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# Proton conducting membranes based on semi-interpenetrating polymer network of Nafion® and polybenzimidazole

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A new strategy to prepare the reinforced composite membranes for polymer electrolyte membrane fuel cells (PEMFCs), which can work both in humidified and anhydrous state, was proposed via constructing semi-interpenetrating polymer network (semi-IPN) structure from polybenzimidazole (PBI) and Nafion®212, with N-vinylimidazole as the crosslinker. The crosslinkable PBI was synthesized from poly(2,2′-(*m*-phenylene)-5,5′-bibenzimidazole) and *p*-vinylbenzyl chloride. The semi-IPN structure was formed during the membrane preparation. The composite membranes exhibit excellent thermal stability, high-dimensional stability, and significantly improved mechanical properties compared with Nafion®212. The proton transport in the hydrated composite membranes is mainly contributed by the vehicle mechanism, with proton conductivity from $\sim 10^{-2}$ S/cm to $\sim 10^{-1}$ S/cm. When the temperature exceeds 100 °C, the proton conductivity of the semi-IPN membranes decreases quickly due to the dehydration of the membranes. Under anhydrous condition, the proton conductivity of the membranes will drop to $\sim 10^{-4}$ S/cm, which is also useful for intermediate temperature (100–200 °C) PEMFCs. The benzimidazole structure of PBI and the acidic component of Nafion® provide the possibility for the proton mobility via structure diffusion involving proton transfer between the heterocycles with a corresponding reorganization of the hydrogen bonded network.

## 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have attracted a lot of attention these years due to their use as the candidate power source in automobile and stationary application [1–5]. Compared with liquid electrolyte systems, PEMFCs with proton exchange membranes (PEMs) as the electrolyte have lots of advantages. They are much easier to be handled, sealed, and assembled [6]. The main roles of PEMs are to convey the protons from the anode to the cathode and separate the reactants. Therefore, the membranes should possess good mechanical and conductive properties. The benchmark materials for PEMs are perfluorosulfonated ionomers, of which the most famous representative is Nafion® from DuPont Co.. This commercial perfluorosulfonated ionomer exhibits high proton conductivity and excellent chemical stability. However, it still suffers from high cost, poor dimensional stability, as well as not high enough mechanical properties for engineering application. As mentioned in the literatures before [7–11], there are two main methods to improve the mechanical properties of Nafion®, including impregnating Nafion® resin into porous Teflon membranes or blending silica with Nafion®. Nafion® blended with the second component can not only reduce the cost, but also improve the mechanical properties and the dimensional stability. Only in the recent past, it was also realized that the hydrated perfluorosulfonated membranes have another disadvantage of temperature limitation due to the dehydration of the membranes at higher temperature, which is important for better electrode kinetics as well as humidity and heat management in PEMFCs [5,9].

Polybenzimidazole (PBI) is a promising polymer, which can be doped with acid and used in intermediate temperature (100–200 °C) PEMFCs due to its high thermal and chemical stability [12,13]. Two methods have been used for the crosslinking of polybenzimidazoles. One is ionic crosslinking [14–17], which is obtained by the preparation of polymeric acid-base blending membranes; the other is covalent crosslinking [18–20], which can be achieved by thermal treatment or an amide-type linkage through imidazole groups of the polymers. Moreover, it has been found that PBI has good compatibility with Nafion® due to the possibility of acid-base interaction between imidazole and sulfonic groups [21–23]. In present work, a new strategy to prepare the reinforced composite membranes for PEMFCs, which can work both in humidified

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environment and at anhydrous state, is proposed via constructing semi-interpenetrating polymer network (semi-IPN) structure from PBI and Nafion®. The crosslinkable PBI will be synthesized from poly [2,2′-(m-phenylene)-5,5′-bibenzimidazole] and *p*-vinylbenzyl chloride. The composite membranes based on semi-IPN of Nafion® and crosslinkable polybenzimidazole with *N*-vinylimidazole as a crosslinker will be prepared. Using *N*-vinylimidazole as the crosslinker may increase the compatibility between PBI and Nafion® as well as the proton conductivity of the composite membranes. The mechanical properties, proton conductivity, and thermal stability of the composite membranes will be discussed.

## 2. Experimental

### 2.1. Materials

3,3′,4,4’-tetraaminobiphenyl (TAB) was purchased from Shanghai Bangcheng Chem. Co., and recrystalized before used. Nafion®212 was from DuPont Co.. NaH was purchased from Fluka Chemical Co. *N*-vinylimidazole and *p*-vinylbenzyl chloride were bought from Aldrich Co. Other chemicals and solvents were from Shanghai Chemical Reagent Co. and all used as received.

### 2.2. Synthesis of poly[2,2′-(m-phenylene)-5,5′-bibenzimidazole]

The synthesis of PBI was similar to the method which described in references [24,25]. TAB (3.2314 g, 15.1 mmol) and polyphosphoric acid (180 g, 532.5 mmol) were placed in a three-necked flask in nitrogen atmosphere. The mixture was stirred using a mechanical stirrer, purged with a slow stream of nitrogen, and heated at 150 °C for 0.5 h. The temperature was then gradually increased to 200 °C. Isophthalic acid (2.5066 g, 15.1 mmol) was added to the flask when the temperature reached 200 °C. $P_2O_5$ (2.94 g, 30 mmol) was then added. Polymerization was carried out at 190–200 °C for 13 h. During the polymerization, the reaction mixture became more and more viscous, and it developed a deep brown color. After polymerization, the mixture was poured into distilled water and isolated as a deep green algoid mass. The mass was washed with distilled water three times, neutralized with ammonium hydroxide, and then boiled in distilled water, pulverized and extracted by Soxhlet with ethanol, and finally dried in vacuum for more than 24 h at 100 °C to obtain the PBI powder.

The Ubbelohde viscometer was used to determine the molecular weight of the polymer. PBI was dissolved in 96% sulfuric acid, and then the flow time of the solution and the solvent was measured respectively, from which the intrinsic viscosity can be calculated. An approximation to the viscosity-average molecular weight ($M_\eta$) of PBI can be obtained through the intrinsic viscosity by Mark–Houwink–Sakurada expression (Eq. (1)) [26],

$$\eta_{int} = 1.94 \times 10^{-4} M_\eta^{0.791} \tag{1}$$

and $M_\eta$ of PBI synthesized in this study was 18.5 kDa.

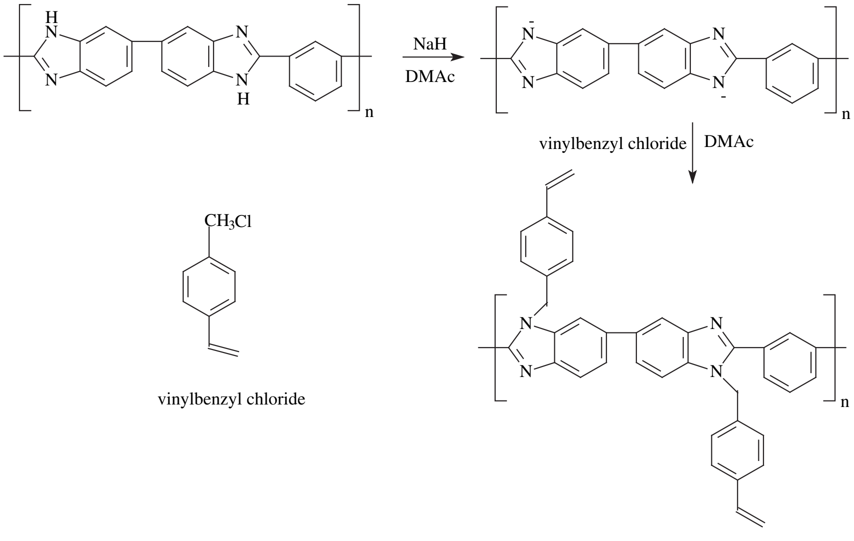
### 2.3. Synthesis of vinylbenzyl substituted PBI

The general synthetic procedure for vinylbenzyl substituted PBI was shown in Scheme 1. PBI is difficult to be dissolved in organic solvent, but 2% (w/v) solution in DMAc can be prepared by heating to 160 °C with stirring to affect the dissolution of PBI. NaH was then added slowly and carefully into PBI solution at a molar ratio of PBI:NaH = 10:3. The reaction mixture was stirred for 18 h under nitrogen at 80 °C. Then, an excess of *p*-vinylbenzyl chloride was added into the solution and stirred for 18 h at 80 °C, which resulted in vinylbenzyl substituted PBI. The reaction mixture was cooled to room temperature and was precipitated in acetone. The precipitate was purified by dissolving in DMAc and precipitated in acetone again, and then washed with deionized (DI) water to remove DMAc from the modified polymer.

### 2.4. Preparation of the composite membranes based on semi-IPN of Nafion® and PBI

Nafion®212 was immersed in 10 wt% NaOH aqueous solution for 24 h. Partial protons of Nafion® can be changed into sodium ions, which can help decrease the possibility of gel-formation when Nafion® was blended with PBI [14,23]. The sodium salt of Nafion® was then dissolved in DMAc at 160 °C. The solution was treated by high speed centrifugal machine (12,000 rpm) to remove insoluble Nafion® and microgels as clearly as possible.

N-vinylimidazole was used as a crosslinker with contents of 5.0, 10.0, 30.0, 40.0, 50.0 wt%, respectively. 20 mL DMAc solution of vinylbenzyl substituted PBI (0.02 g/mL) was mixed with N-vinylimidazole (5.0–50.0 wt%) and AIBN (0.4 wt%) in a 100 mL conical flask, and then was treated in an ultrasonic bath at 25 °C for 1 h to make it



**Scheme 1.** Synthesis of vinylbenzyl substituted PBI.

homogeneous. The solution was mixed with Nafion® 212 solution in DMAc and was poured onto a glass plate. The whole sample was then placed horizontally in an oven and slowly heated from room temperature to 130 °C. During the process, the crosslinking reaction as well as solvent evaporation was performed. The membrane was then stripped off from the plate and placed in the oven at 130 °C for 24 h. The free radicals might be generated from electron-rich styrenic double bonds by thermal heating at 130 °C, which is well known as 'auto-initiation of styrene' in the literature [27]. The produced membranes were first extracted by ethanol in a Soxhlet apparatus to remove the residual monomers, N-vinylimidazole dimers or oligomers, and the residual solvent as clearly as possible. Then, the membranes were soaked in 10% HCl solution at 80 °C for 24 h, and washed with distilled water and dried at 100 °C for 24 h. The membranes with different contents of the crosslinker were noted as M(5%), M(10%), M(15%), and M(20%), M (30%), M(40%), and M(50%) respectively.

### 2.5. Characterization of the composite membranes

The crosslinking degree of the composite membranes was characterized by the gel content of the membranes [28]. Small pieces of the membranes (∼0.05 g) were wrapped with the filter paper. The samples were then placed in excess DMAc (∼30 mL) at 160 °C, and the solvent was replaced after 12 h until no further soluble polymer was found. The samples were then dried until constant weight $w_1$. The gel content was calculated from Eq. (2),

$$W\ (\text{gel}) = \left(\frac{w_1}{w_0}\right) \times 100\% \tag{2}$$

where $w_0$ is the original weight of the dried membrane.

The ion-exchange capacity (IEC) of the composite membranes was measured by titration method. The composite membranes were soaked in saturation NaCl solution for 24 h, and then the solution was titrated with 0.01 M NaOH solutions with phenolphthalein indicator [29]. The value of IEC was calculated using the following formula (Eq. (3))

$$\text{IEC} = \frac{V_{\text{NaOH}} \times C_{\text{NaOH}}}{W} \tag{3}$$

where $V_{\text{NaOH}}$ is the volume of NaOH consumed during the titration, $C_{\text{NaOH}}$ is the concentration of the titrant NaOH and $W$ is the weight of the dried sample.

The measurement of the water uptake of the membranes was carried out by immersing three sheets of membranes (20–30 mg per sheet) into water at 25 °C and 80 °C for 48 h respectively, before which the membranes were dried under vacuum at 100 °C for 2 days and weighed. Then the membranes were taken out, wiped with tissue paper and quickly weighed on a microbalance. The water uptake (WU) of the membranes was calculated from Eq. (4) [30],

$$\text{WU} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \tag{4}$$

where $W_{\text{dry}}$ and $W_{\text{wet}}$ were the weight of dry and corresponding wet membrane sheets, respectively. The water uptake of the membranes was estimated from the average value of at least three measurements for each sheet.

As same to the water uptake, the measurement of the swelling ratio of the membranes was carried out by immersing three square sheets of membranes into water at 25 °C and 80 °C for 5 h respectively, before which the membranes were dried under vacuum at 100 °C for 2 days and the diagonal length of the membrane was measured. Then the membranes were taken out. The diagonal length of the swollen membrane was measured again. The swelling ratio (SR) of the membranes was calculated from Eq. (5) [31],

$$\text{SR} = \frac{D_{\text{wet}} - D_{\text{dry}}}{D_{\text{dry}}} \times 100\% \tag{5}$$

where $D_{\text{dry}}$ and $D_{\text{wet}}$ are the diagonal length of dry and swollen membranes, respectively. Swelling ratio of the membranes was estimated from the average value of at least three measurements for each sheet.

FTIR analysis of the synthesized vinylbenzyl substituted PBI was carried out by a thermo Bruker EQUINOXSS/HYPERION2000 spectrometer. The KBr pellet method was employed. $^1$H-NMR spectra of pure PBI and vinylbenzyl substituted PBI in deuterated dimethyl sulfoxide (DMSO) were recorded on a Varian Bruker AC-250 instrument.

The tensile strength of the composite membranes was measured by a universal material testing machine (Dejie machine Co.) according to ASTM D882-02. The stretching speed was 2 mm/min..

Thermal stabilities of the membranes were investigated by thermogravimetric analyzer (TG) (STA 449C, Netzsch Co.). The samples were heated from room temperature to 700 °C with a heating rate of 10 °C/min under nitrogen atmosphere.

The cross-sectional specimens of the membranes were prepared by breaking the membrane manually after cooling in liquid nitrogen. The fractured surface of the composite membranes was examined on a QUANTA 200 FEG SEM (FEI Company).

Methanol permeability of the composite membranes was determined at 20 °C by a diffusion cell according to a method in Ref. [32]. This diffusion cell consists of two reservoirs. Reservoir A contains 44 wt% methanol aqueous solution and reservoir B contains deionized water. The tested membrane was immersed in water for hydration before measurements for more than 24 h, and then vertically fixed between two reservoirs. A flux of methanol in the pure water reservoir was measured *versus* time by using differential refractometry. The methanol concentration in the receiving reservoir as a function of time is given by the following formula (Eq. (6)) [32,33],

$$C_{\text{B}}(t) = \frac{A}{V_{\text{B}}L} DKC_{\text{A}}(t - t_0) \tag{6}$$

where $C_{\text{B}}$ is the concentration of methanol in reservoir B; $A$ is the membrane area; $V_{\text{B}}$ is the volume of reservoir B; $L$ is the membrane thickness; $C_{\text{A}}$ is the concentration of solution A; $D$ and $K$ are the methanol diffusivity and partition coefficient, respectively. The product $DK$ is the methanol permeability ($P$). $t_0$, which termed time lag, is related to the diffusivity, $t_0 = L^2/6D$.

The proton conductivity ($\sigma$) of the composite membranes was measured by the complex impedance method on an Electrochemical Impedance Lab CHI 604B (CH Instruments Inc.), which worked in the galvanostatic mode and produced a proton current across the membrane. The hydrated membranes was measured in a test cell [34], which was placed in a thermo-controlled water bath for measurement at relatively humidity (RH) of 100%. The anhydrous membranes were measured by sandwiched between two gold electrodes, and the direction of the conducting measurement was perpendicular to the membrane. The applied current was typically of the order of 5 mA. The DC conductivity of the membrane can be calculated from Cole-Cole plots ($Z''$ vs. $Z'$)[35].

## 3. Results and discussion

### 3.1. Chemical structure of vinylbenzyl substituted PBI

FTIR spectra of pure PBI, vinylbenzyl substituted PBI, Nafion®212, and semi-IPN membrane are shown in Fig. 1. FTIR spectra of PBI and

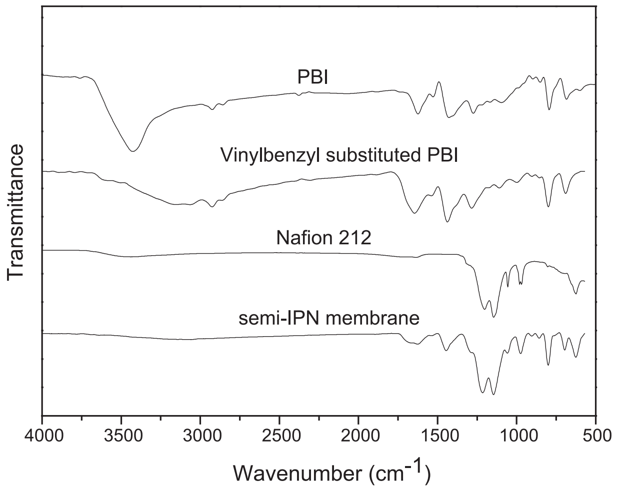


**Fig. 1.** FTIR spectra of pure PBI, vinylbenzyl substituted PBI, Nafion®212, and the semi-IPN membrane (Nafion®212/PBI = 70/30(w/w), crosslinker content is 30%).

its derivatives have been studied extensively in the past [36,37]. The strong band from 2500 to 3500 cm$^{-1}$ in the spectrum of PBI is ascribed to the strong hydrogen bonding of the type N—H···H. This band becomes broader with the addition of vinylbenzyl in the spectrum of vinylbenzyl substituted PBI due to partial N-substitution. The band at 2925 cm$^{-1}$, which corresponds to $-CH_2$ stretching vibration, is enhanced with the addition of $-CH_2$ group from vinylbenzyl substitution. Bands derived from aromatic C=C and C=N stretching modes are found in 1620–1440 cm$^{-1}$ region. There is significant increase in the C=C stretching frequency at 1645 cm$^{-1}$, which indicates the presence of double bonds in vinylbenzyl substituted PBI. The different chemical structures of PBI and vinylbenzyl substituted PBI are also characterized by means of $^1$H-NMR. As shown in Fig. 2, before the substitution, the proton signal of imidazole denoted as $H_a$ can be observed at around 13.30 ppm. The proton signals of biphenyl denoted as $H_b$, $H_c$, and $H_d$ are observed at around 7.61 ppm, 8.03 ppm, and 7.83 ppm. The proton signals of benzene denoted as $H_b$ and $H_f$, are observed at around 9.13 ppm and 8.31 ppm. After substituted by vinylbenzyl, $^1$H-NMR spectra show that the proton peak $H_a$ disappears and peaks at around 7.39 ppm, 7.07 ppm, 6.63 ppm, 5.76 ppm, 5.41 ppm, and 5.17 ppm are attributed to the vinylbenzyl groups. From FTIR and $^1$H-NMR spectra, it can be safely concluded that the vinylbenzyl substituted PBI has been synthesized successfully.

In FTIR spectrum of Nafion®212, the band at 974 cm$^{-1}$ corresponds to the stretching vibration of C—O—C on the side chain of Nafion®. The band around 1055 cm$^{-1}$ is attributed to the symmetric S—O stretching of sulfonic groups [38]. The strong bands at 1140 and 1204 cm$^{-1}$ are assigned to the stretching vibration of C—F on the main chain of Nafion® [39]. The main characteristic absorption bands of Nafion® and PBI remain the same in the spectrum of the semi-IPN membrane, while the C=C stretching frequency (1645 cm$^{-1}$) decreases significantly, which indicates that the C=C at vinylbenzyl substituted PBI will be attacked by initiator AIBN and reacted with N-vinylimidazole to form a network structure. The possible structure of semi-IPN based on crosslinkable PBI, N-vinylimidazole, and Nafion® is shown in Fig. 3. Nafion®212 chains penetrate thoroughly in crosslinked PBI network.

### 3.2. Crosslinking degree of the composite membranes

The gel fraction is employed to determine the crosslinking degree of PBI in the composite membranes. In the present work, the crosslinking degree is designed to be regulated by varying the content of the crosslinker. Because of the steric effect of PBI

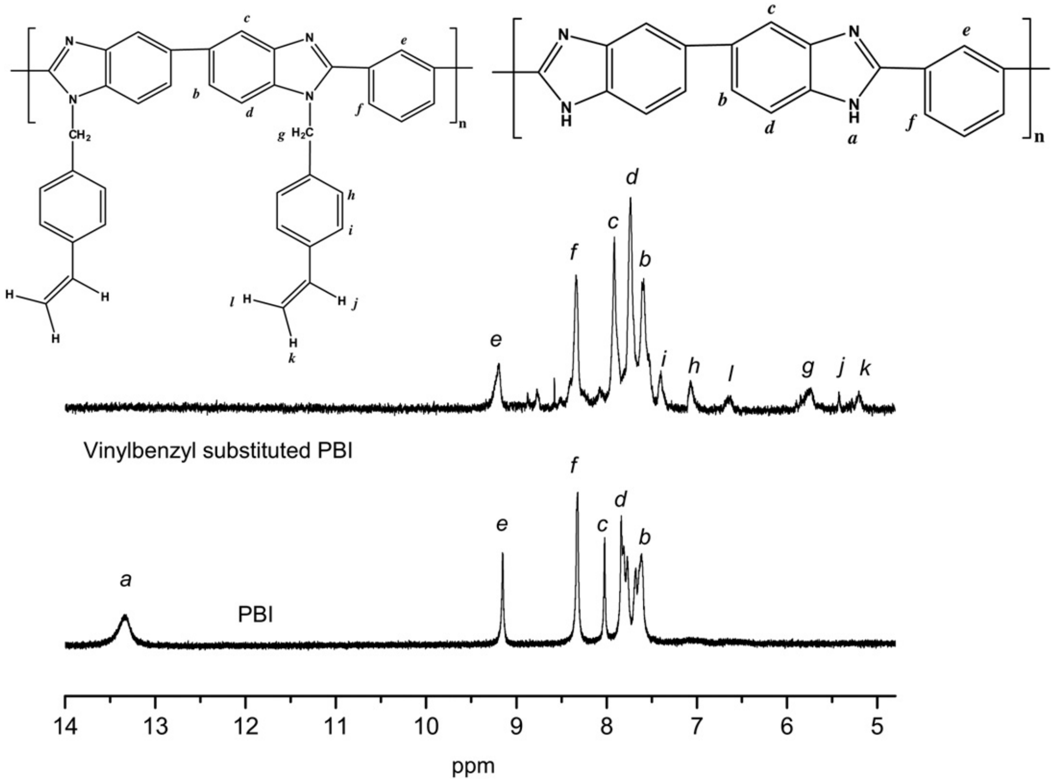


**Fig. 2.** $^1$H-NMR spectra of pure PBI and vinylbenzyl substituted PBI.

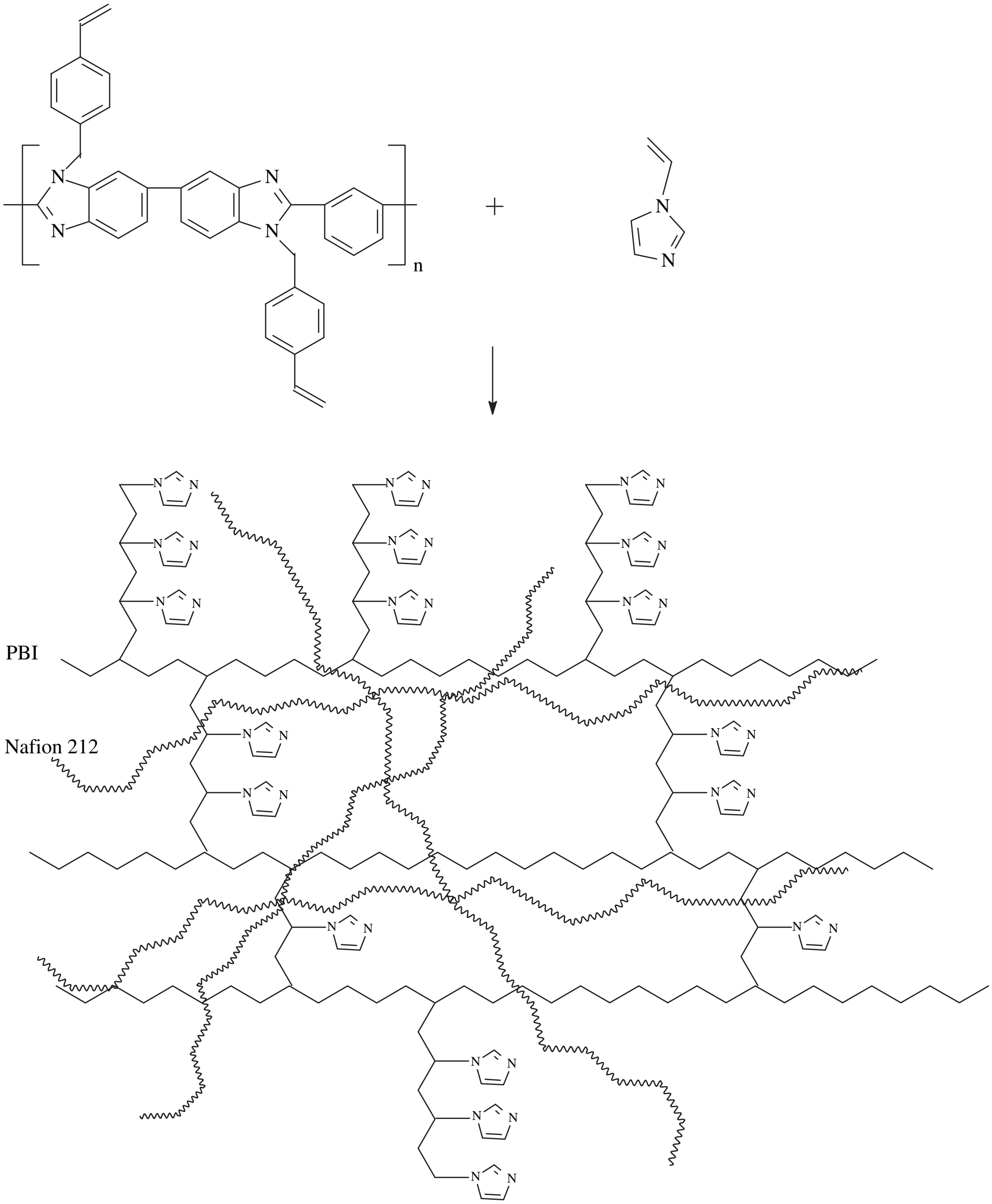


**Fig. 3.** The semi-IPN structure of crosslinkable PBI, N-vinylimidazole, and Nafion®212.

backbone or blocked by Nafion®, it is difficult to exactly determine how much crosslinker will react with the vinylbenzyl group on the crosslinkable PBI during the preparation of the composite membranes. However, as found in Table 1, at the same amounts of vinylbenzyl substituted PBI and AIBN, the higher the content of the crosslinker is, the higher the crosslinking density of the composite membranes can reach. Three possible reactions may exist during the preparation of the composite membranes. First, the crosslinker directly reacts with the crosslinkable PBI; second, the crosslinker reacts with each other at first and then reacts with crosslinkable PBI; third, the crosslinker just reacts with each other. The first and the second reaction will result in the crosslinked network. With the higher crosslinker concentration, the possibility for the crosslinker to get close to the vinylbenzyl group on the crosslinkable PBI will increase, which means that the first and the second reaction will be easier to be realized, and the crosslinking degree will increase.

**Table 1**
Gel contents of the composite membranes.

| Samples | PBI (wt%) | Nafion® 212 (wt%) | Gel content (%) |
|---|---|---|---|
| PBI | 100 | 0 | 0 |
| Nafion® 212 | 0 | 100 | 0 |
| M(5%) | 30 | 70 | 2.32 |
| M(10%) | 30 | 70 | 6.76 |
| M(15%) | 30 | 70 | 8.91 |
| M(20%) | 30 | 70 | 11.12 |
| M(30%) | 30 | 70 | 13.91 |
| M(40%) | 30 | 70 | 17.26 |
| M(50%) | 30 | 70 | 19.35 |

**Table 2**
IEC, water uptake, and swelling ratio of the composite membranes.

| Membranes | IEC(mmol/g) | Water uptake (%, w/w) | | Swelling ratio (%) | |
|---|---|---|---|---|---|
| | | 25 °C | 80 °C | 25 °C | 80 °C |
| Nafion® 212 | 0.96 | 25.6 | 34.7 | 10.3 | 14.8 |
| $M_1$(5%)[a] | 0.85 | 19.9 | 24.7 | 7.8 | 10.2 |
| $M_1$(10%)[a] | 0.84 | 19.1 | 23.5 | 7.6 | 9.8 |
| $M_1$(20%)[a] | 0.84 | 18.5 | 22.9 | 7.1 | 9.2 |
| $M_1$(30%)[a] | 0.82 | 17.8 | 21.3 | 6.7 | 8.2 |
| $M_2$(5%)[b] | 0.68 | 16.7 | 20.6 | 4.4 | 5.7 |
| $M_2$(10%)[b] | 0.66 | 16.3 | 20.4 | 4.0 | 5.3 |
| $M_2$(20%)[b] | 0.66 | 15.9 | 19.9 | 3.7 | 4.5 |
| $M_2$(30%)[b] | 0.64 | 15.1 | 19.3 | 3.5 | 4.4 |
| $M_3$(5%)[c] | 0.61[c] | 12.5 | 18.3 | 2.3 | 3.5 |
| $M_3$(10%)[c] | 0.59 | 12.4 | 18.0 | 2.2 | 3.5 |
| $M_3$(20%)[c] | 0.57 | 12.0 | 17.8 | 2.0 | 3.4 |
| $M_3$(30%)[c] | 0.54 | 11.8 | 17.5 | 1.9 | 3.2 |

[a] Nafion®212/PBI = 70/30(w/w).
[b] Nafion®212/PBI = 50/50(w/w).
[c] Nafion®212/PBI = 30/70(w/w).

### 3.3. Ion-exchange capacity, water uptake, and swelling ratio of the composite membranes

Generally, the proton conductivity of the hydrated membranes is directly related to IEC of the polymers. For the composite membranes based on Nafion®, IEC depends on the molar ratio of the sulfonic group in the membrane. On the other hand, water acts as the vehicle for proton transport in the membranes, thus water uptake of the composite membranes is also closely related to the fuel cell performance [40]. Sufficient water in the membrane will lead to high proton conductivity while excessive water uptake will lead to high-dimensional swelling ratio as well as the decrease of the mechanical properties of the membranes. Since PEMFCs are generally operated at temperature close to 80 °C, the water uptake and the swelling ratio of pure and composite membranes were measured at 25 °C and 80 °C, respectively. As seen from Table 2, the water uptake of the membranes will increase with increasing temperature. With increasing content of Nafion® in the composite membrane, IEC and the water uptake will increase. The reason is obvious that there are more hydrophilic sulfonic groups when the composite membrane contains more Nafion®. IEC remains the same when the crosslinking degree of PBI in the composite membrane increases, while the water uptake of the membranes decreases a little. With the higher crosslinking degree, the main chains of PBI will intertwist more tightly with each other or with Nafion® chain, which may, to a certain extent, block the water molecules from accessing to the hydrophilic sulfonic group.

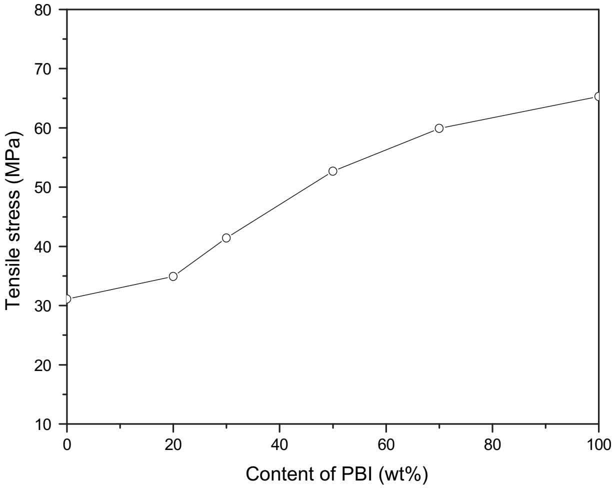


**Fig. 4.** Effects of the crosslinkable PBI contents on the tensile strength of the composite membranes, the crosslinker content is 30%.

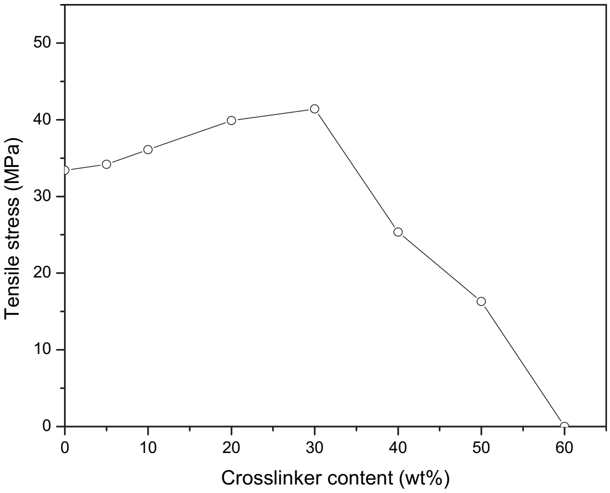


**Fig. 5.** Effects of the crosslinker contents on the tensile strength of the composite membranes, the crosslinkable PBI content is 30%.

To estimate the swelling ratio of the composite membranes, the dimensional change in diagonal length is tested. As seen in Table 2, the swelling ratio increases with increasing temperature, which is similar to that of the water uptake. With higher PBI content and higher PBI crosslinking degree, the swelling ratio of the composite membranes will be reduced. This may be due to the decreased content of the hydrophilic sulfonic group and the introduction of the crosslinked PBI, which restrain the swelling of Nafion®. Thus, the dimensional stability of the composite membranes is improved.

### 3.4. Mechanical properties of the composite membranes

The mechanical properties of the composite membranes are described by two kinds of figures. Fig. 4 shows the effects of the crosslinkable PBI contents on the tensile stress of the composite membranes, and Fig. 5 shows the effects of the crosslinking degree

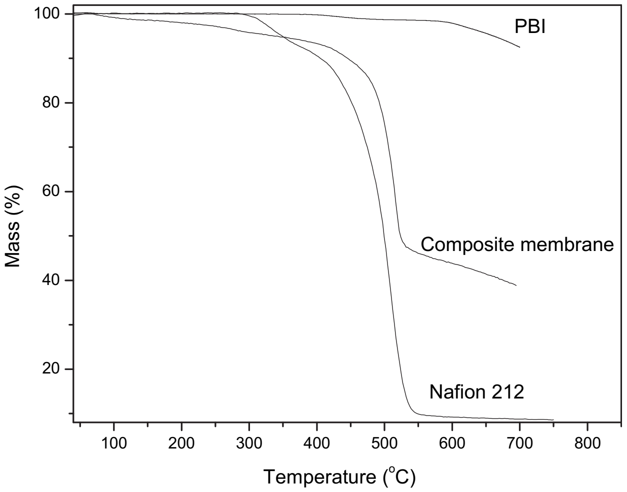


**Fig. 6.** TGA thermograms of pure PBI, pure Nafion®212, and the composite membrane (Nafion®212/PBI = 70/30(w/w), crosslinker content is 30%), $N_2$ atmosphere, heating rate 10 °C/min.

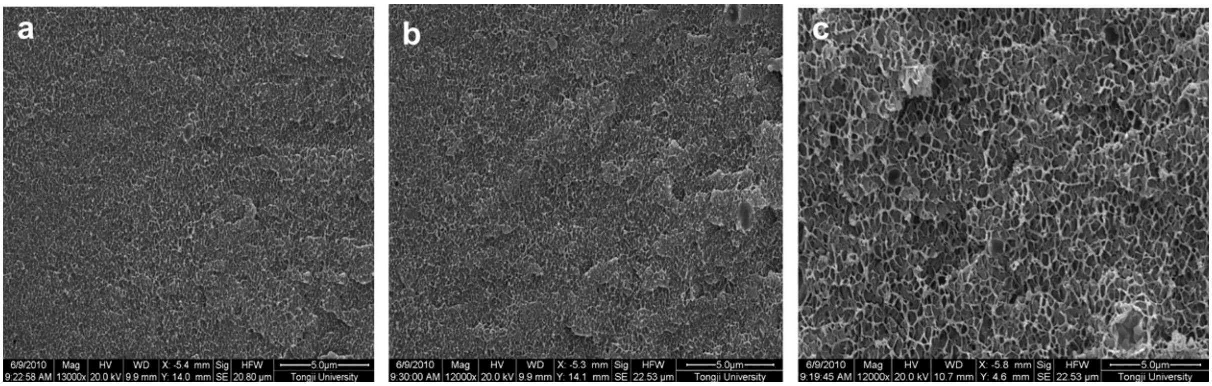


**Fig. 7.** Morphology of the fractured surfaces of the composite membranes with different PBI contents, (a) Nafion®212/PBI = 70/30(w/w); (b) Nafion®212/PBI = 50/50(w/w); (c) Nafion®212/PBI = 30/70(w/w), the crosslinker content of all membranes is 30%.

on the tensile stress of the composite membranes. The mechanical properties of polymer blends mainly depend on the properties of the original polymers and the compatibility of the polymers. The benzimidazole structure in PBI backbone provides good compatibility with Nafion® because of the possibility of acid-base interaction. Moreover, PBI has better mechanical properties than Nafion® due to the wholly aromatic structure of its main chain. As a result, the tensile strength of the composite membranes is improved with increasing PBI contents as shown in Fig. 4. With higher crosslinking degree, the semi-IPN structure of crosslinked PBI and Nafion® can form. As seen in Fig. 5, with the formed network, the macromolecular chain is harder to be broken into small pieces, and the tensile properties can be improved. However, when the crosslinker is amount to 15%, the tensile properties will decrease. With too higher crosslinking degree, the slack anisotropic distributed PBI chains will intertwist more tightly with each other; the segment of the macromolecular chain will be more difficult to diffuse and relax the stress, which will lead to the decrease of the mechanical properties of the composite membranes.

### 3.5. Thermal stability of the composite membranes

TG curves of PBI, Nafion®212, and the composite membranes under nitrogen atmosphere are shown in Fig. 6. For pure PBI, the main weight loss appears at around 600 °C, which can be attributed to the degradation of the backbone of the polymers. For pure Nafion®212, the first weight loss near 329 °C is attributed to the decomposition of the sulfonic acid group, and the major weight loss around 509 °C is due to the degradation of the backbone of Nafion® [41]. For the composite membrane, it exhibits a similar degradation behavior to that of Nafion®. The major weight loss of the composite membrane is around 525–530 °C, which is a little higher than that of Nafion®. The reason is probably that the crosslinked PBI and the semi-IPN structure of the composite membrane restrict the activity of the sulfonic groups and C–F bonds. It indicates that the composite membranes show improved thermal stability compared with Nafion® membranes.

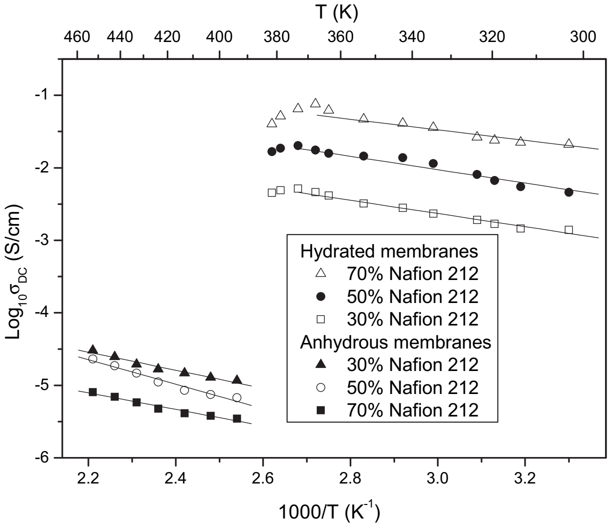


**Fig. 8.** Effects of Nafion® contents on the temperature dependence of the proton conductivity of the composite membranes at 100% relative humidity and anhydrous condition, respectively, the crosslinker content is 30%.

### 3.6. Morphology of the composite membranes

Fig. 7 shows the SEM micrographs for the fractured surfaces of the composite membranes with 30%, 50%, and 70% crosslinkable PBI content, respectively. The cross-sectional surfaces of the composite membranes are homogeneous, which indicates the good compatibility within the semi-IPN structure due to the hydrogen bonds between imidazole and sulfonic groups. The network structures can also be observed significantly from SEM photographs, particularly, when PBI content is higher. The scale of the network chain, which is formed by crosslinked PBI, is about 50–60 nm in Fig. 7(c).

### 3.7. Proton conductivity of the composite membranes

Proton conductivities of the composite membranes are measured in 100% relative humidity and under anhydrous condition, respectively. The results are shown in Fig. 8. With the relative humidity (RH) of 100%, the proton conductivity of the membrane is determined in the temperature range from 30 to 110 °C. As described in the literatures [42,43], the proton transport in Nafion® is vehicle mechanism. It largely depends on the water molecules and offers higher proton conductivity than PBI. Thus, the proton conductivity of the composite membrane increases with increasing Nafion® content in 100% relative humidity. With high relative

**Table 3**
Pre-exponential factor $\sigma_0$ and activation energy $E_a$ of semi-IPN membranes.

| Membranes | $\sigma_0$ (S $cm^{-1}$) | $E_a$ (KJ $mol^{-1}$) |
|---|---|---|
| Nafion®/PBI = 70/30(w/w) | 0.0025 | 21.82 |
| Nafion®/PBI = 50/50(w/w) | 0.1223 | 32.48 |
| Nafion®/PBI = 30/70(w/w) | 0.0162 | 23.90 |

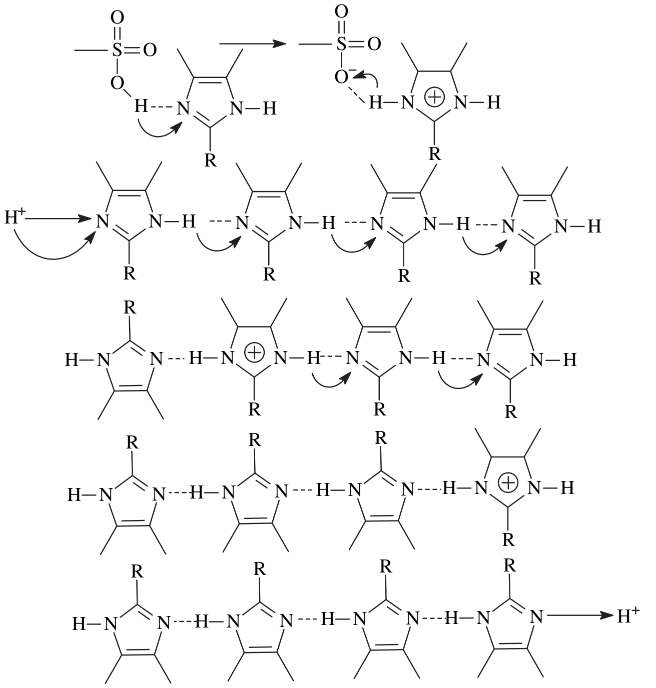


**Fig. 9.** Possible mechanism of correlated proton transfer in PBI/Nafion® semi-IPN membranes.

humidity, the proton conductivity of these materials increases gradually with increasing temperature. However, when the temperature exceeds 95 °C for Nafion®/PBI=70/30(w/w) membrane and 100 °C for Nafion®/PBI = 50/50&30/70(w/w) membranes, the proton conductivity of the composite membranes decreases quickly because of the dehydration of the membranes. The proton transport in the hydrated composite membranes is mainly contributed by the vehicle mechanism.

The anhydrous proton conductivity of the membranes in the temperature range from 110 to 180 °C is also shown in Fig. 8. It can be found that the proton conductivity of all the membranes will drop a lot when the test condition is switched to an anhydrous state. However, the proton conductivity of the membranes also increases gradually with increasing temperature. It can be found that, under the anhydrous condition, the higher the PBI content is, the higher the proton conductivity is, particularly at high temperature.

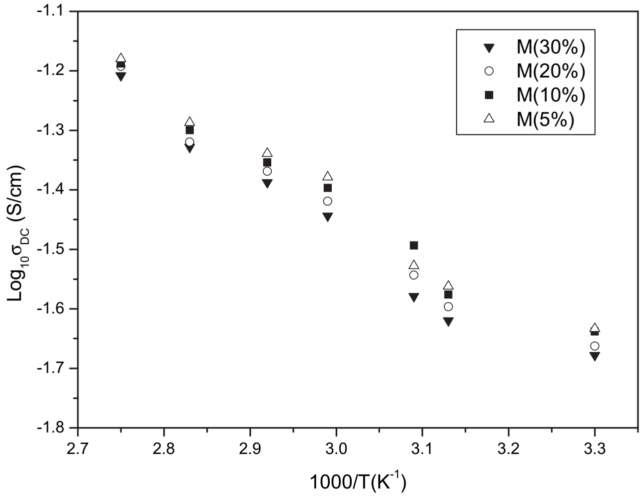


**Fig. 10.** Effects of the crosslinker content on the temperature dependence of the proton conductivity of the composite membranes, the Nafion® content is 70%.

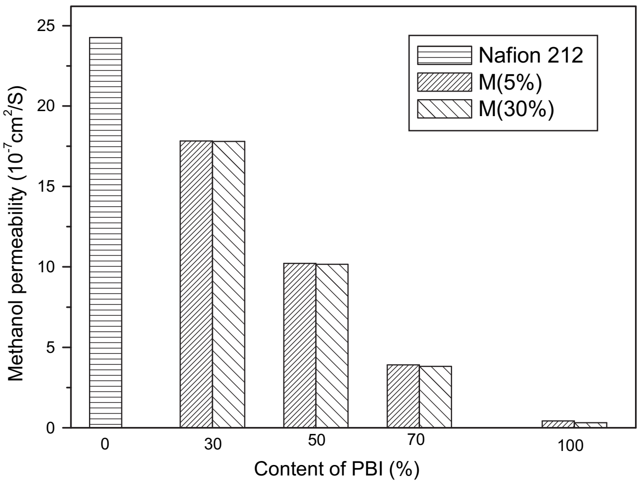


**Fig. 11.** The methanol permeability of the composite membranes with different PBI content.

Temperature dependence of the proton conductivity of anhydrous polymer electrolytes has often been taken as an indicative of a particular type of conduction mechanism [44]. The temperature dependence of proton conductivity follows two different types of equations. Arrhenius law (Eq. (7)) can be used to explain the proton hopping mechanism, while Vogel–Tammann–Fulcher (VTF) equation (Eq. (8)) is usually used to describe the segmental motion mechanism.

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right) \tag{7}$$

$$\sigma = A\exp\left(-\frac{B}{R(T-T0)}\right) \tag{8}$$

In above equations, $\sigma_0$ is the pre-exponential factor; $E_a$ is the apparent activation energy; $R$ is the Boltzmann constant and $T$ is the temperature of the polymer electrolyte. $A$, $B$, and $T_0$ are three constants.

As shown in Fig. 8, temperature dependence of the proton conductivity of PBI/Nafion® semi-IPN membranes under anhydrous condition can be fitted by Arrhenius equation. Table 3 lists the pre-exponential factor $\sigma_0$ and activation energy $E_a$ of PBI/Nafion® semi-IPN membranes. $E_a$ values of the membranes with different Nafion® content are quite approachable, which means that the proton transport in the composite membrane is independent of the segmental motion of Nafion®. The proton transport in the semi-IPN membranes under anhydrous condition can be explained by a Grotthuss-type diffusion mechanism, in which the proton transport in acid–base composite system can occur from protonated molecules to nonprotonated molecules nearby [45]. PBI, a basic polymer ($pK_a = 5.5$ as protonated) with benzimidazole part as the proton donor and acceptor, provides the possibility for proton mobility via structure diffusion involving proton transfer between Nafion® and PBI as well as among PBI chains with a corresponding reorganization of the hydrogen bond network, as shown in Fig. 9.

As shown in Fig. 10, the proton conductivity for the composite membranes will decrease a little when the crosslinking degree increases. The possible reason is that the proton transport under humidified environment mainly depends on the diffusion of water molecules. With the higher crosslinking degree, the main chain of PBI will intertwist more tightly with each other, which may, to a certain extent, retard the diffusion of the water molecules. However, all the composite membranes show proton conductivity values over $10^{-2}$ S/cm under humidified environment, which indicates that they are suitable candidates for PEMs for fuel cell application.

### *3.8. Methanol permeability of the composite membranes*

As a proton exchange membrane in PEMFCs, another key property is the fuel permeability besides the proton conductivity [46]. As shown in Fig. 11, the methanol permeability of the PBI/Nafion® semi-IPN membranes with different crosslinker content decreases dramatically with increasing content of PBI. For Nafion® membranes, there are well-separated hydrophobic/hydrophilic domains, which can transport protons, water, as well as the methanol simultaneously, responding to high methanol permeability of Nafion® [33]. While for PBI/Nafion® semi-IPN membranes, the methanol transport channel will be somewhat blocked by PBI domains. Besides, the benzimidzole structure in PBI main chain is easy to form hydrogen bond with methanol, which also may, to a certain extent, reduce the methanol permeability [32]. Fig. 11 also shows that the methanol permeability for the composite membranes will have a little decrease when the crosslinking degree increases. The possible reason is similar to that discussed in proton conductivity. The main chain of PBI with a higher crosslinking degree will intertwist more tightly with each other, which will not only retard the diffusion of the water molecules but the methanol as well.

## 4. Conclusions

A new strategy to prepare the reinforced composite membranes for PEMFCs with wide working temperature was proposed via constructing semi-IPN structure from PBI and Nafion®212. The crosslinkable PBI was synthesized from poly(2,2′-(m-phenylene)-5,5′-bibenzimidazole) and *p*-vinylbenzyl chloride. PBI was crosslinked during the membrane preparation and formed semi-IPN structure with Nafion®212. The crosslinking degree of PBI in the composite membranes can be evaluated by the gel fraction. The results show that the crosslinking degree can be controlled by the adding amount of the crosslinker. The membranes show higher thermal stabilities and improved mechanical properties compared with pure Nafion®. The composite membranes have high proton conductivity, which range from $\sim 10^{-2}$ S/cm to $\sim 10^{-1}$ S/cm at relative humidity (RH) of 100%. The proton transport in the hydrated composite membranes is vehicle mechanism due to the presence of the water. When the temperature exceeds 100 °C, the proton conductivity of the composite membranes decreases quickly because of the dehydration of the membranes. Under anhydrous condition, the proton conductivity of the membranes will drop to $\sim 10^{-4}$ S/cm, the benzimidazole structure of PBI and the acidic component of Nafion® provides the possibility for the proton mobility via structure diffusion involving proton transfer between the heterocycles with a corresponding reorganization of the hydrogen bonded network.

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