



High-temperature water-free proton conducting membranes based on poly(arylene ether ketone) containing pendant quaternary ammonium groups with enhanced proton transport

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ARTICLE INFO

Article history:

Received 17 June 2011

Received in revised form 2 August 2011

Accepted 2 August 2011

Available online 9 August 2011

Keywords:

High temperature

Poly(arylene ether ketone)

Phosphoric acid

Proton exchange membrane

Fuel cell

ABSTRACT

Poly(arylene ether ketone) containing pendant quaternary ammonium groups (QPAEKs) are anion-conducting polymers synthesized from benzylmethyl-containing poly(arylene ether ketone)s (PAEK-TM). Then QPAEK membranes doped with different concentrations of H_3PO_4 are prepared and evaluated as high temperature proton exchange membranes. The H_3PO_4 doping ability of quaternary ammonium groups in QPAEK system is found to be stronger than that of imidazole groups in polybenzimidazole system. The doping level of resulting QPAEK/ H_3PO_4 composite membranes increases with both the concentration level of soaking H_3PO_4 solution and the ion exchange capacity. For example, the highest doping level of composite membranes is 28.6, which is derived from QPAEK-5 with an ion exchange capacity of 2.02 mmol g^{-1} saturated with concentrated phosphoric acid. A strong correlation between the doping level and the proton conductivity is observed for all the membranes. Besides their low cost, novel high temperature proton exchange membranes, QPAEK/ H_3PO_4 , show really high proton conductivity and possess excellent thermal and mechanical stability, suggesting a bright future for applications in high temperature fuel cell.

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1. Introduction

Proton exchange membrane fuel cell (PEMFC), a new class of power electricity generation device, is well known for its low-pollution and high energy efficiency. Proton exchange membrane (PEM), the key component in a PEMFC, has attracted considerable attentions because it is of vital importance to the cell performance [1–5]. The state-of-the-art PEMs based on perfluorinated sulfonic acid containing ionomers (PFASs), such as Nafion, have demonstrated excellent performances, including superior chemical stability and high proton conductivity under 100% relative humidity. It has been proposed that the proton conduction of the PFASs is governed by a vehicle mechanism, where water acts as a vehicle in the proton transport [6,7]. The proton conductivity of PFASs suffers greatly at temperature above 80°C due to the dehydration of the membrane, which restricts the use of PFASs in high temperature fuel cells. Operating a PEMFC at high temperature without any humidification has many advantages, such as a simple water management and cooling system, higher catalytic activity,

and an increase in efficiency and CO-tolerance [8,9]. Hence, the design and synthesis of novel high temperature anhydrous polymer electrolytes constitutes the main prerequisite for the successful implementation of high temperature proton exchange membrane fuel cells (HT-PEMFCs).

One of the most successful PEMs with outstanding high temperature performance is based on inorganic acids doped polybenzimidazole (PBI) system. PBI serves as the basic support material to immobilize inorganic acids in this system, while the inorganic acids conduct protons [10–12]. Among various inorganic acids, phosphoric acid (PA) is of interest due to its high boiling point and rapid diffusion rate. The proton transport in PA doped PBI under anhydrous condition is considered to follow a proton hopping or so-called Grotthuss mechanism [9,13] and strongly depends on acid doping ability, temperature and humidity [14–18]. Commonly, PA doping level and PA uptake are used to measure the acid doping ability. The doping level of PBI is usually given as the mole percent of phosphoric acid per mole repeating unit of the polymer. For each repeating unit of PBI, two molecules of phosphoric acid are strongly bound to the nitrogen atom in the basic imidazole ring. Exceeding PA in the membrane acts as “free acid”, which contributes significantly to the proton conductivity of PA doped PBI membranes [19–22]. To improve the doping level and the consequent proton conductivity of the resulting PBI/PA composite membranes, a series of membranes based on a sol–gel process or a new porous

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process were intensively studied [23–25]. However, the PA-doped PBI membranes derived from these methods all suffered from high PA loss rate and inferior mechanical properties at high PA doping level [26]. The poor solubility in common organic solvents of PBI has restricted its application for the high cost in the production [27]. Furthermore, 3,3',4,4'-tetraaminobiphenyl, the common reagent to synthesize PBI, is a strong carcinogen and the PA loss and the decrease of conductivity caused by the product water generation was serious at the cathodes and the PA loss rate was closely related to the fuel cell operating temperature [28]. These drawbacks have stimulated the development of alternative polymeric materials with compromised high PA doping level, desirable mechanical properties and relatively moderate conditions. A number of heterocyclic-containing poly(arylene ether)s with improved processability have been prepared and characterized [27,29]. The heterocyclic units in the main chain of the polymer include pyridine, triazine ring, benzoxazole, quinoxaline, oxadiazole and triazole. They exhibit good mechanical and thermal stabilities, excellent film forming property, and easily doped with PA. It is reported that the acid doping ability is affected from the detailed polymeric structure, the content and the type of basic groups. Li et al. reported that quaternized polymers as matrices for H_3PO_4 are quite stable in HT-PEMFCs operating condition and the quaternary ammonium groups have a good bonding with phosphoric acid [30]. However, there are still few reports on the stronger basic groups bearing polymer matrices prepared from a method that are more safer and better for environment.

In this work, the quaternary ammonium group containing poly(arylene ether ketone) (QPAEK) membrane capable of high PA uptake shows promising results for applications in HT-PEMFCs. The quaternary ammonium groups served as the basic connecting sets to immobilize PA ion by electrovalent bond and PA molecule by hydrogen bonds. The quaternary ammoniation of poly(arylene ether ketone) (PAEK) is a positioning and quantitative procedure to the benzylmethyl group on 3,3',5,5'-tetramethyl-4,4'-biphenol (TMBP) monomer. The composite membranes have been found to exhibit high proton conductivity at elevated temperature under anhydrous conditions due to the great basic connecting sets. The resulting PA/QPAEK-*x* series membranes prepared from QPAEK with higher ion exchange capacity (IEC) show higher PA uptake and consequently high proton conductivities compared to the sol-gel PA-doped PBI membranes. The detailed properties of the PA/QPAEK-*x* membranes, including PA doping level, water uptake, proton conductivity and mechanical properties are evaluated in this work, and some insights are also provided on how the quaternary ammonium groups influence the properties of PA/QPAEK composite membranes.

2. Experimental

2.1. Materials

TMBP and *N*-bromosuccinimide (NBS) were obtained from Shanghai Jiachen chemical company and dried at 80 °C for 24 h. 2,2'-Bis(4-hydroxy phenyl) propane (BPA) was got from Sinopharm Chemical Reagent Co. Ltd. 4,4'-Difluorobenzophenone (DFBP) was obtained from Yanbian Longjing chemical company. Benzoyl peroxide (BPO) was obtained from Lanzhou Aokai chemical company and used without further purification. Trimethylamine (TMA) was obtained from Sinopharm Chemical Reagent Co. Ltd. H_3PO_4 solution was bought from Tianjing chemical company and the molar concentration is 14.6 mol L⁻¹. All other solvents were obtained from Tianjin Tiankai chemical company and treated by a standard method prior to use.

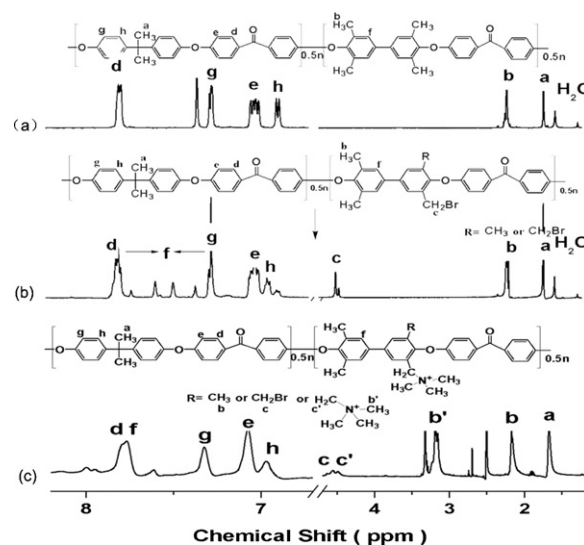


Fig. 1. ¹H NMR spectra: (a) PAEK, (b) BrPAEK and (c) QPAEK.

2.2. Synthesis and bromination of benzylmethyl-bearing PAEK

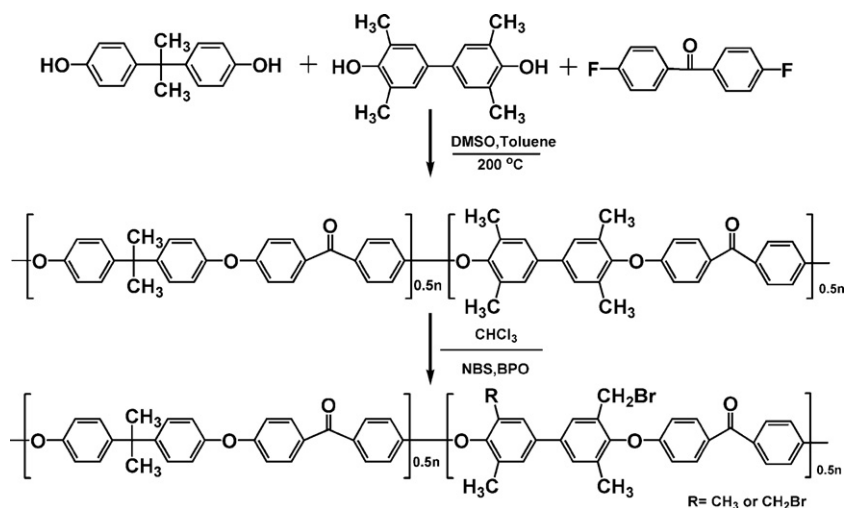
6.05 g (25 mmol) of TMBP, 5.70 g (25 mmol) of BPA, 10.90 g (50 mmol) of DFBB, 4.14 g (30 mmol) of K_2CO_3 , 57 mL of sulfolane (25 wt.%) and 18 mL of toluene were charged into a three-neck flask equipped with a nitrogen inlet, overhead stirrer, condenser, and Dean-Stark trap. The reaction was heated to 150 °C and lasted for 3 h as water was removed as an azeotrope with toluene. Toluene was removed from this system with a strong nitrogen purge. The reaction was then heated to 200 °C and kept at this temperature for 3.5 h. During this time, the reaction became so viscous that it began to wrap around the stirrer shaft. Then the viscous solution was precipitated into water. The white powder was collected by vacuum filtration, followed by stirring in boiling water and boiling methanol. After dried the washed polymer under vacuum overnight at 100 °C, white powder termed benzylmethyl-bearing PAEK (TMPAEK) was obtained. The resulting ¹H NMR spectrum is presented in Fig. 1(a).

The bromination of TMPAEK was taken according to the reaction shown in Scheme 1. 4.2 g (10 mmol) of PAEK, 16.02 g (9 mmol) of NBS and 0.02 g (0.09 mmol) of BPO were dissolved in 100 mL dried chloroform in a 250 mL three-necked flask. The flask was equipped with a mechanical stirrer, a nitrogen inlet and a condenser. The orange mixture was heated until the mixture turned to blood red at 62 °C. Pale yellow precipitate was obtained after precipitation of the blood red mixture in a 50% volume fraction of ethanol and water mixture and filtration. After washed with ethanol for three times, pale yellow powder, BrPAEK-1, was obtained in almost quantitative yield. The corresponding ¹H NMR spectrum is presented in Fig. 1(b).

BrPAEK-2 with higher bromine content was achieved by adjusting the adding content of NBS. The reaction steps followed the similar procedure described above.

2.3. Preparation of QPAEK/PA composite membranes

The preparation steps of PA doped QPAEK composite membranes are shown in Scheme 2. A typical ammoniation procedure was as follows: a three neck round-bottomed flask equipped with a dropping funnel was charged with BrPAEK and tetrahydrofuran (THF). After dissolving BrPAEK in THF totally under intensively stirring, TMA was dripped into the reactions from the dropping funnel drop by drop. Then the reaction device was sealed and the mixture



Scheme 1. Synthesis and bromination of benzylmethyl-bearing PAEK.

was kept at 40 °C for 4 h and a homogeneous solution was achieved. Then the residual solution was casted directly onto a clean glass plate and carefully dried at room temperature for 24 h and vacuum-dried at 120 °C for 24 h to remove solvent and most of excess TMA. Tough and totally dried membrane of QPAEK was obtained after removed from the glass plate, washed with deionized water and dried in oven.

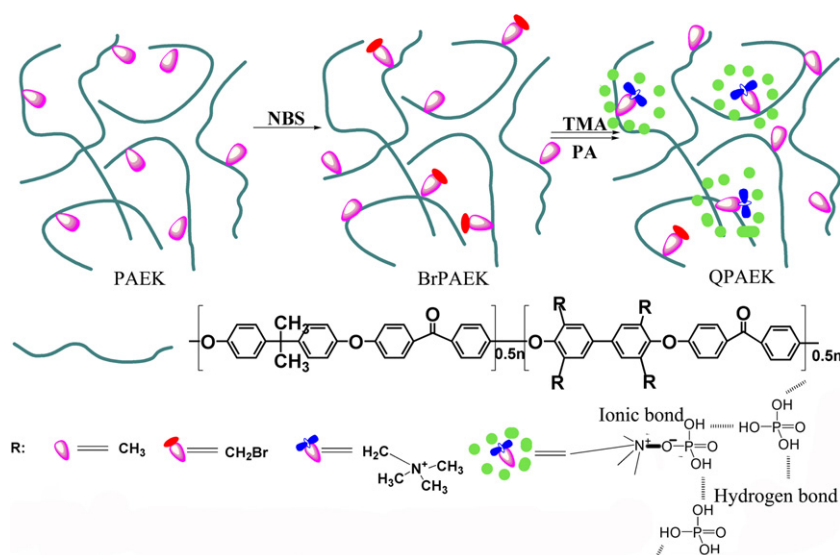
Example for the synthesis of PA/QPAEK composite membranes based on QPAEK with lower quaternary ammonium content: 4.0 g of BrPAEK-1 and 100 mL of THF were charged in a 250 mL neck round-bottomed flask equipped with a dropping funnel. 2 mL of TMA was dripped from dropping funnel to the mixture and conducted according to the above described procedure. A representative ¹H NMR spectrum for polymer QPAEK is shown in Fig. 1(c). The thoroughly dried QPAEK membrane was cut into five pieces in 5 cm × 5 cm and immersed into different concentrations of phosphoric acid solutions (3 M, 6 M, 9 M, 12 M and 14.6 M) at 80 °C, respectively. After an immersion time of 24 h, a series of PA/QPAEK composite membranes were obtained, and these composite membranes were dried in vacuum oven at 120 °C to remove water thoroughly. The weight and length

of these samples were measured pre and post immersion. The totally dried membranes were kept in vacuum drying basin before tests.

Example for the synthesis of PA/QPAEK composite membranes prepared from QPAEK with higher quaternary ammonium content: 4.0 g of BrPAEK-2 and 100 mL of THF were charged in a 250 mL neck round-bottomed flask equipped with a dropping funnel. By adjusting the addition amount of TMA, a series of QPAEK membranes with increasing ammonium contents were obtained according to the above described procedure and termed as QPAEK-x. QPAEK-x series membranes were immersed into a concentrated PA solution to saturate for 24 h at 20 °C. The resulting PA doped membranes were termed as PA/QPAEK-x.

2.4. Membrane characterization

¹H NMR spectra were recorded on a Bruker 510 MHz spectrometer using deuterated chloroform (CDCl₃) and DMSO-*d*₆ to confirm PAEK, BrPAEK and QPAEK, respectively. The average number of bromine per repeat unit of the BrPAEK-1, *D*_{Br}, is evaluated by integration and comparison of the ¹H NMR signals arising from the



Scheme 2. Preparation of PA doped QPAEK membranes.

Table 1
Compositions and properties of PA doped QPAEK membranes prepared from membranes with high IEC values at room temperature.

Samples	IEC (mmol g ⁻¹)	Dimension increase (%)	Weight uptake (%)	Water uptake (%)	PA uptake (%)	Doping level	σ (mS cm ⁻¹) ^a
PA/QPAEK-1	0.71	1.9	100.5	35.2	65.3	9.4	3.2
PA/QPAEK-2	1.14	10.2	141.4	36.6	104.8	9.4	17.6
PA/QPAEK-3	1.41	34.6	245.6	60.5	185.1	13.4	26.4
PA/QPAEK-4	1.75	69.9	550.5	236.1	314.4	18.3	56.9
PA/QPAEK-5	2.02	116.4	1227.7	662.4	565.3	28.6	– ^b

^a Samples were tested at 200 °C, under anhydrous conditions.

^b PA/QPAEK-5 were broken and no proton conductivity was obtained.

methyl protons and the brominated methylene protons. D_{Br} was calculated by the following Eq. (1):

$$D_{Br} = \frac{12A_{Hc}}{3A_{Hc} + 2A_{Hb}} \quad (1)$$

A_{Hc} is the peak area of brominated methylene protons, while A_{Hb} corresponds to the peak area of methyl protons of TMBP moiety.

FT-IR spectra of powder samples were recorded between 4000 cm⁻¹ and 400 cm⁻¹ on a Bruker Vector 22 FT-IR spectrometer. Thermo gravimetric analysis (TGA) was performed in nitrogen with a Pyris 1-TGA (Perkin-Elmer) thermo gravimetric analyzer at a heating rate of 10 °C min⁻¹ from 80 to 720 °C. The tensile measurements were carried out at room temperature at a constant crosshead speed of 2 mm min⁻¹. The uniaxial tensile measurements were conducted on membrane samples of 4 mm width and 15 mm length.

To evaluate the content of active quaternary ammonium groups per unit mass, the IEC of QPAEK was measured by a classical acid–base titration. Firstly, the QPAEK membrane was immersed in a 1 mol L⁻¹ NaOH solution for 24 h and then washed repeatedly with deionized water to remove redundant base. QPAEK in OH⁻¹ was weighted after oven drying and immersed in quantitative hydrochloric solution for 48 h. The solution was then titrated with NaOH standard solution using phenolphthalein as an indicator. The IEC was calculated by the following formula:

$$IEC = \frac{C_{HCl} \times V_{HCl} + C_{NaOH} \times V_{NaOH}}{M} \quad (2)$$

C_{HCl} is the molar concentration of HCl solution, V_{HCl} (mL) is the volume of HCl solution, C_{NaOH} is the molar concentration of NaOH solution, V_{NaOH} (mL) is the volume of NaOH solution, M (g) corresponds to the weight of dry membrane.

The weight uptake, water uptake, dimensional change and doping level were determined by comparing the weight changes between undoped, doped, and vacuum dried doped membranes. PA uptake was calculated by the difference between weight uptake and water uptake. Firstly, the cast membranes were dried at 150 °C in vacuum oven for 24 h and their weights (W_D) were recorded. Second, the dried membranes were then immersed in H₃PO₄ solutions. After 24 h, the membranes were taken out, wiped dry, and weighed (W_W). Then the wiped dry membranes were dried at 120 °C in vacuum oven for 24 h and the thoroughly dried membranes were weighed and termed as W_A . Dimensional increase was measured by length change in the plane direction, which was calculated by Eq. (4). L_W and L_U are the lengths of undried doped membrane and dried undoped membrane, respectively. MW_{PA} is the mole weight of PA. The corresponding equations were listed as follow:

$$\text{Weight uptake (\%)} = \frac{W_W - W_D}{W_D} \times 100 \quad (3)$$

$$\text{Dimensional change (\%)} = \frac{L_W - L_U}{L_U} \times 100 \quad (4)$$

$$\text{Water uptake (\%)} = \frac{W_W - W_A}{W_D} \times 100 \quad (5)$$

$$\text{Doping level} = \frac{W_A - W_D}{MW_{PA} \times IEC \times W_D} \quad (6)$$

The proton conductivity paralleled to the surface (in plane) of the QPAEK/PA composite membranes was determined by a modified four-probe AC impedance method from 0.1 Hz to 100 kHz, 10 mV AC perturbation and 0.0 V DC rest voltage using a Princeton Applied Research Model 2273 potentiostat/galvanostat/FRA. The totally dried PA doped membranes and the electrodes were set in a Teflon cell and the distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber for measurement. The impedance measurement was performed from 80 °C to 200 °C under anhydrous environment. The proton conductivities (σ , S cm⁻¹) of the copolymers were obtained using $\sigma = d/L_s \times W_s \times R$ (d is the distance between reference electrodes, and L_s and W_s are the thickness and width of the PA doped membrane, respectively). The thicknesses of membranes were averaged over several measurements taken by a digital micrometer in different regions of the samples. The membranes were dried and preserved under vacuum prior to measure the thickness at room temperature.

3. Results and discussion

3.1. The bromination and ammoniation of PAEK

BrPAEK-1 was synthesized via a radical bromination reaction of benzylmethyl-containing PAEK and the resulting D_{Br} was calculated to be 0.75. D_{Br} was determined by integration and comparison of the ¹H NMR signals arising from the methyl protons and the brominated methylene protons in Fig. 1(b). Compared with ¹H NMR of TMPAEK (Fig. 1(a)), the new peaks at around 4.47 ppm were assigned to the brominated methylene protons of TMBP. The peaks at 1.19 ppm were assigned to the protons on the benzylmethyl groups of TMBP moiety.

Fig. 1(c) presents the ¹H NMR spectrum of QPAEK derived from BrPAEK-1. Superfluous of TMA was added to the solution of BrPAEK to convert the bromomethylbenzyl groups to the quaternary ammonium groups. Then the resulting solution was equipped with pressure-relief devices to remove the vestige TMA at room temperature and subsequently casted directly onto clean glass plates. After carefully dried at room temperature for 3 h and vacuum-dried at 120 °C for 24 h, a thick, transparent and tough film was obtained. Then the film was washed for several times and dried under vacuum to achieve a neat base membrane of QPAEK. The thickness of this base membrane was 86 μm. After ammoniation, new peaks appeared at about 3.16–3.19 ppm which were assigned to the methyl groups of the newly formed quaternary ammonium groups. Peaks of methylene protons after ammoniation shifted from 4.47 ppm to 4.64 ppm. The theoretical IEC value was calculated to be 0.57 mmol g⁻¹ by comparing the integrations of methyl groups of benzyltrimethylammonium groups with those of methyl groups of TMBP moiety at 1.67 ppm. The IEC value calculated from acid–base titration was 0.50 mmol g⁻¹, which was slightly lower than the theoretical value. According to the independent investigations of

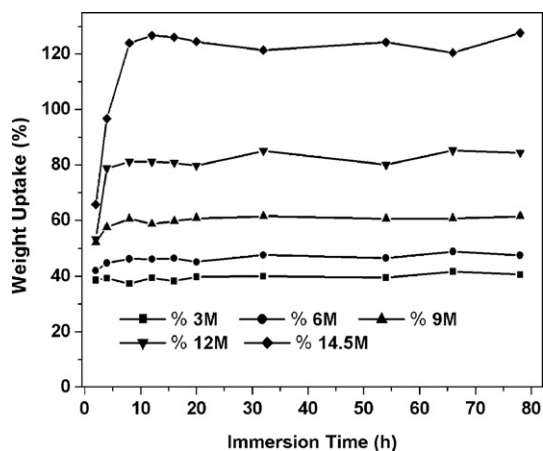


Fig. 2. Weight uptake of QPAEK membranes at room temperature in different concentrations of PA as a function of time.

Yanagi and Fukuta [31,32], QPAEK in OH^{-1} form would be gradually converted into bicarbonate form on exposure to air as a result of the rapid absorption of CO_2 , which caused a corresponding decrease in IEC during the titration process. ^1H NMR spectra of QPAEKs with higher IEC cannot be achieved for its poor solubility in common solvent. The IEC listed in Table 1 were calculated from acid–base titration and the resulting doping level were calculated according to these values.

3.2. Preparation of PA doped composite membranes

To determine the time required to saturate QPAEK membranes in different concentrations of PA solutions, the QPAEK membrane was cut into five pieces and immersed in 3, 6, 9, 12 and 14.6 M PA solutions at room temperature separately. And their weight gains were measured as a function of time. Fig. 2 shows the weight uptake of QPAEK and BrPAEK-1 in different acid concentrations. It can be observed that a longer time was needed to saturate the film in a higher concentration of PA solution. The saturated time increased from 2 h to 12 h as the acid concentration increased. The polymer membrane with quaternary ammonium groups absorbed more phosphoric acid as compared to those with brominated methylene groups, indicating a strong acid–base interaction between quaternary ammonium groups and PA. It is obvious in all cases that the doping ability is drastically increased at elevated concentration of phosphoric acid. QPAEK showed a great weight uptake of 120% even at a low immersion temperature in concentrated PA solution. This is due to the increased volume fraction caused by the pendant quaternary ammonium groups. Furthermore, the strong basicity of quaternary ammonium groups would have specific effect in increasing acid doping level. According to the above results, further doping experiments were all performed for 24 h to obtain the maximum PA doping level.

In order to obtain composite membranes with higher PA doping level for high temperature fuel cells, five pieces of QPAEK membranes were immersed in PA solutions at a higher temperature of 80°C , respectively. For the use of these materials in high temperature fuel cells, an important prerequisite for QPAEK membrane is their ability to be doped in concentrated PA solutions at high temperature, thus resulting in high proton conductive materials. After an immersion time of 24 h, the composite membranes in all cases were still integrated for the further tests. The weights and lengths of these resulting membranes were measured and the results of weight uptake and dimensional change as a function of concentration of acid are shown in Fig. 3. Not surprisingly, the total

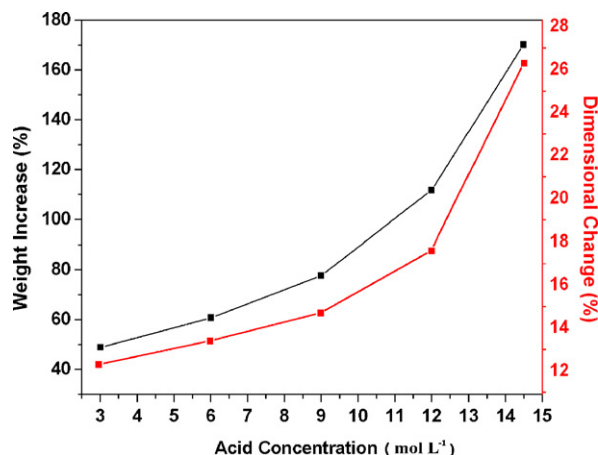


Fig. 3. Weight uptake and dimensional change of PA/QPAEK membranes at 80°C as a function of PA concentration.

weight uptake of QPAEK increased with the increasing acid concentration. The dimensional change of the composite membranes also increased with the concentration of PA increasing. For example, the weight uptake of these membranes increased from 50% to 170%, while the dimensional change increased less than 26.5%. It is concluded that the QPAEK base membranes are favorable for the absorption of PA with a minor dimensional change.

The total weight uptake of PA/QPAEK membranes was attributed to PA and water uptake. To investigate the contribution of both factors in the weight increase, PA/QPAEK membranes were dried in a vacuum oven to remove the water without any loss of PA. Then the water uptake of composite membranes in different PA solution was measured and the results are shown in Fig. 4. The initial water uptake was about 22–24%, when the PA concentration was lower than 9 M. However, a rapid growth of water uptake to 82.6% occurred as the PA concentration increased to 14.6 M. It could be caused by the redundant water absorbed by PA in the composite membranes, indicating that PA/QPAEK composite membranes have great water holding capacity. Operating the fuel cell at high temperature will generate portion of water, and the resulting water was an important factor beneficial to the conductivity of phosphoric acid doped membranes.

As reported in the literature, the maximum doping level of *meta*-PBI by immersing the dry film in the PA solution was 13–16 of PA for each mole repeating unit of *meta*-PBI [33,34]. Fig. 5 shows the doping levels of PA/QPAEK composite membrane as a function of acid concentration. In PA/QPAEK system, the doping level

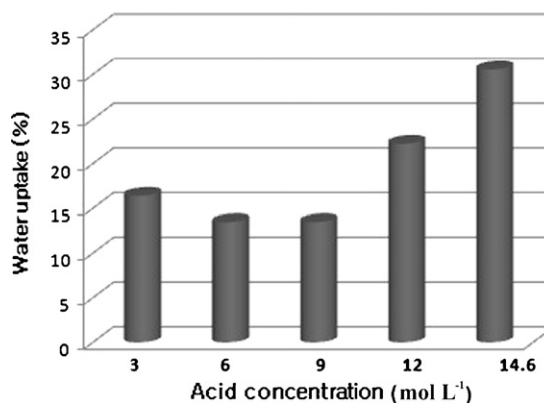


Fig. 4. Water uptake of PA/QPAEK membranes at 80°C as a function of PA concentration.

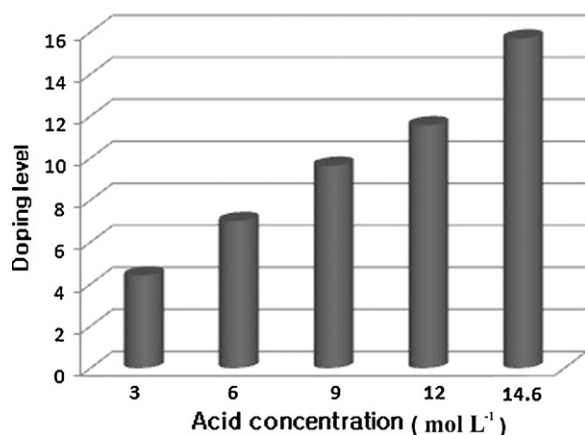


Fig. 5. PA doping level of PA/QPAEK membranes at 80 °C as a function of PA concentration.

was termed as membranes average number of PA bonded by each quaternary ammonium group. The PA/QPAEK exhibited a doping level of 15.7 at the maximum acid concentration, which is really high in comparison with *meta*-PBI. This result can be addressed to both the increased volume fraction caused by the pendant quaternary ammonium groups and the strong basicity of quaternary ammonium groups.

3.3. Influence of doping level on the mechanical properties

The measured stress at break as a function of the acid doping level is shown in Fig. 6. The maximum stress at break of the composite membrane was 38 MPa with a doping level of 4.4, when the concentration of doping acid was 3 M. As the acid doping level further increased, the stress at break decreased to 19 MPa. This is reasonable since increasing PA content would increase the space between polymer chains. The mechanical strength of the membranes results from attractive forces between polymer molecules, including dipole–dipole interaction (including hydrogen bonding), induction forces, dispersion or London forces between non-polar molecules [35]. The increasing space would reduce intermolecular forces and consequently deteriorate the mechanical strength of the membranes.

Surprisingly, the elongation at break of PA doped QPAEK membranes is extremely high (between 87% and 120%), which is significantly higher than that of pure QPAEK membranes (lower than 30%). It indicates that the polymer chains are more flexible to

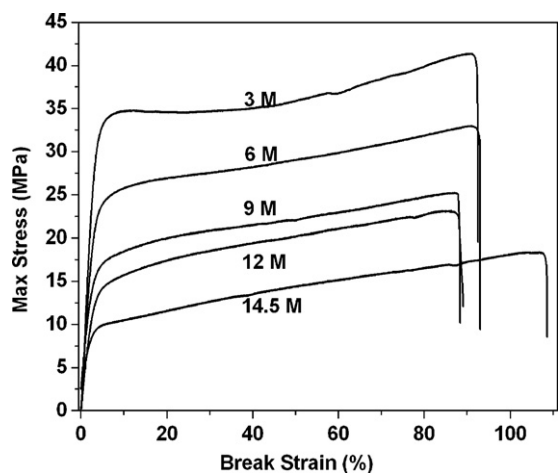


Fig. 6. Mechanical properties of PA/QPAEK membranes with different doping levels.

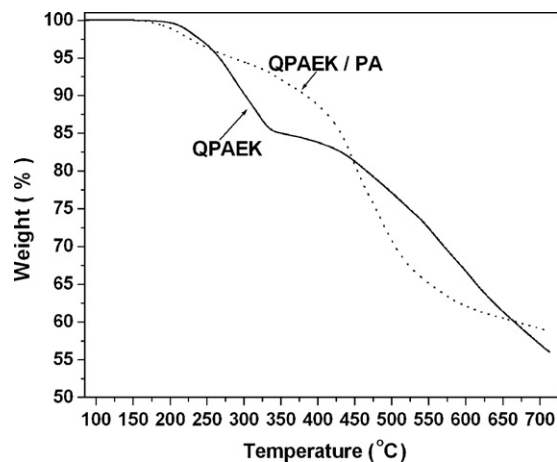


Fig. 7. TGA traces of membranes recorded under a nitrogen atmosphere.

rearrange under load after doping with PA. There might be even a “phase transition” in PA doped composite membranes where the membranes shifted from being completely glassy or solid-like to being more viscoelastic [36].

3.4. Thermal properties of composite membranes

Fig. 7 shows the results of TGA measurements for the QPAEK copolymer and one of the PA/QPAEK composite membranes prepared from concentrated PA. It can be observed that there are two drastic weight loss ranges with the increasing temperature in the TGA curve of QPAEK. One appears at 200–330 °C caused by the loss of benzyltrimethyl ammonium and bromine groups, and the other appears at 431 °C produced by main chain decomposition. For the PA doped composite membrane, the first decomposition temperature at about 155 °C can be assigned to the loss of water mainly produced by acid dimerization and the second weight loss is considered as the loss of benzyltrimethyl ammonium groups [24]. It should be noted that the decomposition temperature of benzyltrimethyl ammonium groups in PA doped membrane is higher than that of QPAEK base membrane. It was attributed to the protecting effect of polyphosphoric acid around the benzyltrimethyl ammonium groups.

3.5. Proton conductivity

Silva et al. reported that the observed conductivity decreased with increasing thickness of Nafion based membranes in tangential direction conductivity measurements [37]. The thicknesses of the present membranes were between 100 and 115 μm after equilibrated in PA solution and carefully dried with paper. The small difference in the thickness ensured that the conductivity values are calculated within the error limits. The proton conductivities of the composite membranes were measured without any external humidification supply. The structures of phosphoric acids are complex and relate to their complicated hydrated and anhydrous forms. Under anhydrous conditions, condensed structures of the *dimer* (pyrophosphoric acid, H₆P₂O₇), *trimer* (*meta*- or *tri*-polyphosphoric acid, H₈P₃O₁₀), and larger fused structures are formed. Clearly, the proton conduction behavior in phosphoric acid systems is carried by both orthophosphoric acid and its condensed structures.

The conductivities of all the obtained membranes were tested every 10 °C from 80 °C to 200 °C. Fig. 8 presents these measured conductivities as a function of temperature. It was expected that the proton conductivity should have an increasing tendency with temperature increasing since at elevating temperature the mobil-

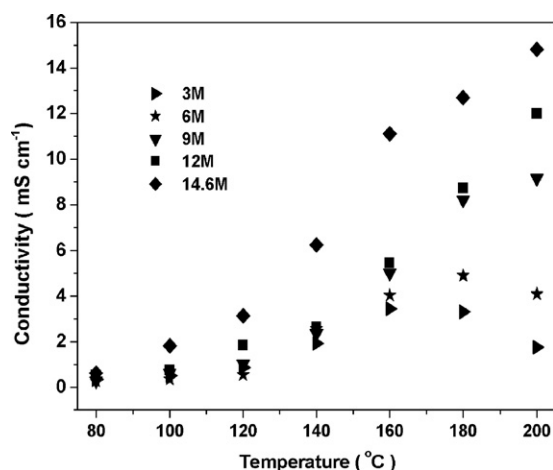


Fig. 8. Proton conductivity of PA/QPAEK series as a function of temperature.

ity of the polymeric chain increases and this enhances the proton's mobility. However, there is a change in the slope observed above 160 °C, which may be attributed to the change of conduction mechanism. As the temperature reached up to 160 °C, dehydration happened between PA molecules and the condensed structures formed, which decreased the mobility of proton. Furthermore, the proton conductivities increased with the increase of doping levels. The maximum proton conductivity among these membranes was about 15 mS cm^{-1} with a doping level of 15.7. The basic groups grafted onto the backbone of PAEK were expected to enhance PA doping ability and consequently the proton conductivity of the membranes. Considering the relatively low IEC of QPAEK, the PA uptake of PA/QPAEK (136.1%) was really low and the proton conductivity value was comparable. As the IEC of QPAEK increased, there will be a much space for promotion in proton conductivity.

3.6. Preparation and characterized of PA doped QPAEK-x membranes with higher IEC

Since the quaternary ammonium groups were the only group in QPAEK membranes that interact with the phosphoric acid and result in high doping ability. QPAEK-x membranes with higher IEC were prepared to improve the PA doping ability. The IEC value of QPAEK-x series increased with the addition amount of TMA and the results are listed in Table 1. QPAEK-x membranes with increasing IEC were immersed into a concentrated PA solution to saturate for 24 h at 20 °C and the corresponding thickness were between 120 and 144 μm after equilibrated in PA solution. The corresponding composition and the properties of PA doped membranes are tested and the results are also listed in Table 1.

Fig. 9 shows the conductivity of PA/QPAEK-x composite membranes as a function of temperature. As expected, the proton conductivity of PA doped QPAEK-4 membrane was greatly improved when compared to PA/QPAEK-x composite membranes derived from QPAEK with lower IEC. For example, the composite membrane PA/QPAEK-4 showed the most outstanding proton conductivity of 56.9 mS cm^{-1} at 200 °C, due to its good water and PA absorption ability. The conductivity of PA/QPAEK-5 was not obtained because of the partial dissolving of the basic membrane and the loss of mechanical stability in the high PA concentration. The decrease in the conductivity is also observed in Fig. 9, which could be related to the change in the amounts of free PA in the composite membranes. Then the FTIR measurement (shown in Fig. 10) was taken and compared between the PA/QPAEK-4 composite membrane before and after high temperature treatment. FTIR spectrum of the final product, PA/QPAEK-4 after long term

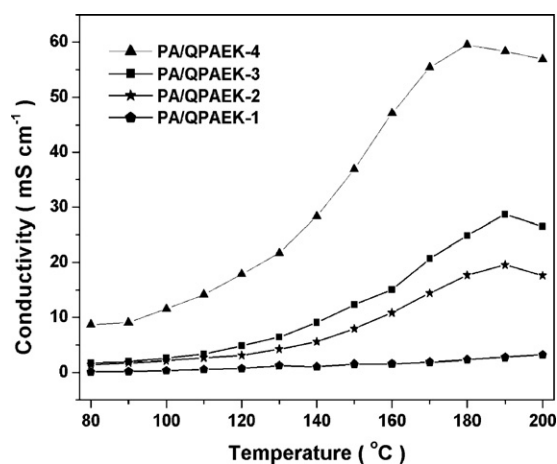


Fig. 9. Proton conductivity of PA/QPAEK-x composite membranes prepared from membranes with high IEC values at room temperature.

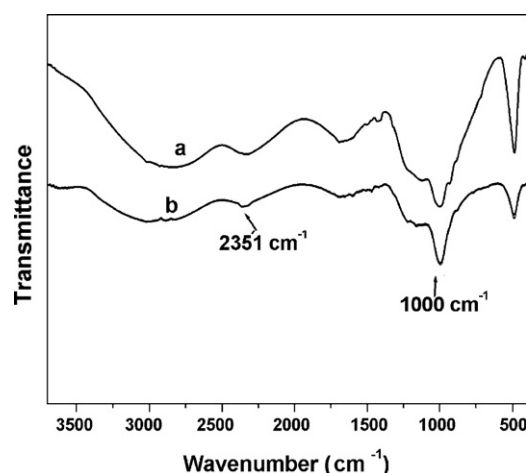


Fig. 10. The infrared spectra of PA/QPAEK-4 composite membranes: (a) pre high temperature treatment and (b) after high temperature treatment.

high temperature treatment, demonstrated several characteristic absorption bands at 1000 cm^{-1} assigning to the stretching vibrations of $\text{P}=\text{O}$ in the $-\text{P}(\text{O})(\text{OH})_2$ group. Simultaneously, a broad peak relating to the $-\text{P}-\text{O}-\text{H}$ groups appeared at 2351 cm^{-1} . All these characteristic peaks were similar to PA/QPAEK-4 before heat treatment. That is to say, the hydrolysis of $\text{P}-\text{O}-\text{P}$ anhydrides and dimerization of PA carried out at the same time; thus, the conductivity was carried by both orthophosphoric acid and its condensed structures.

4. Conclusions

High temperature proton exchange membranes based on PA/QPAEK have been prepared from quaternary ammoniation of BrPAEK. Quaternary ammonium groups that located on the side-chain of polymer played an important role in improving the doping ability and the proton conductivity of the resulted composite membranes. The PA/QPAEK-x composite membranes showed a really high doping level ranging from 4.2 to 26.8. It was observed that the proton conductivity of PA/QPAEK-x membranes exhibited a significant increase with increasing PA doping ability in composite membranes. The PA/QPAEK composite membranes showed a maximum conductivity of 56.9 mS cm^{-1} at 200 °C under anhydrous

conditions. The value was much higher than those of most of PA doped PBI membranes and that of sol-gel processed membranes (47 mS cm^{-1}). The ionic conductivity study also revealed that there was a strong dependency on temperature, doping level and anhydrides and dimerization of PA in the samples. The water production at cathode was still the major degradation mechanism of the PA-based high temperature PEM fuel cell. Further work will be devoted to reducing the dimensional change of the composite membranes with high IEC and improving the mechanical stability and to detailing the correlation between the membrane PA loss and the fuel cell performance degradation rate.

Acknowledgement

The authors would like to thank the National Natural Science Foundation of China (Grant No. 21074044) for financial support of this work.

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