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ARTICLE TYPE

## Quaternized poly(ether ether ketone)s doped with phosphoric acid for high temperature polymer electrolyte membrane fuel cells

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Quaternized poly(ether ether ketone)s (QPEEKs) which were aminated by trimethylamine (TMeA), triethylamine (TEtA), tripropylamine (TPrA) and 1-methylimidazole (MeIm) were prepared and used as phosphoric acid (PA) doped high temperature proton exchange membranes. These QPEEK membranes showed high glass transition temperature ( $T_g$  was higher than 483 K) and high thermal stability ( $T_{5\%}$  was higher than 486 K). The tensile strengths of these QPEEK membranes were higher than 60 MPa. The PA doped im-QPEEK which was aminated by MeIm had the highest  $W_{\text{doping}}$  (159 wt.%) and proton conductivity ( $0.05 \text{ S cm}^{-1}$  at 473 K). For other three PA doped QPEEK membranes, the  $W_{\text{doping}}$  and proton conductivity decreased with increasing of the length of trialkyl side chains on quaternary ammonium groups. According to our study, the PA absorbing ability was subjected to the structures of quaternary ammonium groups instead of the basicities of quaternary aminating reagents. All PA doped membranes had great oxidative stability and could last for more than 5 h in 3 wt.%  $\text{H}_2\text{O}_2$ , 4 ppm  $\text{Fe}^{2+}$  Fenton solution at 353 K.

### Introduction

With the environmental pollution and energy shortage becoming worse, clean and efficient renewable energy has been widely studied. In recent years, proton exchange membrane fuel cells (PEMFCs) have received more and more attention because of their high efficiency, high energy density and low emission of pollutants<sup>[1]</sup>. And they seem to benefit from operation at high temperature (373–473 K)<sup>[2–4]</sup>. There are several advantages for operating at high temperature: (1) electrochemical kinetics rates are enhanced; (2) water and heat management are simplified; (3) higher CO-rich reformed hydrogen can be used; (4) use of non-platinum catalyst is possible.

Proton exchange membrane (PEM) is the core of PEMFC. At present, commercial PEM materials are perfluorosulfonic acid membranes represented by Nafion<sup>®</sup> series (DuPont). They own excellent chemical stability and high proton conductivities when hydrated<sup>[5,6]</sup>. However, Nafion<sup>®</sup> shows poor mechanical strength and loses its long-term stability at high temperature (higher than 353 K). In addition, the proton conductivity of Nafion<sup>®</sup> is water-dependent. When the temperature is above 373 K, free water is unable to act as the proton carrier because of its boiling point. Therefore, the widely studied methods to prepare high temperature proton exchange membrane (HTPEM) are improving water retaining capability at high temperature and substituting water for high boiling proton solvent. Three strategies have fallen into this category. Firstly, the hydrophilic materials (almost are inorganic materials, such as silicon oxide) are introduced into sulfonic acid membranes to improve water retaining capability at the temperature above 373 K<sup>[7–10]</sup>. Secondly, new electrolytes which were based on the polymers owning nitrogen-containing heterocycles were employed to act as proton solvents, such as imidazole, benzimidazole and pyrazole<sup>[11–13]</sup>. Thirdly,

replacement of proton carrier has been extensively used in the field of HTPEM, such as ionic liquid<sup>[14,15]</sup>, phosphoric or sulfonic acid containing an oxo-acid in the molecule<sup>[16–19]</sup>. Among them, the phosphoric acid (PA) is the most widely used as proton carrier. The phosphoric acid has remarkably high conductivity in pure state because of its self-dissociation<sup>[20]</sup>. When doped in basic polymer, phosphoric acid is attached onto polymer through ionic bonds, besides other phosphoric acid is bonded to each other by hydrogen bonds network. The protons transport through this network by breaking and rebuilding of hydrogen bonds<sup>[21, 22]</sup>.

At present, PBI doped with phosphoric acid has been widely studied as the HTPEM<sup>[23–26]</sup>. As is well known, PBI has high thermal stability due to the hydrogen bonds among molecules. However, PBI with high molecular weight has poor solubility in common solvents such as dimethyl sulfoxide (DMSO) and *N*-methyl-2-pyrrolidone (NMP), except in limited solvent such as polyphosphoric acid (PPA). Alternative materials of HTPEMs are poly(aryl ether ketone/sulfone)s bearing polar functional groups or *N*-heterocycle on the main or side chain<sup>[27–30]</sup>. Poly(ether ether ketone) (PEEK) is widely used in traffics, aeronautics, astronautics, medicines and other fields due to its good mechanical properties, high thermal stability (glass transition temperature was 416 K and melting temperature was 616 K), excellent chemical stability and resistance to radiation damage<sup>[31]</sup>. The PEEK with 3,3',5,5'-tetramethyl-4,4'-bisphenol (TMBP) as the bisphenol monomer (TMBP-PEEK) has a high  $T_g$  (526 K)<sup>[32]</sup>. The outstanding thermal stability makes it possible to play an important role in HTPEM. In our previous work, the quaternized PEEK copolymers which were based on TMBP and 2, 2'-bis(4-hydroxy phenyl) propane were studied as HTPEM<sup>[33]</sup>. Compared with PBI, TMBP-PEEK is relatively cheap. And the amount of

quaternary ammonium group which determines the PA doping level is controllable by the adding amount of brominating reagent (*N*-bromosuccinimide). It is easier to control the PA doping level by controlling the concentration of quaternary ammonium group.

In this work, various quaternized poly(ether ether ketone) (QPEEK) membranes with trimethylamine (TMeA), triethylamine (TEtA), tripropylamine (TPrA) and 1-methylimidazole (MeIm) as quaternary aminating reagents were prepared. The  $T_g$  of these QPEEK membranes was varied because of different pendent side-chains. And we supposed that the PA absorbing ability of these membranes would be influenced by the structures of quaternary ammonium groups and the basicities of quaternary aminating reagents. So the PA absorbing ability of these membranes was studied in this work. The dynamic mechanical analyses (DMA), thermal gravimetric analyses (TGA), mechanical properties and oxidative stability of these QPEEK and PA doped membranes were also studied in detail.

## Experimental

### Materials

TMBP and 4,4'-difluorobenzophenone (DFBP) were purchased from Yanbian Longjing Chemical Company. *N*-bromosuccinimide (NBS), benzoyl peroxide (BPO), trimethylamine aqueous solution (33 %), triethylamine (98 %), tripropylamine (99 %) and phosphoric acid solution (85 wt.%) were purchased from Sinopharm Chemical Reagent Co.,Ltd.. Chloroform, DMSO, NMP, potassium carbonate and toluene were obtained from Tianjin Tiantai Fine Chemicals Co.,Ltd.. Hydrogen peroxide aqueous solution (30 %) was purchased from Xilong Chemical Co.,Ltd.. 1-Methylimidazole was obtained from Shanghai Dibo Chemical Reagent Co.,Ltd.. All chemicals were used as received without further purification.

### Characterization and measurements

The nuclear magnetic resonance (NMR) spectra were performed by the Bruker 510 spectrometer (500 MHz). The mechanical properties were studied by SHIMADZU AG-1 1KN equipment at a test speed of 2 mm min<sup>-1</sup>. All the samples were cut into 15 mm × 4 mm and at least ten samples were measured to obtain an average value. The TGA were performed by the Perkin-Elmer TGA-1 thermo-gravimetric analyzer in nitrogen atmosphere at a heating rate of 10 K min<sup>-1</sup> from 373 K to 973 K. Before test, all the membranes were preheated at 373 K for 24 h in vacuum oven to remove water completely. The DMA were performed on TA Q800. The membranes were cut into 6 mm × 4 cm with an approximate thickness of 70 μm. 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 tan delta were obtained at a heating rate of 5 K min<sup>-1</sup> in air.

### Preparation of polymers

Poly(ether ether ketone) was synthesized as follows. TMBP (4.84 g, 0.02 mol), DFBP (4.36 g, 0.02 mol), potassium carbonate (3.04 g, 0.02 mol), 25 ml DMSO and 10 ml toluene were added into a three-neck reaction flask which was equipped with an overhead mechanical stirrer, a nitrogen inlet and a Dean-Stark trap with a condenser. Firstly, the mixtures of reaction were heated to 403 K and held for 3 h to remove the water from the reaction. Secondly,

toluene was removed and the temperature rose to 453 K and was held for several hours until the mixtures of reaction became very viscous. Finally, the viscous solution was poured into water to precipitate out the polymer. The precipitates were crushed into powder and washed with distilled water for three times and then dried at 393 K.

The brominating reaction of PEEK was performed in a controllable and mild way with NBS as the brominating reagent and BPO as the initiator. The degree of bromine-substituted (DS) was controlled by the amount of NBS. Taking the brominated polymer DS=0.8 as an example, the process of bromination was described as follows. The PEEK polymer (4.2 g 0.01mol), NBS (1.8 g 0.01 mol) and BPO (0.2 g, 0.001 mol) were dissolved in 42 ml chloroform. The reaction took place at the reflux temperature of chloroform. After 6 h, the mixtures of reaction were poured into acetone to precipitate out the brominated polymer. The brominated polymer (BrPEEK) was washed with acetone for three times and dried at 333 K.

The preparation of quaternized PEEK (QPEEK) was similar, taking the methyl-QPEEK which was aminated by trimethylamine as an example. The BrPEEK polymer (1 g) was dissolved in 10 ml NMP solution. After the BrPEEK polymer was dissolved completely, trimethylamine aqueous solution (0.35 ml) was dropped into the BrPEEK solution. Then the mixtures of reaction were heated to 323 K and maintained for 6 h. The methyl-QPEEK solution was poured into acetone and washed with acetone for three times. The obtained methyl-QPEEK polymer was dried at 333 K for 24 h. The QPEEK polymer which was aminated by triethylamine was marked as ethyl-QPEEK. The QPEEK polymer which was aminated by tripropylamine was marked as propyl-QPEEK. The quaternary aminating reagent of im-QPEEK was 1-methylimidazole. The obtained QPEEK polymers were dissolved in NMP to form 10 wt.% casting solution, then poured on the glass plate, respectively. The membranes were kept at 333 K for 48 h in oven to remove the solvent.

### PA doping level ( $W_{\text{doping}}$ and $V_{\text{doping}}$ ) and volume swelling ratio ( $V_{\text{swelling}}$ )

Each QPEEK membrane was cut into 4 cm × 4 cm and dried at 413 K for 24 h to reach an unchanged weight ( $W_{\text{undoped}}$ ). Then the membrane was immersed in phosphoric acid solution (85 wt.%) at 333 K for 6 h, then taken out, wiped the phosphoric acid solution on surface, and dried in vacuum oven at 373 K for 24 h to remove water. The weight of anhydrous PA doped membrane was marked as  $W_{\text{doped}}$ . Meanwhile, the length, width and thickness of each membrane were recorded before and after being doped with phosphoric acid. The PA doping level in weight ( $W_{\text{doping}}$ ) was calculated by following equation:

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

The volume swelling ratio ( $V_{\text{swelling}}$ ) was the volume change of membrane before and after being doped with phosphoric acid.

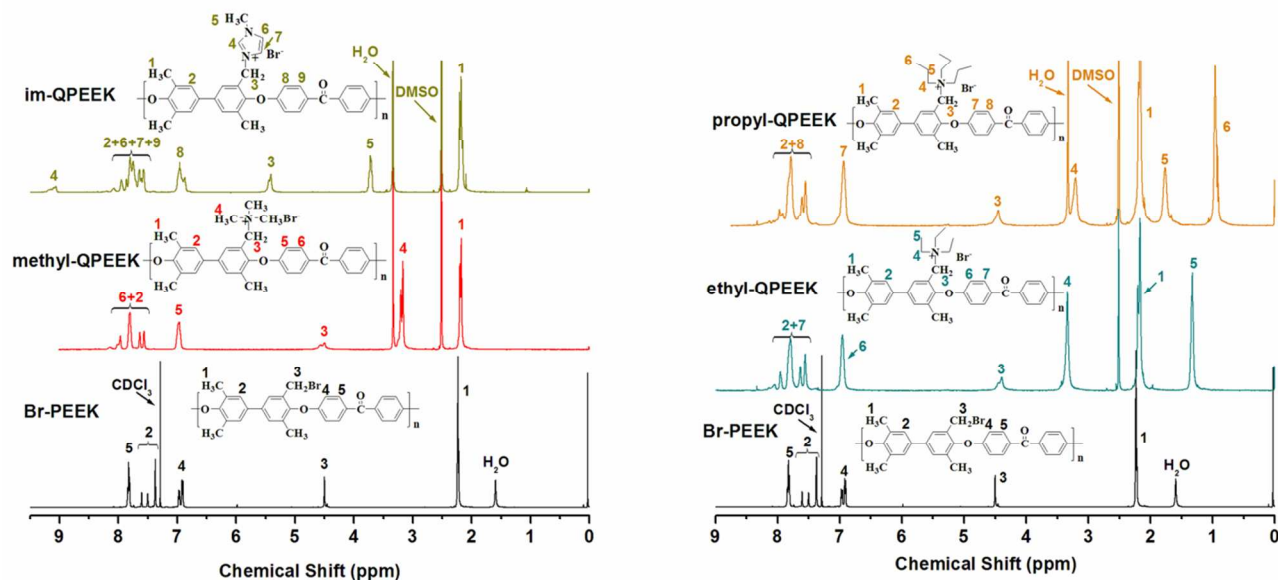


Figure 1. The  $^1\text{H-NMR}$  spectra of BrPEEK, methyl-QPEEK, ethyl-QPEEK, propyl-QPEEK and im-QPEEK.

$$V_{\text{swelling}} =$$

$$\frac{L_{\text{doped}} \times I_{\text{doped}} \times T_{\text{doped}} - L_{\text{undoped}} \times I_{\text{undoped}} \times T_{\text{undoped}}}{L_{\text{undoped}} \times I_{\text{undoped}} \times T_{\text{undoped}}} \times 100\% \quad 2$$

where  $L_{\text{doped}}$ ,  $I_{\text{doped}}$  and  $T_{\text{doped}}$  were the length, width and thickness of the anhydrous PA doped membrane, and  $L_{\text{undoped}}$ ,  $I_{\text{undoped}}$  and  $T_{\text{undoped}}$  were the length, width and thickness of the QPEEK membrane.

The PA doping level in volume ( $V_{\text{doping}}$ ) was calculated by following equation.

$$V_{\text{doping}} = \frac{W_{\text{doped}} - W_{\text{undoped}}}{L_{\text{doped}} \times I_{\text{doped}} \times T_{\text{doped}} \times \text{Mr}(\text{H}_3\text{PO}_4)} \quad 3$$

where the unit of weight was gram (g) and the units of length, width and thickness were centimetre (cm),  $\text{Mr}(\text{H}_3\text{PO}_4)$  was  $97.97 \text{ g mol}^{-1}$ .

### In-plane proton conductivity ( $\sigma$ ) and oxidative stability

The in-plane proton conductivity ( $\sigma$ ) 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  $1 \text{ cm} \times 4 \text{ cm}$  and the thicknesses were measured. The proton conductivity was calculated by following equation:

$$\sigma = \frac{L}{RS} \quad 4$$

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

The oxidative stability of anhydrous PA doped membrane was tested. All membranes were cut into  $15 \text{ mm} \times 3 \text{ mm}$  and immersed in different solutions (details in footnote of Table 1) at water bath under 353 K. The time that membrane took to begin to break was recorded to evaluate the stability. The longer time the

membrane endured in Fenton solution, the better stability the membrane had.

## Results and Discussion

### NMR

The preparation of methyl-QPEEK, ethyl-QPEEK, propyl-QPEEK and im-QPEEK was similar and easy. The reaction was  $\text{S}_{\text{N}}2$  alkylation reaction and occurred under very mild condition. The NMR spectra of BrPEEK, methyl-QPEEK, ethyl-QPEEK, propyl-QPEEK and im-QPEEK are shown in Figure 1. For the  $^1\text{H-NMR}$  spectrum of BrPEEK, the chemical shift of peak 3 ( $\delta=4.499 \text{ ppm}$ ) belonged to the hydrogen atoms of benzyl bromide group ( $\text{ph-CH}_2\text{Br}$ )<sup>[32]</sup>. Comparing the NMR spectrum of methyl-QPEEK with that of BrPEEK, the thin and tall peak 3 ( $\text{ph-CH}_2\text{Br}$ ,  $\delta=4.499 \text{ ppm}$ ) disappeared and the new peaks at  $\delta=4.505\text{-}4.577 \text{ ppm}$  (peak 3) and  $\delta=3.167\text{-}3.201 \text{ ppm}$  (peak 4) appeared. The new peaks 3 and 4 in methyl-QPEEK were assigned to the hydrogen atoms of  $-\text{CH}_2\text{-N}$  and  $-\text{N}(\text{CH}_3)_3$  groups, respectively. The ratio of integral peak area of 3 to 4 was 2:9 which was same with that of hydrogen atoms of  $-\text{CH}_2\text{-N}$  and  $\text{N}(\text{CH}_3)_3$ . This result indicated the  $\text{ph-CH}_2\text{Br}$  reacted with TMeA completely. For the NMR spectrum of im-QPEEK, the new peaks at  $\delta=9.058\text{-}9.103 \text{ ppm}$  (peak 4),  $\delta=7.890 \text{ ppm}$  (peak 7),  $\delta=7.611 \text{ ppm}$  (peak 6) and  $\delta=3.720 \text{ ppm}$  (peak 5) belonged to the hydrogen atoms of MeIm in im-QPEEK. After being aminated by MeIm, the peak of benzyl hydrogen atoms ( $\delta=4.499 \text{ ppm}$ ) was shifted to  $\delta=5.408\text{-}5.442 \text{ ppm}$  (peak 3). The results confirmed the im-QPEEK polymer had been synthesized successfully.

For the  $^1\text{H-NMR}$  spectrum of ethyl-QPEEK, the chemical shifts of peak 4 ( $\delta=3.335 \text{ ppm}$ ) and peak 5 ( $\delta=1.324 \text{ ppm}$ ) were assigned to the methylene and methyl hydrogen atoms of TETA in ethyl-QPEEK. The chemical shift of benzyl hydrogen atoms was transferred from  $\delta=4.499 \text{ ppm}$  to  $\delta=4.395 \text{ ppm}$  (peak 3) after the benzyl bromide was alkylated by TETA. For the NMR spectrum of propyl-QPEEK, the chemical shifts of peak 4 ( $\delta=3.203 \text{ ppm}$ ),



peak 5 ( $\delta=1.767$  ppm) and peak 6 ( $\delta=0.939$  ppm) belonged to the hydrogen atoms of N-CH<sub>2</sub>-C, C-CH<sub>2</sub>-C and C-CH<sub>3</sub> groups on TPrA in propyl-QPEEK, respectively. The chemical shift at  $\delta=4.450$  ppm was attributed to benzyl hydrogen atoms (ph-CH<sub>2</sub>-N). The ratio of integral area was same with that of the number of hydrogen atom for all QPEEKs. All the results confirmed that the quaternized polymers had been synthesized successfully and the conversion of benzyl bromide groups to quaternary ammonium groups was almost complete.

### 10 PA doping level and volume swelling ratio

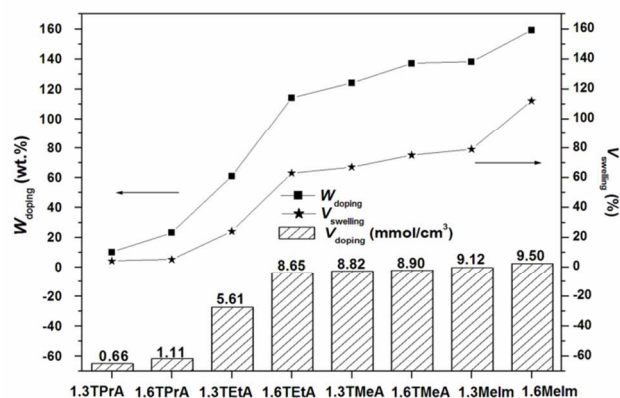


Figure 2. The  $W_{\text{doping}}$ ,  $V_{\text{swelling}}$  and  $V_{\text{doping}}$  of PA-methyl-QPEEK, PA-ethyl-QPEEK, PA-propyl-QPEEK and PA-im-QPEEK (1.3 or 1.6 was the degree of bromine-substituted).

15 The  $W_{\text{doping}}$ ,  $V_{\text{swelling}}$  and  $V_{\text{doping}}$  of PA-methyl-QPEEK, PA-ethyl-QPEEK, PA-propyl-QPEEK and PA-im-QPEEK membranes are shown in Figure 2. It could be seen that the  $W_{\text{doping}}$  and  $V_{\text{doping}}$  increased with the increasing of DS for the same QPEEK membranes. And for different QPEEK membranes, the  $W_{\text{doping}}$  and  $V_{\text{doping}}$  were in the order of PA-im-QPEEK > PA-methyl-QPEEK > PA-ethyl-QPEEK > PA-propyl-QPEEK, even the DS increased, for example, PA-im-QPEEK(1.3) > PA-methyl-QPEEK(1.6), PA-methyl-QPEEK(1.3) > PA-ethyl-QPEEK(1.6), PA-ethyl-QPEEK(1.3) > PA-propyl-QPEEK(1.6). Both basicities  
25 of amines and structures of quaternary ammonium groups were supposed to influence the PA doping levels. In fact, the basicities of amines did not show obvious influence to the PA doping levels. The  $pK_a$  of four various aminating reagents from SciFinder was list as follows,  $pK_a$  (TMeA)= $9.75\pm 0.28$ ,  $pK_a$  (TEtA)= $10.62\pm 0.25$ ,  $pK_a$  (TPrA)= $9.99\pm 0.50$ ,  $pK_a$  (MeIm)= $7.01\pm 0.10$ . The basicities of them should be in order of TEtA > TPrA > TMeA > MeIm, which showed almost an opposite order of PA doping levels from experiment. Meanwhile, it was found that the PA doping levels were closely related to the  
35 structures of quaternary ammonium groups. The structures of quaternary ammonium groups directly determined the PA doping levels of QPEEK membranes. Increasing the length of trialkyl side chains on quaternary ammonium group led to weaker ionic bond between cation and phosphoric acid molecule. As shown in  
40 Figure 3, the  $W_{\text{doping}}$  and  $V_{\text{doping}}$  of PA doped membranes decreased obviously with the length of trialkyl side chains on N atoms increasing, especially for the PA-propyl-QPEEK which almost had no PA absorbing ability. The three flexible and hydrophobic side chains of N atom could move freely, which

45 hindered the approach of phosphoric acid and led to the weakest ionic bonds. The PA-im-QPEEK membrane had the highest  $W_{\text{doping}}$  and  $V_{\text{doping}}$  for two reasons. First, the heterocyclic MeIm was a conjugated and nearly plane ring which provided a larger space to approach phosphoric acid molecule. Second, the  
50 conjugated structure of MeIm delocalized the positive charge in the whole ring, which facilitated the formation of ionic bond between the imidazolium cation and phosphoric acid molecule. Therefore, the PA-im-QPEEK had the highest  $W_{\text{doping}}$  and  $V_{\text{doping}}$ . In this work, the  $V_{\text{swelling}}$  of PA doped membranes increased with  
55 the increasing of  $W_{\text{doping}}$  and  $V_{\text{doping}}$ .

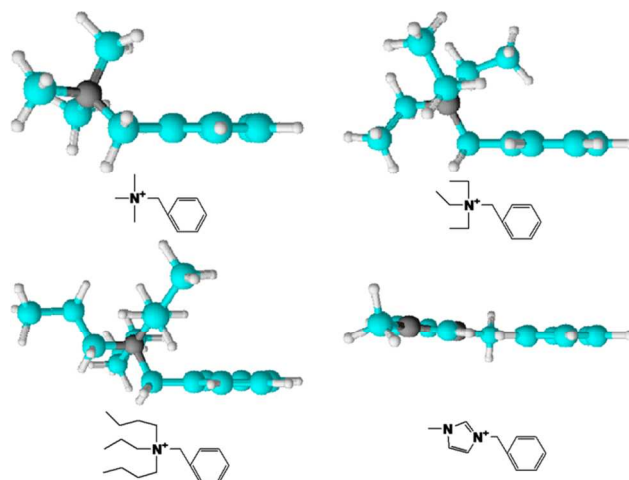


Figure 3. Atomic arrangement diagram of different quaternary ammonium groups (the white was H atom, the gray was N atom and the cyan was C atom).

### 60 Proton conductivity

The proton conductivities of PA doped membranes are shown in Figure 4. The proton conductivity increased with the temperature increasing. The PA-im-QPEEK (1.6) had the highest proton conductivity of  $0.05 \text{ S cm}^{-1}$  at 473 K under anhydrous condition.  
65 The proton conductivity of PA-ethyl-QPEEK (1.3) is lower than  $0.01 \text{ S cm}^{-1}$ . For the PA-propyl-QPEEK membranes, they had too low  $W_{\text{doping}}$  and  $V_{\text{doping}}$  to obtain a measureable resistance. It was found that the proton conductivity showed the same trend with the  $W_{\text{doping}}$  and  $V_{\text{doping}}$  as shown in Figure 2. The proton transport  
70 in PA doped membrane at high temperature mainly followed the proton hopping or Grothuss mechanism. The proton hopped along the hydrogen bonds which were formed by phosphoric acid. And the proton conductivity was determined by the hydrogen bond transport channels. The volume swelling changed  
75 the distance of polymer molecules. And the larger volume swelling led to the larger molecular spacing. Both the amount of phosphoric acid and volume swelling of membranes influenced the proton transport. Because more PA molecules were needed to keep the continuity of hydrogen bonds in PA doped membrane  
80 with larger molecular spacing. Therefore, the  $V_{\text{doping}}$  played a more important role than  $W_{\text{doping}}$  in proton transport. The proton conductivity mainly depended on the  $V_{\text{doping}}$ . As shown in Figure S1, regardless of how the acid uptake was achieved, e.g. TMeA, TEtA or MeIm, the proton conductivities of PA doped membranes  
85 increased along with the increasing of  $V_{\text{doping}}$ .

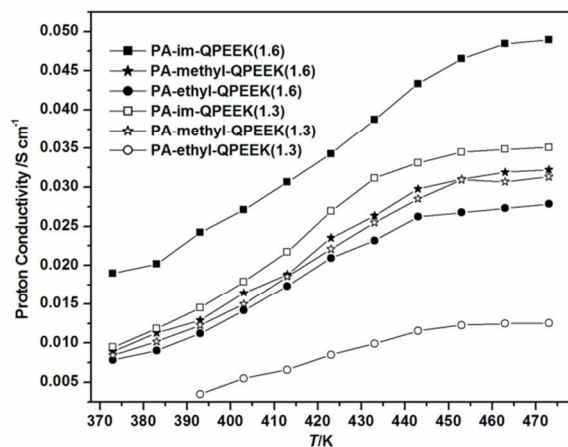


Figure 4. The proton conductivities of PA-methyl-QPEEK, PA-ethyl-QPEEK, PA-propyl-QPEEK and PA-im-QPEEK under anhydrous condition (1.3 or 1.6 was the degree of bromine-substituted).

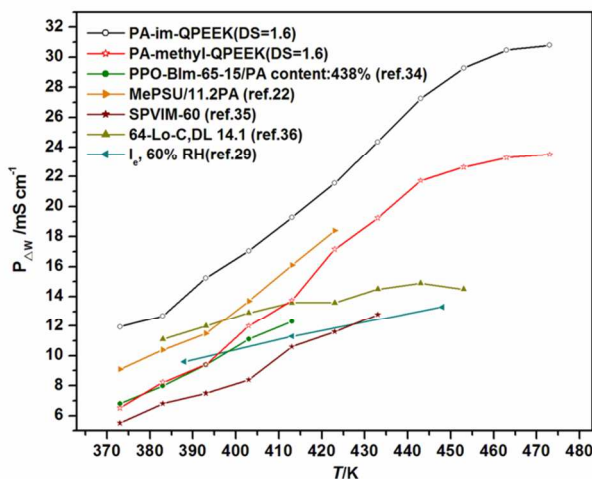


Figure 5. The  $P_{\Delta W}$  of PA-im-QPEEK(DS=1.6), PA-methyl-QPEEK(DS=1.6) and polymers from references.

Since the polymer structure determines PA doping level, PA doping level determines proton conductivity. In order to compare proton conductivity among different polymers, the ratio of proton conductivity to  $W_{\text{doping}}$  ( $P_{\Delta W}$ ) was calculated.  $P_{\Delta W}$  is the contribution of per PA doping level (wt.%) to the proton conductivity. The highest proton conductivity of different polymers from previous works was summarized and compared with that of this work. Figure 5 shows the  $P_{\Delta W}$  of PA-im-QPEEK (DS=1.6), PA-methyl-QPEEK (DS=1.6) and polymers from references. It could be seen that the  $P_{\Delta W}$  of PA-im-QPEEK (DS=1.6) was highest. The  $P_{\Delta W}$  of PA-methyl-QPEEK (DS=1.6) membrane was also higher than those of PPO-BIm-65-15 (PPO system)<sup>[34]</sup> and SPVIM (polystyrene system)<sup>[35]</sup>. Although the  $P_{\Delta W}$  of PA-methyl-QPEEK (DS=1.6) was lower than those of 64-Lo-C (PBI system)<sup>[36]</sup> and  $I_e$  (aromatic polyether system)<sup>[29]</sup> at the temperature lower than 413 K, it was far higher than those of 64-Lo-C and  $I_e$  at the temperature higher than 413 K. The results indicated that PA-im-QPEEK and PA-methyl-QPEEK showed

high conductivity at higher temperature, which was more suitable to be used as HTPEM.

## TGA and DMA

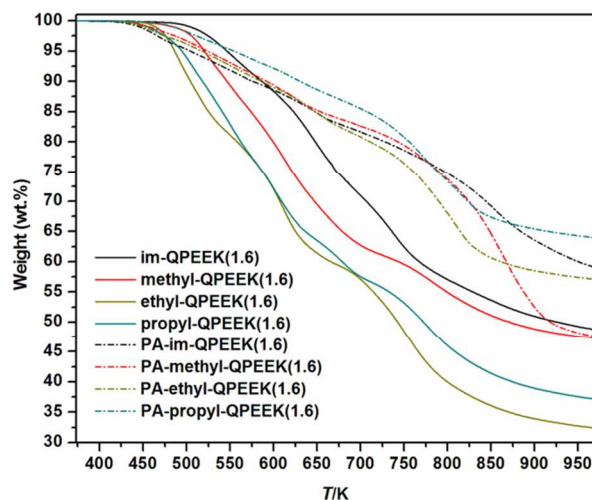


Figure 6. The TGA curves of QPEEKs and PA doped membranes.

The excellent thermal stability is indispensable in HTPEM field. The temperature where the weight loss reached 5% was used to evaluate the thermal stability of material and was marked as  $T_{5\%}$ . The TGA curves of QPEEKs and PA doped membranes are shown in Figure 6. The  $T_{5\%}$  of the im-QPEEK, methyl-QPEEK, ethyl-QPEEK and propyl-QPEEK membranes was 547, 521, 486 and 494 K, respectively. The thermal stability of im-QPEEK and methyl-QPEEK was better than those of ethyl-QPEEK and propyl-QPEEK. The  $T_{5\%}$  of the PA-im-QPEEK, PA-methyl-QPEEK, PA-ethyl-QPEEK and PA-propyl-QPEEK membranes was 504, 524, 518 and 554 K, respectively. The PA doped membranes began to lose weight at about 423 K. This was because the phosphoric acid molecules lost water and turned into pyrophosphates ( $H_4P_2O_7$ ) and then triphosphoric acids ( $H_5P_3O_{10}$ ) at higher temperature. The high  $W_{\text{doping}}$  and the easy loss of side chain always led to the low  $T_{5\%}$ . The im-QPEEK had the highest  $T_{5\%}$ . However, after doped with phosphoric acid, the  $T_{5\%}$  of PA-im-QPEEK was lowest. This was because the PA-im-QPEEK had the highest  $W_{\text{doping}}$ . When the phosphoric acid molecules began to lose water, the weight loss was also largest. Although the PA-methyl-QPEEK had higher PA doping level than PA-ethyl-QPEEK,  $T_{5\%}$  of PA-methyl-QPEEK was higher than that of PA-ethyl-QPEEK. This was mainly because the ethyl-QPEEK had the easy lost side chains. When the temperature was higher than 743 K, the thermal decomposition of main chain began to occur. The results of TGA indicated that all membranes had great thermal stability.

Table 1. The mechanical properties and oxidative stability of PA doped membranes.

Samples	Young's Modulus (MPa)	Elongation at the break (%)	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation at the break (%)	Tensile Strength (MPa)	stability(h)							
							298 K		403 K		Fenton solution <sup>a</sup>	Fenton solution/PA <sup>b</sup>	Fenton solution <sup>c</sup>	Water <sup>d</sup>
							PA-im-QPEEK(1.6)	101	115	9	6	457	2	5
PA-methyl-QPEEK(1.6)	207	52	13	21	207	6	15.4	15.6	21.2	intact				
PA-ethyl-QPEEK(1.6)	197	29	12	38	171	9	26.7	30.1	35.8	intact				
PA-propyl-QPEEK(1.6)	597	7	22	672	61	20	- <sup>e</sup>	-	-	-				
PA-im-QPEEK(1.3)	169	105	11	10	377	3	10.4	10.9	16.1	intact				
PA-methyl-QPEEK(1.3)	188	40	12	92	230	11	18.8	19.5	25.6	intact				
PA-ethyl-QPEEK(1.3)	573	14	29	431	126	25	>50	>50	>50	intact				
PA-propyl-QPEEK(1.3)	854	6	35	427	109	31	-	-	-	-				

<sup>a</sup> The PA doped membranes were immersed in 4 ppm Fe<sup>2+</sup>, 3 wt.% H<sub>2</sub>O<sub>2</sub> solution at water bath under 353 K.

<sup>b</sup> The QPEEK membranes were immersed in 4 ppm Fe<sup>2+</sup>, 3 wt.% H<sub>2</sub>O<sub>2</sub> and phosphoric acid solution at water bath under 353 K.

<sup>c</sup> The QPEEK membranes were immersed in 4 ppm Fe<sup>2+</sup>, 3 wt.% H<sub>2</sub>O<sub>2</sub> solution at water bath under 353 K.

<sup>d</sup> The PA doped membranes were immersed in water bath under 353 K.

<sup>e</sup> The sample was not measured because the proton conductivity of propyl-QPEEK membrane was too low to use as the HTPEM.

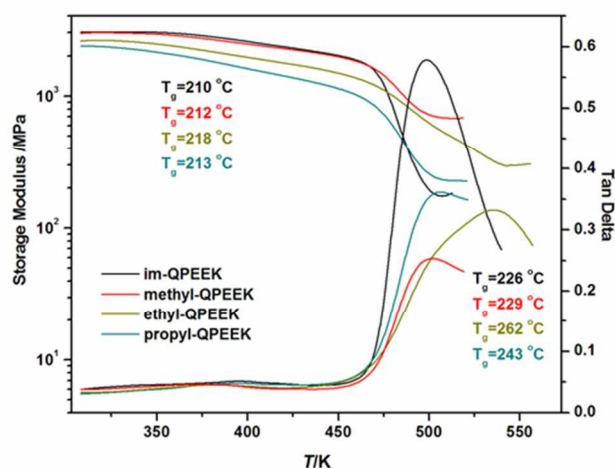


Figure 7. The DMA curves of QPEEK.

The  $T_g$  of all QPEEK membranes was measured by DMA and the results are shown in Figure 7, which was all higher than 473 K. The  $T_g$  which was derived from tan delta was higher than that derived from storage modulus. There are many factors that influence the  $T_g$  of polymer, such as the structure of main chain, the flexibility of side chain and the intermolecular force. The side chain could affect  $T_g$  of polymer in different way, such as, the flexible side chain could act as a plasticizer, which leads to a low  $T_g$ ; the side chain with large volume could increase the steric hindrance of intermolecular rotation, which leads to a high  $T_g$ . For the QPEEK with different length of trialkyl side chains, the ethyl-QPEEK had the highest  $T_g$  among methyl-QPEEK, ethyl-QPEEK and propyl-QPEEK. This was because the side chains of methyl-QPEEK and ethyl-QPEEK were too short to show the flexibility. On the contrary, the large side chain of ethyl-QPEEK made the  $T_g$  higher than that of methyl-QPEEK. The propyl-QPEEK had three C atoms on each side chain of quaternary ammonium group, which was able to show flexibility, so the propyl-QPEEK had a lower  $T_g$  than that of ethyl-QPEEK. After

all, the  $T_g$  of these QPEEK was higher than 483 K and these QPEEK membranes could be used as HTPEM. The DMA of PA doped membranes were measured and the results are shown in Figure S2. Compared with QPEEK membranes, PA doped membranes had lower storage modulus and  $T_g$ . This was mainly because the phosphoric acid which acted as a plasticizer led to

### Mechanical properties and oxidative stability

Excellent mechanical property is prerequisite for all polymer materials. The mechanical properties of these QPEEK membranes before and after PA doping were measured and the results are shown in Figure 8 and Table 1. It could be seen that the tensile strengths of QPEEK membranes were higher than 60 MPa, and the elongation at the break was lower than 10%. After doping with phosphoric acid, the tensile strengths of membranes decreased sharply and the elongation at the break increased obviously. For example, the Young's modulus and tensile strength of PA-im-QPEEK (DS=1.6) with the  $W_{\text{doping}}$  of 159 wt.% decreased to 101 MPa and 9 MPa, respectively. However, the elongation at break increased up to 115%. It was also found that the Young's modulus and tensile strength almost decreased with the increasing of  $W_{\text{doping}}$  and the elongation at the break increased (Figure S1). This was mainly because the phosphoric acid acted as a plasticizer in membranes. Since these PA doped membranes were supposed to be used as HTPEMs, the mechanical properties of PA doped membranes at 403 K were measured and the results are shown in Figure S3 and Table 1. It could be seen from Table 1 that the high temperature brought a lower tensile strength and a higher elongation at the break than the mechanical properties which were measured at 298 K. And it was found that the PA doped membrane with higher  $W_{\text{doping}}$  showed a more obvious reduction in tensile strength. The deterioration of mechanical stability at high  $W_{\text{doping}}$  existed in all various basic polymer membranes including PBI [37]. Xiao prepared high temperature PBI fuel cell membrane via a sol-gel process and the obtained PA-PBI membrane had the tensile strength only 1.0-3.5 MPa [38], which was even lower than those of PA doped membranes which



were measured in 403 K in this work. In our previous work, the tensile strength of pristine PA-PBI membrane (333 K in 85 wt.% phosphoric acid solution) was about 5 MPa which not only was lower than those of PA doped membranes at 298 K but also lower than those of most PA doped membranes at 403 K in this work [23].

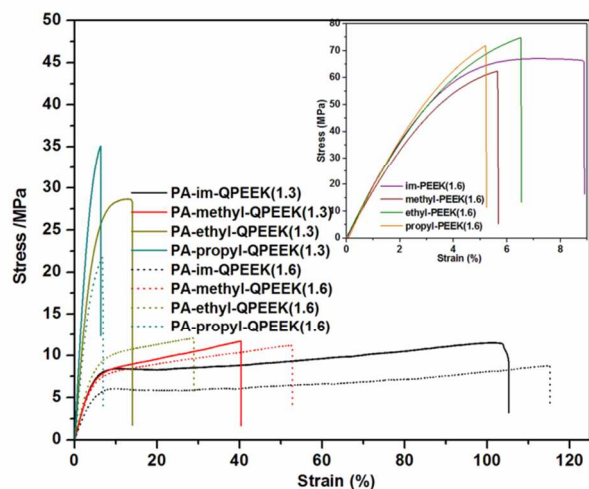


Figure 8. The mechanical properties of QPEEKs and PA doped membranes.

There are two main tests to evaluate the oxidative stability of proton exchange membrane: the test of ex situ durability and the test of in situ continuous durability. In this work, the test of ex situ durability was used, which was performed by accelerated aging with membrane exposing to 3 wt.%  $\text{H}_2\text{O}_2$ , 4 ppm  $\text{Fe}^{2+}$  Fenton solution in water bath at 353 K. The time that the membrane took to begin to break into pieces after being shaken was recorded to evaluate their oxidative stability (the breaking time). The breaking time of PA doped membranes in Fenton solution is listed in Table 1. Meanwhile, the oxidative stability of QPEEK membranes was measured in Fenton solution within and without phosphoric acid as a stabilizer at 353 K. All the results of oxidative stability are listed in Table 1. In order to prove that those membranes did not break mechanically, the PA doped membranes were immersed in water bath at 353 K as a blind experiment. The PA doped membranes, especially PA-im-QPEEK (1.6 and 1.3), showed swollen obviously in the blind experiment. And all these PA doped membranes remained intact after being shaken. This could prove the PA doped membranes did not break mechanically in water bath at 353 K. Comparing with the results from Fenton solution within phosphoric acid, the QPEEK membranes had better oxidative stability in Fenton solution without phosphoric acid. The result indicated that the phosphoric acid in the membranes was unfavorable to oxidative stability. For the oxidative stability of PA doped membranes, it could be seen that the breaking time became short with the increasing of  $W_{\text{doping}}$ . One reason was the phosphoric acid was unfavorable to oxidative stability and the higher  $W_{\text{doping}}$  would lead to worse oxidative stability. The other reason was the membrane had larger volume swelling with higher  $W_{\text{doping}}$ , and the larger volume swelling provided more opportunities for the Fenton solution to attack the polymer chain. With the largest  $W_{\text{doping}}$  (159 wt.%), the PA-im-QPEEK (1.6) membrane began to break into pieces after 5 h.

Moreover, the PA-ethyl-QPEEK (1.3) with the lowest  $W_{\text{doping}}$  could last more than 50 h. The oxidative stability of all PA doped membranes in this work was better than those of pristine linear PBI reported by Li [39] and Kerres [37]. They exposed the linear PBI membrane to 3 wt.%  $\text{H}_2\text{O}_2$  solution containing 4 ppm  $\text{Fe}^{2+}$  at 341 K. The linear PBI membrane was broken into small pieces after 30 min.

## Conclusions

QPEEK polymers with trimethylamine, triethylamine, tripropylamine and 1-methylimidazole as quaternary aminating reagents were prepared successfully and confirmed by NMR. These membranes had high  $T_g$  ( $T_g$  was higher than 483 K) and thermal stability ( $T_{5\%}$  was higher than 486 K). The quaternary ammonium groups which were located on the polymer main-chain could bond phosphoric acid by acid-base interactions and form ionic bonds. So these polymer membranes could be used as HTPEMs after being doped with phosphoric acid. The PA absorbing ability of QPEEKs was in the order PA-im-QPEEK > PA-methyl-QPEEK > PA-ethyl-QPEEK > PA-propyl-QPEEK.

According to our study, the PA absorbing ability was subjected to the structures of quaternary ammonium groups instead of the basicities of quaternary aminating reagents. The im-PEEK had the highest PA doping level, because the MeIm ring was a conjugated and nearly plane ring which facilitated the formation of ionic bond between the imidazolium cation and phosphoric acid molecule. For the methyl-QPEEK, ethyl-QPEEK and propyl-QPEEK, increasing the length of trialkyl side chains led to the decreasing of PA doping levels. The proton conductivity depended on  $W_{\text{doping}}$  and  $V_{\text{doping}}$ . The PA-im-QPEEK (1.6) had the highest proton conductivity among these membranes, up to 0.05  $\text{S cm}^{-1}$  at 473 K. The tensile strengths of these membranes decreased with  $W_{\text{doping}}$  and temperature increasing, and the elongation at the break increased. All PA doped membranes had great oxidative stability and could last for more than 5 h in 3 wt.%  $\text{H}_2\text{O}_2$ , 4 ppm  $\text{Fe}^{2+}$  Fenton solution at 353 K. Above all, the im-QPEEK and methyl-QPEEK showed great potential in HTPEMs.

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