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ARTICLE TYPE

Macromolecular covalently cross-linked quaternary ammonium poly(ether ether ketone) with polybenzimidazole for anhydrous high temperature proton exchange membrane

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Poly (ether ether ketone) bearing benzyl bromide groups (Br-PEEK) was synthesized. And a series of cross-linked membranes (Br-PEEK-x%PBI) based on Br-PEEK with polybenzimidazole (PBI) as a macromolecular cross-linker was prepared to improve the dimension stability and tensile strength without reducing proton conductivity. The X-ray photoelectron spectroscopy (XPS) confirmed the success of cross-linking reaction. After being ammoniated, the quaternary ammonium PEEK membranes were immersed in phosphoric acid and the anhydrous phosphoric acid doped membranes were obtained. The phosphoric acid doped membranes without PBI as the cross-linker had excess volume swelling and could not keep integrated. The others cross-linked membranes had good dimensional stabilities. Because PBI could absorb phosphoric acids, the proton conductivities of cross-linked membranes first increased and then decreased with the content of PBI increasing. The highest proton conductivity was 0.081 S cm^{-1} at 200 ^{o}C for PA-PEEK-20%PBI membrane. The dimensional stabilities, oxidative stabilities and tensile strength of PA-PEEK-x%PBI membranes improved. The PA-PEEK-30%PBI membrane could last for 7.5 h in 3 wt. % H_2O_2, 4 ppm Fe^{2+} Fenton solution at 80 ^{o}C before breaking into pieces. The energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM) and dynamic mechanical analysis (DMA) were used for detail research.

Introduction

Fuel cells, which are able to directly generate electric energy from chemical energy of fuel, are considered to be the most promising alternative energy conversion advice for both mobile and stationary applications [1-4]. In recent years, proton exchange membrane fuel cell (PEMFC) has drawn more and more attention because of their high efficiency and high energy density. And they seem to benefit from operating at high temperature (Here, the high temperature is 100-200 ^{o}C.). There are several advantages for high temperature proton exchange membrane fuel cells (HTPEMFCs) [5-7], such as enhanced electrochemical kinetics, simplified water and heat management, utilization of higher CO-rich reformed hydrogen and less demand for coolant and humidification. In the last few years, polybenzimidazole doped with phosphoric acids (PBI-PA) has been widely studied as the high temperature proton exchange membrane (HTPEM) material [8-11]. In this system, phosphoric acids act as the proton acceptors and donors to build the hydrogen bond network. The protons pass through this network by breaking and forming of hydrogen bond [12]. So the proton conductivity of PA doped membrane is mainly determined by PA doping level. As the PEM materials, the polymers must own enough high molecule weight to ensure the appropriate mechanical strength for preparation of membrane electrode assembles. The PBI with high molecule weight always has poor solubility, which hinders its extensive use.

Alternative and promising polymers, which can be doped with phosphoric acids and then used as HTPEMs, are the aromatic polyether polymers bearing polar functional groups or N-heterocycle on the main or side chain. These aromatic polyether polymers have excellent chemical and thermal stabilities, high mechanical strength and good solubility. Kallitsis *et al*. prepared kinds of polymers with polar pyridine groups on the main or side chain [13-17]. These polymers exhibited excellent thermal and chemical stabilities and could be used as HTPEM. Wang *et al*. synthesized a series of poly(arylene ether sulfone)s bearing imidazole groups as HTPEM [18]. In order to increase the PA doping level without deteriorating mechanical properties, the cross-linking method was used in this work. Yang *et al*. synthesized polysulfone containing methylimidazole, ethylimidazole and butylimidazole [12]. And they found that the calculated molar free volumes and van der Waals volumes of ImPSU membranes were much larger than those of PBI membrane. So the ImPSU membranes showed lower volume swelling ratio with the same PA doping level when compared with PBI membrane. Scott *et al*. prepared the PA doped quaternary 1,4-diazabicyclo-[2.2.2]-octane polysulfone membrane and poly($R_1R_2R_3$)–N^+/H_3PO_4 composite membrane[19,20]. Tigelaar *et al*. prepared the sulfonated and unsulfonated poly (arylene ether triazine)s with pendant diphenylamine groups as the HTPEM [21]. In our previous work, we prepared PA doped PEMs based on PEEK. These membranes had higher PA doping level compared with that of PBI [22, 23]. However, the higher PA doping level these membranes had, the higher volume swelling ratio and poorer mechanical properties these membranes exhibited. Therefore, many researchers have been making great efforts to solve this problem.

Cross-linking is an excellent method to improve mechanical strength, thermal and oxidative stabilities, and especially limit excess swelling in the field of PEM. A lot of researches about cross-linking have been done in the field of HTPEM, but the cross-linking always leads to the decrease of PA doping level [24-26]. Some cross-linkers with N atom in molecule seem to contribute to PA doping level [27-28]. In our previous work, both 4,4′-diaminodiphenylmethane and 1,6-diaminohexane were used as the cross-linkers. The PA doping level of cross-linked membranes increased with the content of cross-linkers increasing. Macromolecular cross-linkers have been studied in the last few years [4.29.30]. Compared with small molecular cross-linkers, macromolecular cross-linkers have reactive functional groups in each repeating unit, which results in much denser network structure. Then the dimensional stability and mechanical properties of material will be obviously improved in spite of lower cross-linker content.

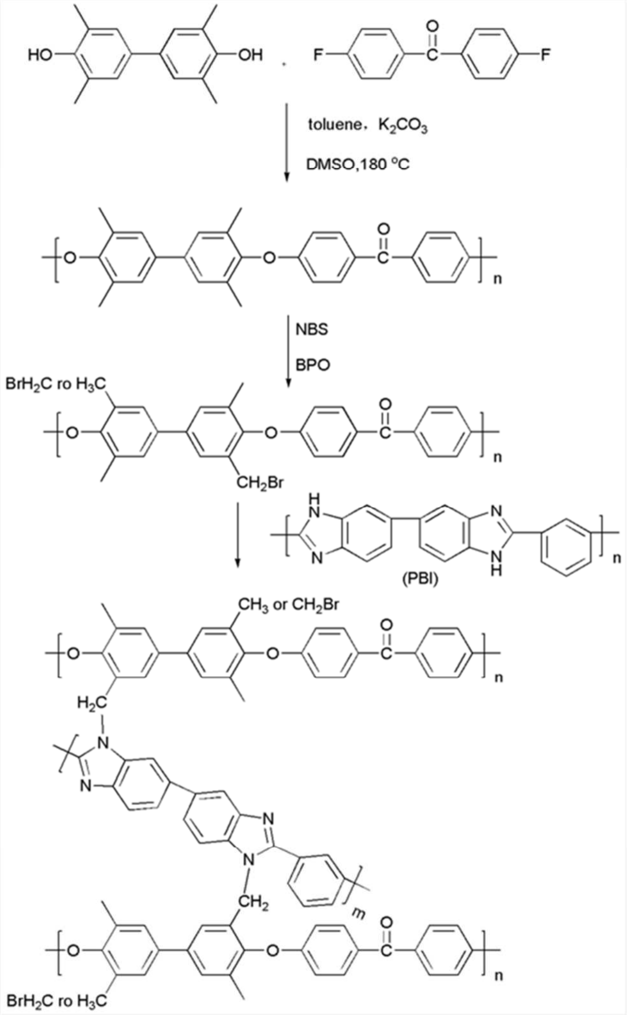
Therefore, in this work, we prepared cross-linked quaternary ammonium PEEK membranes (Q-PEEK-x%PBI) with PBI as the macromolecular cross-linker for anhydrous HTPEMs. The quaternary ammonium reaction was based on PEEK bearing benzyl bromide groups (Br-PEEK). The Br-PEEK polymer was synthesized in a mild way without the use of extremely toxic substance, such as chloromethylether. PBI was chosen as the macromolecular cross-linker. Because PBI possesses the strong ability of absorbing PA and owns two reactive -NH- functional groups in each unit which can react with -CH$_2$Br on Br-PEEK polymer. It is expected to improve thermal stability, oxidative stability and mechanical properties without any damage to proton conductivity. The cross-linking reaction is very easy to take without any catalyst and just needed to be heated. The Q-PEEK-x%PBI membranes were immersed in phosphoric acid solution and dried to obtain the anhydrous PA doped membranes (PA-PEEK-x%PBI). The PA doping level in weight (W_{doping}) and volume (V_{doping}), proton conductivities, mechanical properties, thermal stabilities and oxidative stabilities of anhydrous PA-PEEK-x%PBI membranes were studied in detail.

Experiment

Materials

3,3,5,5-Tetramethyl-4,4-bisphenol （TMBP） was obtained from Shanghai Jiachen Chemical Company. 4,4-Difluorobenzophenone (DFBP) was purchased from Yanbian Longjing Chemical Company. Potassium carbonate, N-bromosuccinimide (NBS) and benzoyl peroxide (BPO) were purchased from Sinopharm Chemical Reagent Co., Ltd. Chloroform, Dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP) and toluene were purchased from Tianjin Tiantai Fine Chemicals Co., Ltd. Trimethylamine aqueous solution (33 %) and phosphoric acid solution (85 wt.%) were purchased from Tianjin Guangfu Fine Chemicals Co., Ltd. Hydrogen peroxide aqueous solution (30 %) was purchased from Xilong Chemical Co., Ltd. 3,3-Diaminobenzidine (DAB) and diphenyl-mphthalate (DPIP) were purchased from Sigma–Aldrich. All chemicals were used as they received without further purification.

Preparation of polymers



Scheme1. The preparation process of cross-linked Br-PEEK-x%PBI

The preparation of poly(ether ether ketone) was described as followed: TMBP (0.02 mol), DFBP (0.02 mol), potassium carbonate (0.02 mol), dimethyl sulfoxide (DMSO) and toluene were added into a three-neck flask, which was equipped with a nitrogen inlet, an overhead mechanical stirrer and a Dean-Stark trap with a condenser. The reaction mixture were heated to 130 °C and held for 3 h to remove the water from the reaction. Then toluene was removed. The temperature was raised to 180 °C and held for several hours until the reaction mixture became very viscous. The viscous solution was poured into water and the PEEK polymer precipitated out of the viscous solution. The precipitate was crushed into powder and washed with distilled water for three times and then dried at 120 °C in the vacuum oven.

The brominating reaction of PEEK was performed in a controllable and mild way as described in our previous work [31]. The degree of bromine substitution (DS) was controlled by the addition amount of NBS. NBS and BPO were used as brominating agent and initiator, respectively. PEEK (0.02 mol), NBS (0.04 mol), BPO (0.004 mol) and chloroform (100 ml) were added into a three-necked flask equipped with an overhead mechanical stirrer and a condenser. The reaction was carried out at the boiling point of chloroform and lasted for 12 h. Then the mixture was poured into acetone and Br-PEEK polymer precipitated out of solution. The Br-PEEK polymer was crushed into powder and washed with acetone for three times and then dried at 80 °C in the vacuum oven. The synthesis of PBI by the condensation of DAB and DPIP in a two-step process was performed according to our previous work [26].

The preparation of cross-linked PA doped membranes

The Br-PEEK polymer was dissolved in NMP at a concentration of 7 % (w/v) and appropriate PBI was added into the Br-PEEK solution. After PBI was dissolved, the solution was cast on the glass plate and dried at 80 °C for 24 h. During the process of membrane forming, the reaction between -CH_2Br and -NH- on PBI took place as shown in Scheme1. Then the cross-linked Br-PEEK-x%PBI membranes were immersed in trimethylamine aqueous solution for 72 h to accomplish the quaternary ammonium reaction, the Q-PEEK-x%PBI membranes were obtained. Finally, the Q-PEEK-x%PBI membranes were immersed in phosphoric acid solution (85 wt.%) at 40 °C for 6 h and dried at 80 °C vacuum oven for 72 h to remove the water, the anhydrous PA-PEEK-x%PBI membranes were obtained. Here, the x% was the mol ratio of -NH- to -CH_2Br.

Characterization and measurements

Nuclear magnetic resonance (NMR) spectrum was measured on a Bruker 510 spectrometer (500 MHz). The X-ray photoelectron spectroscopy (XPS) was measured on a VG Scientific ESCALAB 250 system. The dynamic mechanic analysis (DMA) was performed on TA Q800. The membranes were cut into 6 mm × 4 cm with about 70 μm thickness. The tests were carried out with a fixed frequency of 1 Hz, 1 N applied pre-force and oscillation amplitude of 10 μm. The storage modulus (E′) and loss modulus (E") were obtained at a heating rate of 5 °C min^{-1} in air. Energy dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) were performed by SHIMADZU SSX-500 scanning electron microscope. The mechanical properties of all the membranes were studied by SHIMADZU AG-I 1KN equipment at a test speed of 2 mm min^{-1} in the room temperature. Before the test, all the samples were treated as 15 mm × 4 mm. For each test, at least ten samples were measured and the average value was obtained. The thermal gravimetric analyses (TGA) of all the membranes were performed by a Perkin-Elmer TGA-1 thermo-gravimetric analyzer at a heating rate of 10 °C min^{-1} in nitrogen atmosphere. All the membranes were preheated at 120 °C for 24 h in vacuum oven to make sure that the solvent and water had been removed completely, and then the membranes were heated from 100 °C to 700 °C.

PA doping level (W_{doping} and V_{doping}) and volume swelling ratio

The Q-PEEK-x%PBI membranes were cut into 5 cm × 5 cm and dried at 120 °C for 24 h to reach an unchanged weight and marked as $W_{undoped}$ (g). After being immersed in phosphoric acid solution (85 wt.%) at 40 °C for 6 h, the membranes were taken out, wiped the phosphoric acid solution on surface, and dried in vacuum oven at 80 °C for three days to remove water. Then the weight was recorded and marked as W_{doped} (g). The PA doping level in weight (W_{doping}) was calculated by following equation:

$$W_{doping}=\frac{W_{doped}-W_{undoped}}{W_{undoped}}\times 100\% \quad (1)$$

The volume swelling ratio was reflected as the volume change of membrane before and after PA doping.

$$V_{swelling}=\frac{L_{doped}\times I_{doped}\times T_{doped}-L_{undoped}\times I_{undoped}\times T_{undoped}}{L_{undoped}\times I_{undoped}\times T_{undoped}}\times 100\% \quad (2)$$

where L_{doped}(cm), I_{doped} (cm) and T_{doped} (cm) were the length, width and thickness of the PA doped membrane, and $L_{undoped}$, $I_{undoped}$ and $T_{undoped}$ were the length, width and thickness of the PA undoped membrane.

The PA doping level in volume (V_{doping}) was calculated in this work by following equation.

$$V_{doping}=\frac{W_{doped}-W_{undoped}}{L_{doped}\times I_{doped}\times T_{doped}\times M(H_3PO_4)} \quad (3)$$

where the M(H_3PO_4) was molar mass of H_3PO_4 and was 97.97 g mol^{-1}.

Solubility test and ionic exchange capacity (IEC)

The cross-linked Br-PEEK-x%PBI membranes of 0.01g were put into 3 ml NMP which was used as the solvent of Br-PEEK polymer. Then the samples were kept at room temperature for 20 days to observe if the membrane was dissolved. The ionic exchange capacity was measured with Q-PEEK-x%PBI membranes. Each membrane was immersed in 0.01 mol L^{-1} (M), 40 ml NaOH aqueous solution for three days. Then the membranes were taken out and the solution was titrated with 0.01 M HCl aqueous solution. The consumed volume of HCl aqueous solution was recorded. The membranes were dried at 120 °C for 24 h and the weights were measured. The IEC was calculated by the following formula:

$$IEC=\frac{40\times 0.01-v\times 0.01}{W_{dry}} \quad (4)$$

where v (ml) was the volume of HCl aqueous solution was consumed, and W_{dry} (g) was the weight of dry membrane.

Measurement of in-plane proton conductivity (σ)

The in-plane proton conductivity (σ) of anhydrous PA doped membrane was measured by a four-probe AC impedance method from 0.1 Hz to 100 kHz with a Princeton Applied Research Model 2273 potentiostat/galvanostat/FRA. All the membranes were cut into 1 cm × 4 cm and the thickness were measured. The proton conductivity was calculated by the following equation:

$$\sigma=\frac{L}{RS} \quad (5)$$

where L was the distance of two electrodes (cm), R was the membrane resistance and S was the cross-sectional area of the membrane (cm^2).

Oxidative stability test

All the membranes were cut into 30 mm × 3 mm and then immersed in 30 ml Fenton solution with 3 wt.% H_2O_2, 4 ppm Fe^{2+} at 80 °C. The time that membrane could last for before breaking into pieces was used to evaluate the oxidative stability. The longer the membrane could last for, the better oxidative stability the membrane had.

Results and discussions

Nuclear Magnetic Resonance

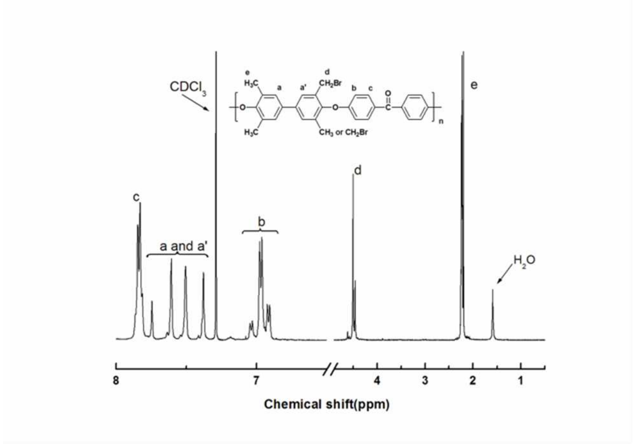


Fig.1 ^{1}H NMR spectrum of Br-PEEK

The ^{1}H NMR spectrum of Br-PEEK polymer is shown in Fig.1. All chemical shifts (integral area) were 7.8 (4H), 7.7-7.3 (4H), 7.0-6.9 (4H), 4.5-4.4 (3.4H) and 2.2 (6.9H) ppm. The chemical shift at 4.4-4.5 ppm belonged to the hydrogen in benzyl bromide group (-CH$_2$Br). According to the integral area in NMR spectrum, the degree of bromine substitution was calculated and was 42.5 %.

X-ray photoelectron spectroscopy and solubility test

The X-ray photoelectron spectroscopy can be used for element qualitative and quantitative analysis, and chemical shift in the binding energy of the inner electron can be used to determine the chemical structure of compound. In this work, XPS analysis of Br-PEEK-25%PBI membrane was performed to confirm if the cross-linking reaction was complete. Fig.2 shows the narrow scan spectra of C1s and N1s. From Fig.2 (a), it could be observed that the carbon signal was divided into five signals, including C-C/C-H (284.7 eV), C-N/C-O (286.0 eV), C-Br (286.6 eV), C=O (288.0 eV) and C=N (289.0 eV) [32]. The appearance of C=N signal indicated that PBI had been incorporated into the cross-linked membrane. In Fig.2 (b), the nitrogen signal was divided into two signals, N(C)$_3$ (401.2 eV) and C=N (399.7 eV). As reported, the binding energy of -NH- and C=N on PBI were 400.2 and 398.4 eV [33]. After cross-linking, the H atom was replaced by C atom, both the binding energy of N(C)$_3$ and C=N showed a slightly increase. And the integral area ratio of N(C)$_3$ to C=N was 1 indicating that the reaction between -NH- and -CH$_2$Br on PBI almost completed.

The cross-linking reaction always leads to the formation of three-dimension network structure which will make the membrane insoluble in general solution. During the solubility test, all Br-PEEK-x%PBI cross-linked membranes had volume swelling and could not be dissolved in NMP solution. The results of solubility test proved that the cross-linking reaction had been accomplished successfully. All the results of XPS and solubility test confirmed the cross-linking reaction took place between -NH- and -CH$_2$Br successfully.

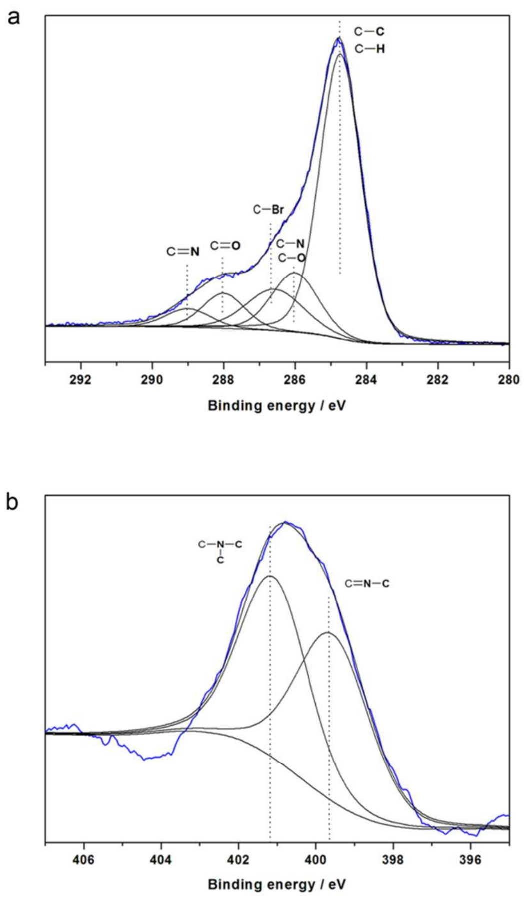


Fig.2 The XPS spectra of C1s (a) and N1s (b)

Dynamic mechanical analysis

Dynamic mechanical analysis is indispensable analytical means for polymer materials study. In the program control temperature, polymer is applied to a periodic stress or strain, and then the storage modulus (E′) and loss modulus (E") are recorded. DMA is a powerful measurement to determine the glass transition temperature (T$_g$) and application temperature of material. The E′ and E" curves of Br-PEEK-x%PBI membranes are shown in Fig.3 (a). All the membranes were kept in 60 ^{o}C vacuum oven for 24 h before test. It could be seen that the T$_g$ of membranes increased with the content of PBI increasing. The T$_g$ of Br-PEEK, Br-PEEK-10%PBI, Br-PEEK-20%PBI and Br-PEEK-30%PBI membranes were 117, 130, 133 and 140 ^{o}C, respectively. Although the introduction of benzyl bromide side chains might lead a lower T$_g$, which were less than 140 ^{o}C. It seemed unreasonable to the high temperature resistance of PEEK. Reviewing the whole process of membrane formation to find the reason for low T$_g$, we found that maybe it contributed to the remaining solvent. The remaining solvent played a role of plasticizer, which led to the low T$_g$. Therefore, all the membranes were kept in 140 ^{o}C vacuum oven for 12 h to remove the remaining solvent as much as possible. Fig.3 (b) shows the E′ and

E" curves of Br-PEEK-x%PBI membranes after heat-treatment. The T_g of Br-PEEK, Br-PEEK-10%PBI, Br-PEEK-20%PBI, Br-PEEK-30%PBI membrane were 186, 189, 187 and 196 °C, respectively. They were much higher than those of unheat-treatment membranes. The similar study had been studied in detail by E. Segreccia *et al* [34]. They prepared sulfonated aromatic polymer membrane with different solvents at different temperatures and performed the stress-strain test and dynamical mechanical analysis of these membranes. The residual solvent as the plasticizer was inserted in macromolecular chains and weakened the intermolecular forces which led to the low E′ and E". The results in Fig.3 confirmed that it was the solvent remaining in membranes that led to the low T_g. And it could be concluded that the heat-treatment was very important for the application of HTPEMs.

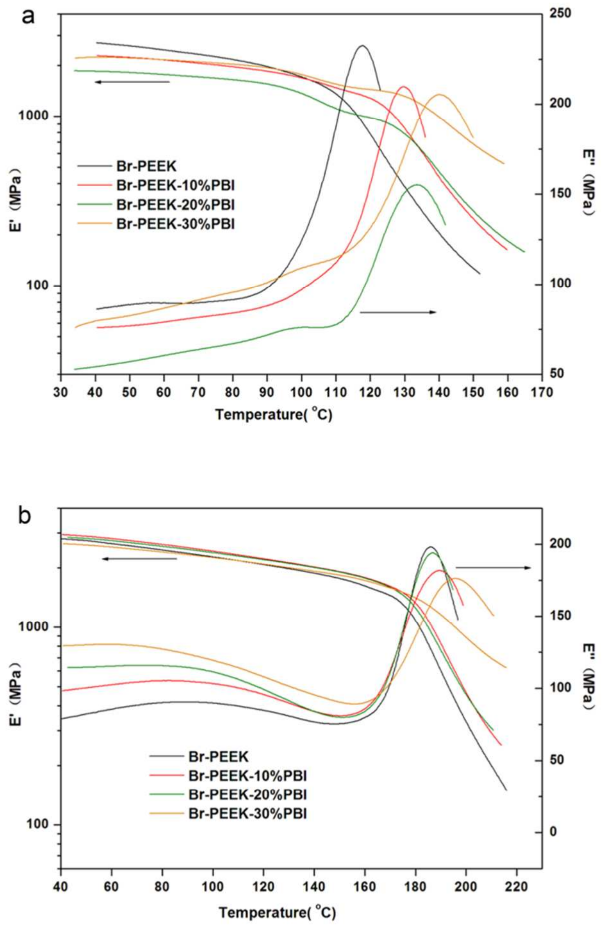


Fig.3 The curves of E′ and E" of Br-PEEK-x%PBI membranes without heat-treatment (a) and Br-PEEK-x%PBI membranes with heat-treatment at 140 °C for 12 h (b)

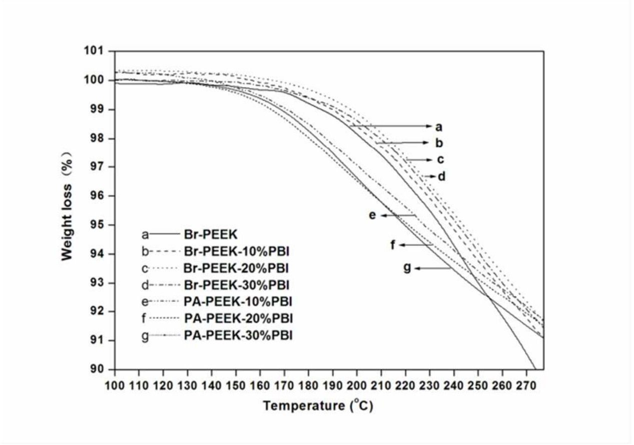


Fig.4 The TGA curves of Br-PEEK-x%PBI and PA-PEEK-x%PBI membranes.

The curves of thermal gravimetric analysis (TGA) are shown in Fig.4. The temperature where the membrane loses 5 % weight ($T_{5\%}$) is recorded and used to evaluate the thermal stability of membrane. The $T_{5\%}$ of Br-PEEK, Br-PEEK-10%PBI, Br-PEEK-20%PBI and Br-PEEK-30%PBI membranes were 234, 238, 242 and 245 °C, respectively. The $T_{5\%}$ of Br-PEEK-x%PBI membranes was higher than 230 °C and the weight loss decreased with the content of PBI increasing. The $T_{5\%}$ of PA-PEEK-10%PBI, PA-PEEK-20%PBI and PA-PEEK-30%PBI membranes were 219, 221 and 227 °C, respectively. The results from Fig.4 indicated the introduction of PBI improved the thermal stabilities of Br-PEEK-x%PBI and PA-PEEK-x%PBI membranes.

Ionic exchange capacity, PA doping level in weight (W_{doping}) and volume swelling ratio ($V_{swelling}$)

Table1. The W_{doping}, V_{doping}, $V_{swelling}$ and proton conductivities of PA-PEEK-x%PBI membranes.

Sample	W_{doping} (wt.%)	$V_{swelling}$ (%)	V_{doping} (mmol cm^{-3})	Proton conductivity (mS cm^{-1})	
				140 °C	200 °C
PA-PEEK	—^{a}	—^{a}	—^{a}	—^{a}	—^{a}
PA-PEEK-10%PBI	246	172	16.18	43	69
PA-PEEK-15%PBI	254	179	16.66	48	75
PA-PEEK-20%PBI	277	183	17.74	54	81
PA-PEEK-25%PBI	243	164	16.80	49	74
PA-PEEK-30%PBI	224	142	16.52	45	73

^{a}The membrane had excess swelling and could not be tested.

The IEC is defined as the amount of quaternary ammonium cations ($–N^+(CH_3)_3$) in unit mass. The benzyl bromide took place SN2 N-alkylation reaction with trimethylamine to generate quaternary ammonium cation ($–N^+(CH_3)_3Br^-$) which could absorb phosphoric acid by ionic bond. The amount of quaternary ammonium cations determined the PA doping level for this kind of basic membrane. The IEC of Q-PEEK, Q-PEEK-10%PBI, Q-PEEK-15%PBI, Q-PEEK-20%PBI, Q-PEEK-25%PBI and Q-PEEK-30%PBI membranes were 5.60, 3.43, 2.95, 2.39, 1.44 and 1.18 mmol g^{-1}, respectively. The IEC values decreased with the content of PBI increasing. Because the cross-linking reaction took place between the -CH_2Br and -NH- on PBI and consumed a number of -CH_2Br functional groups, which directly led to the decrease of -$N^+(CH_3)_3Br^-$ functional groups. The doping level in weight (W_{doping}) and volume (V_{doping}) of all the membranes were measured in 85 wt.% phosphoric acid solution at 40 °C. The PA-PEEK membrane had an excess swelling ratio and was unable to keep integrated. Therefore the PA-PEEK membrane was not studied. The W_{doping} of PA-PEEK-x%PBI membranes was much higher than 224 wt.% which was higher than that of pure PBI (146 wt.%, immersing in 85 wt.% PA solution at 80 °C for 48 h) in our previous work [10]. Compared with various PBI-*im* and PBI-*ph* in reported work [35], the PA-PEEK-x%PBI membranes also had a higher W_{doping}. It could be seen from Table1 that when the content of PBI was lower than 20 %, W_{doping} and V_{swelling} increased with the content of PBI increasing; when the content of PBI was higher than 20 %, W_{doping} and V_{swelling} decreased with the content of PBI increasing. This was because there were two factors for PBI to affect the PA-PEEK-x%PBI membranes. Firstly, PBI could absorb phosphoric acids which could increase W_{doping}. Secondly, PBI as the macromolecular cross-linker could form dense cross-linking network structure which could decrease W_{doping} and V_{swelling}. When the content of PBI was low and the density of cross-linking structure was also low. The volume of cross-linked membrane was able to enlarge to accommodate more phosphoric acids. The existence of PBI was benefit for high W_{doping}. On the contrary, when the content of PBI was high and the density of cross-linking structure was also high. Although the membrane was able to absorb more phosphoric acids, the volume of membrane was not able to enlarge to accommodate phosphoric acids because of high density cross-linking network structure. Then both W_{doping} and V_{swelling} decreased. The existence of PBI was benefit for low V_{swelling}. Therefore, W_{doping} and V_{swelling} first increased and then decreased with the content of PBI increasing.

PA doping level in volume (V_{doping}) and proton conductivity

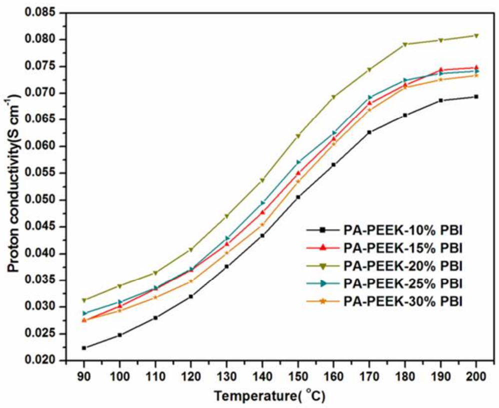


Fig.5 The proton conductivities of PA-PEEK-x%PBI membranes

The proton conductivities of PA-PEEK-x%PBI membranes were measured and are shown in Fig.5. As expected, the proton conductivities increased with the temperature increasing from 90 °C to 200 °C under anhydrous condition. The highest proton conductivity was 0.081 S cm^{-1} for PA-PEEK-20%PBI at 200 °C. When temperature was higher than 170 °C, the increasing trends of proton conductivities became slow. This was because the dehydration reactions among phosphoric acids begin to take place. Meanwhile, the proton conductivities first increased and then decreased as the content of PBI increasing. The same trend was also observed for their W_{doping} and V_{doping} values. Comparing proton conductivities in Fig.6 with W_{doping} and V_{doping} in Table 1, it could be seen that the V_{doping} was more able to reflect the changing trend of proton conductivities than W_{doping}. For example, the W_{doping} of PA-PEEK-10%PBI was 246 wt.% which was higher than that of PA-PEEK-30%. However, both the V_{doping} and proton conductivity of PA-PEEK-10%PBI were lower than that of PA-PEEK-30%. For PA doped PEM, the proton conductivity almost depended on the amount of phosphoric acids. One portion of phosphoric acids was attached to polymer by acid-base reaction forming ion pair [12]; another portion of phosphoric acids dispersed in intermolecular space by formation of the hydrogen bond among phosphoric acids. The continuity of the hydrogen bonding network within the phosphoric acids was crucial to the efficiency of proton hopping and could be significantly disrupted at low content of phosphoric acids [36]. All the membranes showed high volume swelling ratios after being doped with phosphoric acids, which led to the enlarged intermolecular distance. Therefore, more phosphoric acids were needed to build the continuous proton transport path to accomplish proton conduction. Therefore, the amount of phosphoric acids in unit volume of membrane determined the proton conductivity; this was PA doping level in volume (V_{doping}).

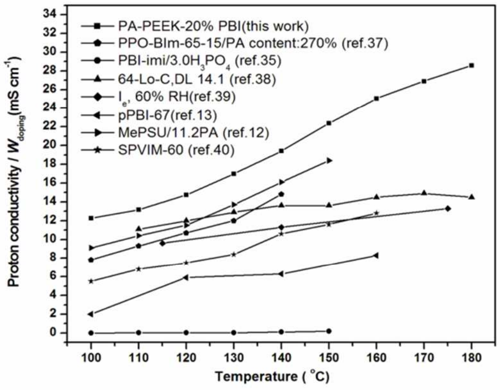


Fig.6 The proton conductivities/W_{doping} at different temperature

In order to compare the proton conductivities with different PA doping level membranes, the ratio of proton conductivity to W_{doping} ($P_{\triangle W}$) was calculated. $P_{\triangle W}$ is the contribution of per PA doping level (wt.%) to the proton conductivity. The highest proton conductivity of polymer membranes with different structure were selected from previous works and the $P_{\triangle W}$ were calculated showing in Fig.6. It could be observed that the $P_{\triangle W}$ of PA-PEEK-20%PBI membrane was higher than those of membranes in references [12,13,35,37-40]. The W_{doping} of PPO-BIm-65-15 (PA content: 270 %) was similar to that of PA-PEEK-20%PBI (PA content: 277 %). The latter had obviously higher proton conductivity, because the structure of PA-PEEK-20%PBI membrane was more suitable for proton transport. The results from Fig.6 indicated that the proton conductivities in this work were higher those of PBI, PSU and PPO systems.

Mechanical properties

Table2 The mechanical properties of Br-PEEK-x%PBI and PA-PEEK-x%PBI membranes.

Sample	Tensile strength (MPa)	Young Modulus (MPa)	Elongations at the break (%)
Br-PEEK-10%PBI	100	1597	12
Br-PEEK-15%PBI	95	1639	11
Br-PEEK-20%PBI	92	1788	14
Br-PEEK-25%PBI	87	1817	18
Br-PEEK-30%PBI	98	1982	11
PA-PEEK	—[a]	—[a]	—[a]
PA-PEEK-10%PBI	5	48	55
PA-PEEK-15%PBI	6	52	57
PA-PEEK-20%PBI	5	50	40
PA-PEEK-25%PBI	7	65	33
PA-PEEK-30%PBI	7	83	31

[a] The membrane had excess swelling and could not be tested.

The excellent mechanical properties are required to prepare membrane electrode assembles. The mechanical properties of Br-PEEK-x%PBI membranes and PA-PEEK-x%PBI membranes were summarized in Table 2. It could be seen the tensile strength and elongations at the break of Br-PEEK-x%PBI membranes were 92-98 MPa and 11-14 %. They did not show regular tend with the content of PBI increasing. The formation of cross-linking structure improved mechanical properties of cross-linked membranes. The tensile strengths of PA-PEEK-x%PBI membranes were almost less than a tenth of those of Br-PEEK-x%PBI membranes. The tensile strength deceased sharply. This was mainly because of plasticization of phosphoric acids. And also due to plasticization of phosphoric acids, the elongations at the break of PA-PEEK-x%PBI membranes increased. The more phosphoric acids the membrane absorb, the lower tensile strength and the larger elongation at break the membrane had. In general, the tensile strength and young modulus of PA-PEEK-x%PBI membranes increased with the content of PBI increasing. The deterioration of mechanical stability at high H_3PO_4 concentration existed in all various basic polymer membranes including PBI used as PA doped HTPEM [41]. Xiao prepared high temperature PBI fuel cell membrane via a sol-gel process and the obtained PBI-PA membrane had the tensile strength only 1.0-3.5 MPa [42]. Here, the tensile strengths of PA-PEEK-x%PBI membranes were comparable to or higher than that of pure PBI membrane (60 °C immersing temperature in 85 wt.% phosphoric acid solution) reported in our previous work [26].

Oxidative stability

Generally, there are two methods to measure the durability of materials: ex situ durability test and in situ continuous durability test. In this work, the ex situ durability test is used. The PA-PEEK-x%PBI membranes were exposed to the Fenton solution with 3 wt.% H_2O_2, 4 ppm Fe^{2+} at 80 °C. The time that membrane could last for before breaking into pieces was used to evaluate the oxidative stability. PA-PEEK-10%PBI, PA-PEEK-20%PBI and PA-PEEK-30%PBI membranes took 3.5 h, 5.5 h and 7.5 h to begin to break, respectively. On the one hand, the dense cross-linking structure was able to hinder the entry of free radicals. On the other hand, the covalent bond network could resist the attack of free radicals in some degree. So the oxidative stabilities improved with the content of PBI increasing. The oxidative stabilities of PA-PEEK-x%PBI membranes were better than those of pure linear PBI reported by Li [43] and Kerres [41]. They exposed the linear PBI membrane to 3 wt.% H_2O_2 solution containing 4 ppm Fe^{2+} at 68 °C. The linear PBI membrane was broken into small pieces after 30 min.

Scanning electron microscopy and energy dispersive X-ray spectroscopy

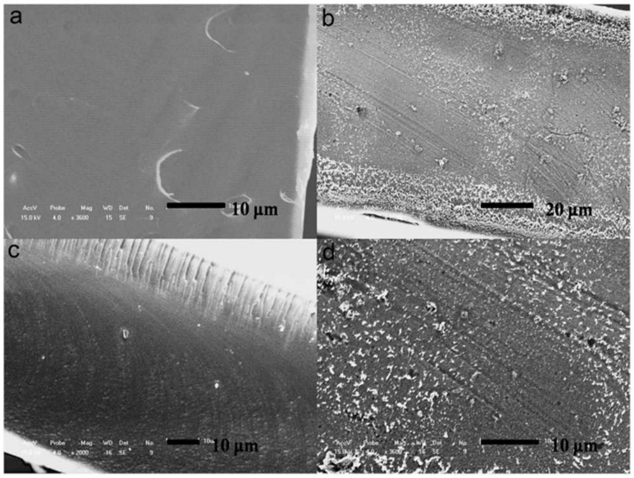


Fig.7 The cross-sectional morphology of Br-PEEK-25%PBI (a), PA-PEEK-25%PBI (b) and sub-PA-PEEK-25%PBI (c). (d) is the partial enlarged view of (b).

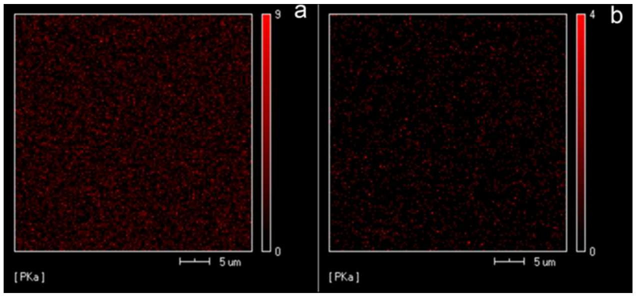


Fig.8 The EDX spectra of PA-PEEK-25%PBI (a) and sub-PA-PEEK-25%PBI (b) membrane

The cross-sectional morphology of Br-PEEK-25%PBI and PA-PEEK-25%PBI are shown in Fig.7 (a) and (b). And Fig.7 (c) shows the cross-sectional morphology of sub-PA-PEEK-25%PBI which is obtained by immersing the PA-PEEK-25%PBI membrane in water at 80 °C for three days and then heating at 150 °C. The Fig.7 (d) shows the partial enlarged view of Fig.7 (b). It could be seen that there were many small particles in cross-section of Fig.7 (b) and this phenomenon could not be found in Fig.7 (a) and (c). So it could be concluded that small particles formed in Fig.7 (b) due to the PA doping. In SEM spectra, PA doped membrane showed white clustering region because of PA doping, which was found in our previous work [10]. From Fig.7 (b) and (d), it could be concluded that phosphoric acids had a good dispersion in the membrane. By immersing in water at 80 °C, was there phosphoric acid still in the sub-PA-PEEK-25%PBI membrane? The EDX analysis of P element was measured. Fig.8 shows the EDX spectra of P element of PA-PEEK-25%PBI and sub-PA-PEEK-25%PBI membrane. From Fig.8 (a), it could be seen that phosphoric acids had a good dispersion and the phosphoric acid clusters were connected with each other. In Fig.8 (b), the phosphoric acid clusters were almost unattached with each other but it showed that there still were phosphoric acids in sub-PA-PEEK-25%PBI membrane.

Conclusions

In this work, a series of anhydrous PA-PEEK-x%PBI membranes with PBI as the N-type macromolecular cross-linker were prepared for high temperature fuel cell. The results of XPS and solubility test confirmed the cross-linking reaction was accomplished successfully. The results of DMA demonstrated that the heat-treatment process was necessary for HTPEMs. Both PA doping level in weight (W_{doping}) and PA doping level in volume (V_{doping}) were calculated in this work. And it was found that the V_{doping} was more able to reflect the changing trend of proton conductivities. With the content of PBI increasing, the proton conductivities first increased and then decreased. The PA-PEEK-20%PBI had the highest proton conductivity among these cross-linked membranes. The oxidative stabilities, tensile strength and dimensional stabilities of cross-linked PA-PEEK-x%PBI membranes improved with the content of PBI increasing. The results of SEM and EDX indicated that phosphoric acids had a good dispersion in membrane. All results indicate that the use of PBI as the macromolecular cross-linker makes it possible for quaternary ammonium PEEK to be used in high temperature fuel cell and the PA-PEEK-20%PBI membrane has the highest potential.

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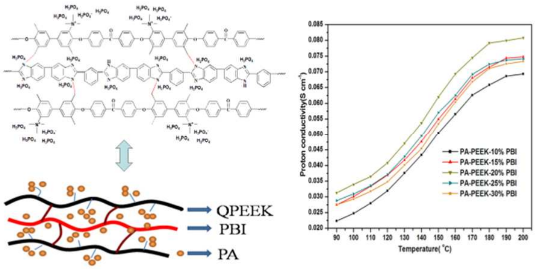
* Colour graphic:



* Text: The phosphoric acid doped quaternary ammonium poly(ether ether ketone) membranes cross-linked with PBI showed improved performance.