.

Water removal stage in SPEEK disappears after the introduction of hydrophobic PBa in SPEEK, which also leads to the decrease in the amount of hydrophilic –SO$_3$H after Ba crosslinking reaction. It is found that the first mass loss region for the crosslinked membranes all occurs between 290 and 410°C with T$_{max}$ approximately at 360°C, indicating that the pyrolysis of sulfonic acid group is not influenced by the crosslinked PBa structure. This implies the presence of –SO$_3$H in SPEEK/PBa matrix as SPEEK. The mass loss between 430 ^{o}C and 630 ^{o}C is associated with the thermal decomposition of the main-chain SPEEK and the crosslinked PBa structure. The rate of mass loss decreases with increase of PBa loading, implying that the PBa crosslinking improves the thermal stability of SPEEK/PBa membranes. The TGA curves clearly reveal that the char yield of the crosslinked membranes increases with PBa loading. The stable intra-molecular hydrogen bonding between –Ar-OH and nitrogen atoms of the Mannich bridge [30] accounts for the excellent thermal stability of SPEEK/PBa membranes. Therefore, the crosslinked structure of SPEEK/PBa exhibits significantly improved thermal stability, making the membranes attractive for fuel cell applications.
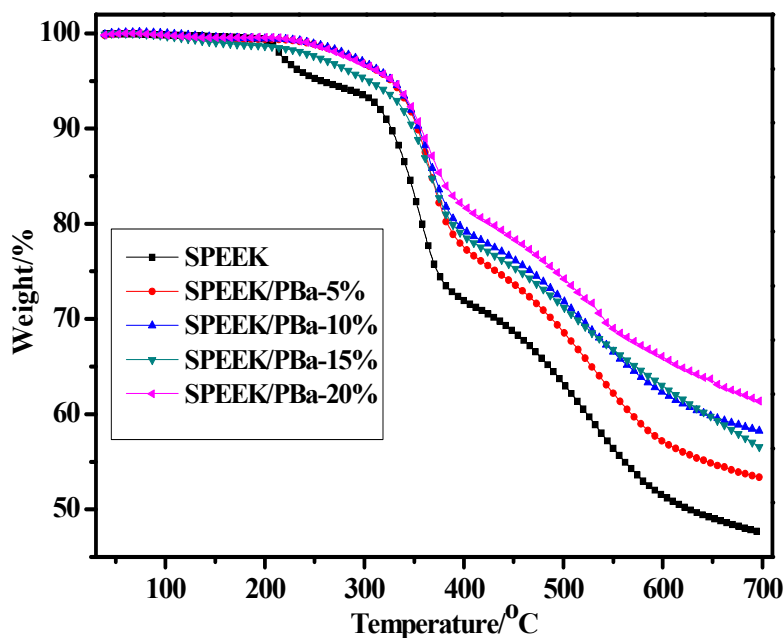
Fig. 3 TG curves of SPEEK and SPEEK/PBa membranes under nitrogen at a heating rate of 20

^{o}C/min.

Tensile properties and morphology

Table 2 shows the typical engineering tensile properties of the dry and wet membranes. The crosslinked membranes exhibit higher tensile strength and Young's modulus than those of the neat SPEEK in both dry and wet conditions. Under dry condition, SPEEK/PBa-15% and SPEEK/PBa-20% samples show better tensile properties than others. Tensile strength and Young's modulus of the wet membranes increase proportionally with the amount of PBa introduced. However, the elongation at break of the wet membranes decreases with increasing PBa content.

The degree of crosslinking due to PBa addition, the level of hydrogen bonding, and the amount of water uptake can strongly influence the tensile properties of SPEEK/PBa membranes. According to the TGA data, there is no detectable water removal in dry SPEEK/PBa membranes. The incorporation of PBa and the crosslinking reaction between SPEEK and PBa minimizes hydrogen bonding between polymer chains and water in SPEEK matrix. As shown above, a suitable level of

PBa-induced crosslinking is essential for enhancing membrane performance. However, embrittlement would ensue if excess PBa is introduced. In the case of the wet membranes, the absorbed water acts as an effective plasticizer, which increases the elongation at break of the membranes directly. The crosslinking and hydrophobic chemical structure of PBa results in significantly reduced plasticization of the membranes.

Table 2 Mechanical properties of SPEEK and SPEEK/PBa crosslinked membranes in dry and wet states.

Sample	Tensile Strength (MPa)		Young's modulus (MPa)		Elongation at break (%)	
	dry[a]	wet[b]	dry[a]	wet[b]	dry[a]	wet[b]
SPEEK	35.7±0.6	30.7±0.4	1300±12	809.4±7	22.6±0.2	204.0±1.0
SPEEK/PBa-5%	39.9±1.2	40.1±0.5	1437±10	1413.9±6	35.3±0.1	112.9±0.9
SPEEK/PBa-10%	43.6±0.8	42.3±1.3	1475±15	1463.6±13	39.5±0.4	101.8±0.6
SPEEK/PBa-15%	56.7±0.4	54.7±0.8	1628±9	1781.0±11	43.3±0.6	91.3±0.7
SPEEK/PBa-20%	62.7±0.9	58.4±0.5	1654±5	1773.6±10	29.8±0.4	62.2±0.5
SPEEK/PBa-25%	53.8±1.1	60.8±1.0	1843±9	1919.4±8	20.1±0.5	19.3±0.4
Nafion-117	31.9±0.5	27.5±0.6	264±4	139.2±5	213.9±1.4	165.2±0.7

[a] "dry" stands for the original dry membranes;

[b] "wet" stands for wet membranes. Wet membranes were obtained by immersing the original dry membranes in deionized water at 30 °C for 12 h.

The cross-sectional SEM images of SPEEK/PBa membranes (Fig. 4 a, b, d and e) show evidence of good compatibility and dispersion of PBa in SPEEK matrix. This morphological feature was further characterized by EDS (Fig. 4c and f). EDS results of the area outlined by a rectangle show a good distribution of S element in SPEEK/PBa membranes, indicating no large-size agglomeration of the PBa phase. This good dispersion is at least partially caused by the crosslinking

between SPEEK/PBa, which results in less segmental mobility of the SPEEK molecules to reduce

diffusion. As expected, the elongation at break is reduced (Table 2) with increased PBa.
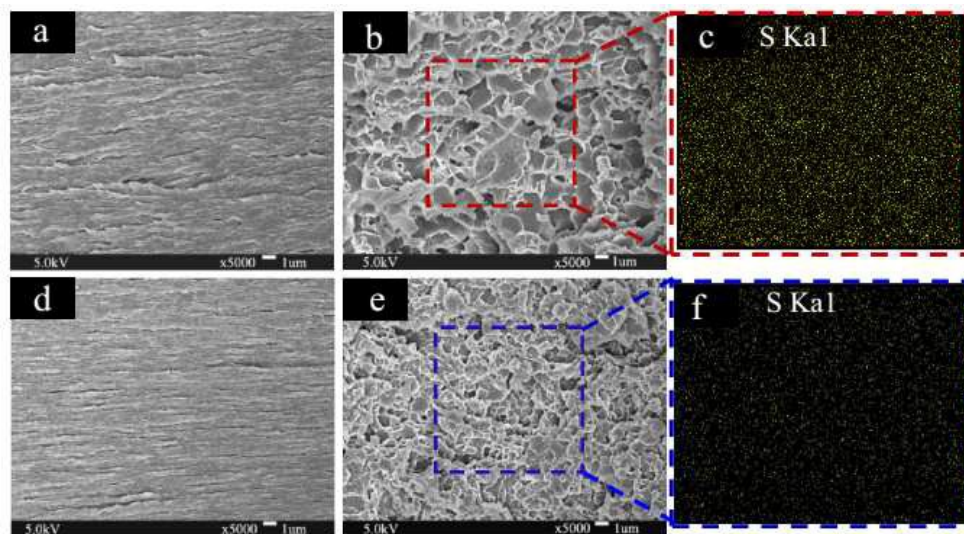

Fig. 4 Cross sectional SEM photographs of SPEEK/PBa-15% membrane (a) wet state, (b) dry state,
(c) corresponding EDS maps; cross sectional SEM photographs of SPEEK/PBa-20% membrane, (d)
wet state, (e) dry state, (f) corresponding EDS maps. The bright dots in EDS images indicate the
sulfur element.

Figure 5 shows direct TEM evidence of formation of well-dispersed nano-domains of SPEEK

having an average size of about 3.5 nm (Fig. 5c) in SPEEK/PBa-15% membrane. The darker regions

correspond to SPEEK stained by lead metal ions in 1N lead acetate solution and representing the

hydrophilic domains, while the lighter parts represent hydrophobic moieties formed by the

hydrophobic SPEEK backbones and crosslinked structure (Fig 5a and b). The sizes of sulfonated

ionic clusters in SPEEK/PBa-15% are mostly in the range between 2.5-4.5 nm (Fig 5c). The pure

SPEEK membrane possessed non-uniform ionic clusters from a few nm up to 100nm according to

the published work [31]. The better hydrophilic/hydrophobic distribution within the SPEEK/PBa-15%

membrane can be attributed to the existence of the crosslinked PBa. This structure can prevent the

hydrophilic sulfonic groups of the neat SPEEK from aggregating into larger ionic clusters and lead to a random distribution of ion channels [32]. The photographic image of SPEEK/PBa-15% shown in Fig. 5d exhibits reasonable transparency with a thickness of approximately 70 μm. SPEEK/PBa membrane appears to be flexible and can be bent easily without causing crazing or crack formation (Fig. 5d and e).
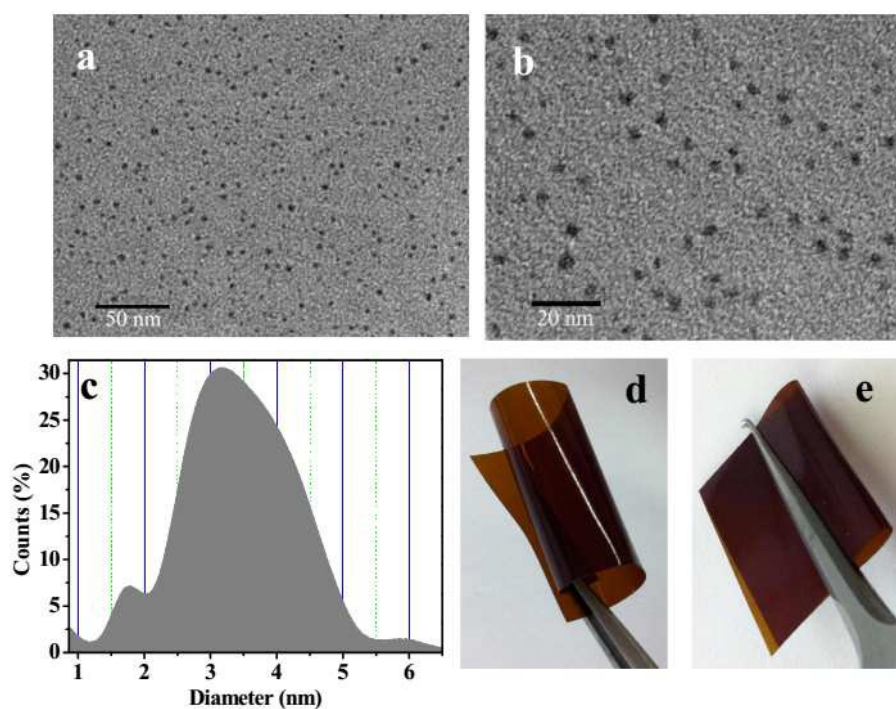

Fig. 5 (a) and (b) TEM of SPEEK/PBa-15% at two different magnifications; (c) Size distribution of sulfonated ionic clusters; (d) and (e) photographic images of SPEEK/PBa-15% dry membrane.

Water uptake and dimensional stability

Appropriate amount of water uptake of the membrane is essential for proton transportation. However, high water content always decreases the mechanical property and dimensional stability of the membranes [33]. The amounts of water uptake of the membranes at 30^oC and 80^oC are shown in Table 3. The water uptake for PBa-crosslinked membranes is much lower than that of SPEEK at 30^oC. The

water uptake of SPEEK/PBa-15% membrane is around 19% at 30°C and about 44% at 80°C. The membrane with SPEEK alone dissolves in water in 2 min, while SPEEK/PBa-5% membrane forms a swollen gel in 10 min at 80°C. The hydrophobic PBa main chains and crosslinking with SPEEK help impede water absorption and preserve dimensional stability. As the temperature increases, water solubility of the membrane increases accordingly. A lower swelling ratio, which indicates better dimensional stability, is required to ensure stable fuel cell operation. As expected, the dimensional change of the SPEEK/PBa membranes is considerably suppressed compared with that of the SPEEK membrane (Table 3). This demonstrates that the crosslinking through PBa in the membrane effectively mitigates the dimensional change caused by water absorption. Notably, the swelling ratio of the SPEEK/PBa-15% membrane measured in water absorption at 30°C is lower than that of the Nafion-117 membrane. The SPEEK/PBa-20% membrane and the Nafion-117 membrane has a similar swelling ratio and water uptake at 80°C in water, suggesting SPEEK/PBa membrane can potentially replace Nafion-117 for DMFC applications.

The swelling ratios of SPEEK and SPEEK/PBa crosslinked membranes in methanol solution vary in the same trend as those tested in water. A lower dimensional swelling ratio corresponds to a more compact membrane structure [14, 18]. With increased crosslinking, the SPEEK/PBa matrix becomes more resistant to methanol diffusion. Furthermore, some sulfonic acid groups in SPEEK have been consumed during the crosslinking reaction, minimizing the hydrophilic channels for methanol diffusion. Crosslinked structure in SPEEK/PBa membranes serves as an effective means to prevent methanol from crossover in DMFC.

Table 3 Water uptake and swelling ratio of the membranes at 30°C and 80°C.

Sample	Swelling ratio in water (%)		Water uptake (wt.%)		Swelling ratio in methanol solution (%)	
	30 $^{\circ}$C	80 $^{\circ}$C	30 $^{\circ}$C	80 $^{\circ}$C	30 $^{\circ}$C	80 $^{\circ}$C
SPEEK	105.3	Dissolved	114.3	Dissolved	250.9	Dissolved
SPEEK/PBa-5%	52.2	Gel-like	95.2	Gel-like	59.8	Dissolved
SPEEK/PBa-10%	33.9	89.2	57.9	96.4	39.0	98.4
SPEEK/PBa-15%	18.8	43.9	37.1	52.3	30.2	31.9
SPEEK/PBa-20%	15.7	39.4	17.6	42.5	22.9	24.9
SPEEK/PBa-25%	9.2	20.7	9.3	23.9	11.3	13.8
Nafion-117	22.9	34.2	38.0	41.9	13.9	29.4

Ion exchange capability, methanol permeability, proton conductivity, and selectivity

The ion exchange capability (IEC), methanol permeability, proton conductivity, and selectivity of the SPEEK/PBa crosslinked membranes are listed in Table 4. The corresponding data for commercial Nafion-117 and pure SPEEK under the same testing conditions are also given for reference. IEC depends on the density of –SO$_3$H groups and plays an important role in proton conductivity for proton exchange membranes. The IEC of SPEEK/PBa membranes varies from 1.174 to 0.479 mmol.g^{-1}. When the PBa content is between 5% and 25%, the IEC value of the membrane decreases slightly with an increase of PBa content (Table 4). PBa as a neutral base exhibits no proton dissociation ability relative to sulfonic acid group. Therefore, incorporation of PBa decreases the concentration of sulfonic acid group per unit mass of the membrane. Meanwhile, crosslinking reaction between PBa and SPEEK consumed the hydrophilic –SO$_3$H groups, reducing the number of dissociable H$^+$ ions in SPEEK/PBa membranes.

Table 4 IEC and proton conductivity of SPEEK/PBa membranes.

| Sample	IEC/(meq.g^{-1})	Methanol permeability (cm^2 s^{-1})		Proton conductivity (S cm^{-1})		Selectivity parameter (S s cm^{-3})	
		30 °C	80 °C	30 °C	80 °C	30 °C	80 °C
SPEEK	1.327	5.79×10^{-5}	----	7.76×10^{-2}	----	1.34×10^{3}	----
SPEEK/PBa-5%	1.174	1.23×10^{-6}	----	5.45×10^{-2}	----	4.43×10^{4}	----
SPEEK/PBa-10%	0.871	1.93×10^{-7}	9.64×10^{-6}	6.18×10^{-3}	4.21×10^{-2}	3.20×10^{4}	4.37×10^{3}
SPEEK/PBa-15%	0.794	1.26×10^{-7}	5.53×10^{-6}	4.25×10^{-3}	2.46×10^{-2}	3.12×10^{4}	4.45×10^{3}
SPEEK/PBa-20%	0.583	2.23×10^{-7}	3.42×10^{-6}	7.97×10^{-4}	1.34×10^{-2}	3.57×10^{3}	3.92×10^{3}
SPEEK/PBa-25%	0.479	5.46×10^{-7}	2.12×10^{-6}	1.61×10^{-4}	8.21×10^{-3}	2.98×10^{2}	3.87×10^{3}
Nafion-117	0.881	1.88×10^{-6}	2.58×10^{-5}	8.91×10^{-2}	9.03×10^{-2}	4.84×10^{4}	3.50×10^{3}

Low methanol crossover of the membrane will reduce the open-circuit potential and poison the electro-catalysts on the cathode for long term DMFC operation. As expected, a lower swelling ratio of membranes (Table 3) leads to lower methanol permeability (Table 4). The methanol permeability in all of the SPEEK/PBa crosslinked membranes decreases as PBa content is increased. When PBa content is increased from 5% to 10%, the methanol permeability of SPEEK/PBa decreases from 1.93 × 10^{-6} cm^2 s^{-1} to 1.26 × 10^{-7} cm^2 s^{-1} at 30°C, and from 9.64 × 10^{-6} cm^2 s^{-1} to 5.53 × 10^{-7} cm^2 s^{-1} at 80°C. The methanol permeability of SPEEK/PBa-20% membrane is 2.23 × 10^{-7} cm^2 s^{-1} at 30°C and 3.42 × 10^{-7} cm^2 s^{-1} at 80°C, which are an order of magnitude lower than those of Nafion-117 at the same measurement conditions (1.88 × 10^{-6} cm^2 s^{-1} at 30°C and 2.58 × 10^{-5} cm^2 s^{-1} at 80°C). The introduction of rigid PBa backbone into the membrane inhibits the mobility of SPEEK molecular chains and the crosslinking reaction between PBa and SPEEK reduces the size of channels for swelling of methanol. Additionally, the presence of the crosslinked structure interrupted the diffusion pathway for methanol.

The selectivity parameter, i.e., the ratio of proton conductivity to methanol permeability, is usually used as a measure of methanol resistance [34]. The SPEEK/PBa-15% crosslinked membrane exhibits a selectivity of 4.45×10^3 S s cm^{-3} at 80°C, which is about 1.3 times higher than that of Nafion-117 at 3.50×10^3 S s cm^{-3}. It is evident that the PBa-induced crosslinking can dramatically suppress the methanol crossover of SPEEK/PBa membranes.

Proton conductivity is considered to be a critical factor for membrane performance in fuel cell application. In this work, we studied the effect of PBa content and temperature on the proton conductivity of the membranes. The proton conductivity of all the SPEEK/PBa membranes decreases with increasing PBa content (Table 4). It is noted that a significant increase in proton conductivity is observed in membranes with PBa 15%~25% as the temperature increases from 30°C to 80°C. The proton conductivity of SPEEK/PBa-15% increases from $4.25\text{-}\times\text{-}10^{-4}$S-cm^{-1} at 30°C to $2.46\text{-}\times\text{-}10^{-2}$-S-cm^{-1} at 80°C. It is concluded that the proton conductivity behavior is related to the amount of water absorbed in the membranes, which is influenced by the chemical structure of the membranes.

The protons are transported through channels formed by ion clusters of hydrophilic sulfonic acid groups and water through two main mechanisms, Grotthuss mechanism and vehicular mechanism [35]. Scheme 4 illustrates the possible proton transport mechanism of SPEEK/PBa membranes under wet conditions. The vehicular mechanism may dominate in the hydrophilic regions where water molecules act as vehicle by carrying along protons in the forms as hydrated protons [36]. Grotthuss mechanism works in the regions where loose acid-base interaction between the sulfonic acid groups in SPEEK and nitrogen atoms in PBa occurred through hydrogen bond formation [37]. Both mechanisms are strongly related to water uptake. The more water uptake in SPEEK/PBa membranes, the more hydrated species and hydrogen bonds are generated, thereby facilitating the transport of protons more quickly. The compact structures formed by crosslinking reaction give better thermal and mechanical properties, and dimensional stability, which will greatly enhance performance in DMFC environments. However, the PBa chemistry is likely to reduce both proton

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transportation channel sizes and amount of sulfonic groups, which will lower proton conductivity of SPEEK membrane. The temperature effect on proton conductivity is mainly caused by thermally activated process. As the temperature increases, water diffusion and segmental motion of polymer chains become more active. Therefore, it allows hydrophilic clusters in membranes move more freely, which improves the formation of transport channels and increase the probability of proton transport.
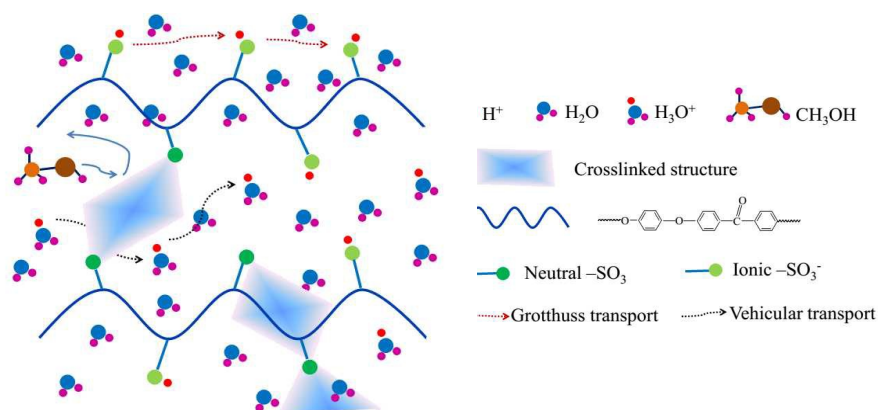
Scheme 4 Proposed mechanism of proton transport within SPEEK/PBa membranes.

Conclusions

A novel high-performance crosslinked proton exchange membrane based on SPEEK and Benzoxazine (Ba) was synthesized and characterized. Homopolymerization of Ba and crosslinking between PBa and SPEEK was conducted at 150 ^{o}C for 3 h. The water resistance, thermal stability, and mechanical properties of the SPEEK/PBa membranes were enhanced significantly due to the rigid hydrophobic segments of PBa and a dimensionally stable crosslinked structure. The SPEEK/PBa-15% and SPEEK/PBa-20% samples exhibited balanced properties for DMFC applications. The SPEEK/PBa-15% crosslinked membrane demonstrated the highest selectivity, measuring 4.45×10^3 S s cm^{-3} at 80 ^{o}C, which is about 1.3 times higher than that of Nafion-117. At 30 ^{o}C, the proton conductivity of the SPEEK/PBa-20% crosslinked membrane was 7.97×10^{-4} S cm^{-1}, and was dramatically increased to 1.34×10^{-2} S cm^{-1} at 80 ^{o}C. The effect of temperature on

proton conductivity was mainly due to the thermally stimulated process of proton transport, changes in the segmental motion of the polymer chains, and water diffusivity. The prepared SPEEK/PBa membranes had high stability and conductivity, and show great potential as proton conducting membranes in direct methanol fuel cells.

Acknowledgements

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