



# Quaternized cardo polyetherketone anion exchange membrane for direct methanol alkaline fuel cells

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## ABSTRACT

Quaternized cardo polyetherketone (QPEK-C) membranes for alkaline fuel cells were prepared via chloromethylation, quaternization and alkalization of cardo polyetherketone (PEK-C). The chemical reaction for PEK-C modification was confirmed by nuclear magnetic resonance ( $^1\text{H}$  NMR) and energy-dispersive X-ray spectroscopy (EDAX). The QPEK-C membrane was characterized by X-ray photoelectron spectroscopy (XPS) and thermo gravimetric analysis (TG). The ion-exchange content (IEC), water and methanol uptakes, methanol permeability and conductivity of the QPEK-C membranes were measured to evaluate their applicability in alkaline methanol fuel cells. The ionic conductivity of the QPEK-C membrane varied from  $(1.6 \text{ to } 5.1) \times 10^{-3} \text{ S cm}^{-2}$  over the temperature range 20–60 °C. The QPEK-C membrane showed excellent methanol resistance. When the concentration of methanol was 4 M, the methanol permeability was less than  $10^{-9} \text{ cm}^2 \text{ s}^{-1}$  at 30 °C.

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## 1. Introduction

Recently alkaline direct methanol fuel cells (ADMFCs) have attracted more and more research interest. Compared with the traditional proton exchange membrane fuel cells (PEMFCs), the ADMFCs have lower methanol crossover, higher catalyst efficiency and lower cost [1–4]. Many investigators have developed various exchange membranes for application in ADMFCs [5–13].

There are many ways to prepare anion exchange membranes, such as radiation grafting of styrene onto polymer films [7,8], dipping with an alkali metal hydroxide [13], and electrophilic substitution [5,6]. Chloromethyl groups can be introduced onto the phenyl ring of the aromatic compounds via the Blanc chloromethylation reaction. Following this reaction, quaternary ammonium groups can be introduced into the aromatic compounds via quaternization and alkalization and hence an anion exchange membrane is produced. Many polymers, such as polysiloxane [14], polyarylether sulfone (PSF) [15], poly(phthalazinon ether sulfone ketone) (PESK) [11], cardo polyethersulfone (PES-C) [9], poly(ether-imide) [16], have been used in this manner to produce anion exchange membranes for application in ADMFCs. Chloromethylether (or bichloromethylether), paraformaldehyde ( $\text{CH}_2\text{O}$ )<sub>n</sub>, hydrochloric

acid (HCl) gas, chloromethyl alkyl ether, etc. are normally used for chloromethylation [11,17–23]. Of those chloromethylation reagents, chloromethylether and bichloromethylether are toxic and carcinogenic, and chloromethyl alkyl ether needs to be produced from chloromethylether. In order to avoid using those toxic substances and to simplify the reaction route, we used paraformaldehyde and HCl gas as the chloromethylation reagents. Fang and Shen [11] prepared quaternized poly(phthalazinon ether sulfone ketone) anion exchange membrane using paraformaldehyde and HCl gas as the chloromethylation reagents.

Cardo polyetherketone (PEK-C) is an excellent resistance polymer with strong mechanical properties and good thermal stability. With the bulky cardo group on a side chain, PEK-C can dissolve in some organic solvents, such as NMP, DMF,  $\text{CHCl}_3$  to produce membranes with ease. Based on the above advantages, PEK-C membranes have potential applications as functional materials, such as for pervaporation and fuel cells [24–26]. Basile et al. [26] prepared sulfonated PEEK-WC (another name for PEK-C) membranes, and applied them in an  $\text{H}_2$ /air fuel cell. The sulfonated PEEK-WC membranes exhibit comparable electrochemical performance. These studies show the ideal potential applications of PEK-C materials for fuel cells.

To our knowledge, quaternized PEK-C membranes have not been reported as having been used for alkaline direct methanol fuel cells. The objective of this work was thus to prepare QPEK-C membranes, using PEK-C as a starting material for the quaternized membranes, for application in alkaline direct methanol fuel cells.

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### Nomenclature

$A$	the cross-sectional area of the membrane ( $\text{cm}^2$ )
$E_a$	the ion transport activation energy (kJ)
IEC	ion-exchange capacity ( $\text{meq g}^{-1}$ )
$l$	the distance between two stainless steel electrodes (cm)
$m_d$	the mass of the dried membrane (g)
$m_h$	the mass of a wet membrane (g)
$M_{o,\text{HCl}}$	the milliequivalents of HCl required before equilibrium (meq)
$M_{e,\text{HCl}}$	the meq of HCl required after equilibrium (meq)
$R$	the membrane resistance from the AC impedance data ( $\Omega$ )
$W_c$	the percentage water or methanol content

### Greek letters

$\sigma$	ionic conductivity ( $\text{S cm}^{-1}$ )
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## 2. Experimental

### 2.1. Materials

Cardo polyetherketone (polymerization degree of 101) was supplied from Xuzhou Engineering Plastic Factory (China). N-methyl-2-pyrrolidone (NMP) and paraformaldehyde  $(\text{CH}_2\text{O})_n$  were purchased from the Shanghai Chemical Reagent Store (China) and used as received.

### 2.2. Chloromethylation of PEK-C

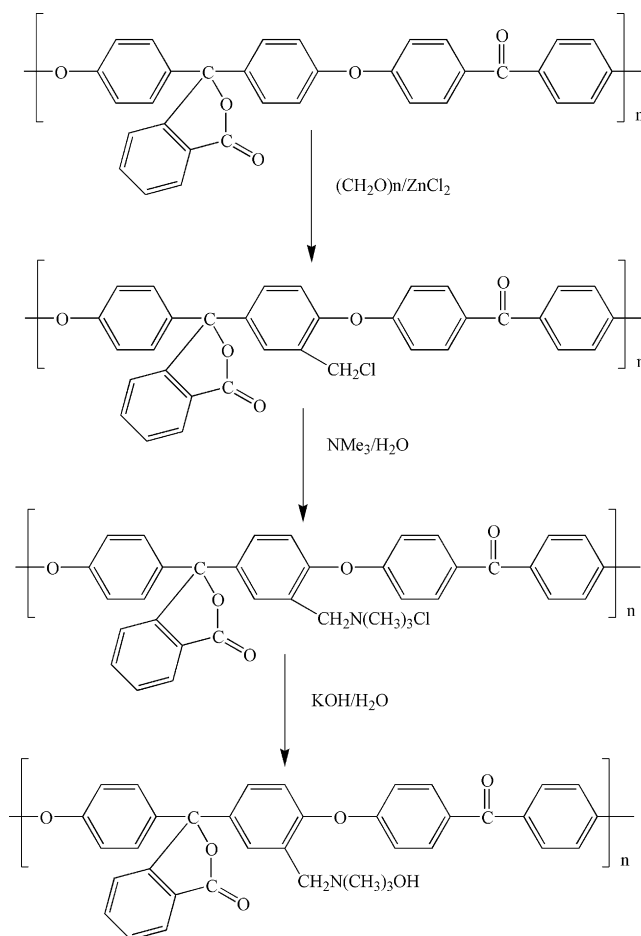
The chloromethylation reaction of the PEK-C was carried out according to the scheme reported in the literature [11,21–23], where the chloromethyl groups were successfully introduced onto the aromatic ring. The ketone group is electron withdrawing and decreases the electron cloud density in the linked aromatic ring. The phenoxy oxygen group is an electron donor and thus increases the electron cloud density of the linked aromatic ring. Hence the chloromethyl group is introduced into the position of the aromatic ring that is linked with the phenoxy oxygen group.

Based on our observations, the best reaction conditions are: a temperature of 30–50 °C and reaction time of 2–4 h. After the chloromethylation reaction, the elemental Cl content in the CPEK-C was measured using EDXA, as shown in Table 1. It was found that the best reaction condition is at 50 °C for 2 h. 10 g of PEK-C was dissolved in 200 mL of NMP in a three necked bottle at room temperature. An excess of paraformaldehyde  $(\text{CH}_2\text{O})_n$  and dry hydrochloric acid gas were used as the chloromethylation agents, and zinc chloride ( $\text{ZnCl}_2$ ) was used as a catalyst to catalyze the chloromethylation reaction of the PEK-C membranes. The reaction was continued at 50 °C under stirring for 2 h. The resulting chloromethylated PEK-C (CPEK-C) was precipitated and washed with deionized water. The CPEK-C was filtered and air dried in a fume hood and then dried for 4 h in an oven at 60 °C.

**Table 1**

The relation of reaction temperature, time and the Cl content in the CPEK-C membranes.

Reaction temperature (°C)	Reaction time (h)	Cl (wt.%)
30	2	0.09
30	4	0.23
50	2	0.58
50	4	0.28



**Scheme 1.** Synthesis of the quaternized PEK-C membranes.

### 2.3. Quaternization and alkalinization of PEK-C membranes

5 g of CPEK-C was dissolved in 100 mL of NMP to make a 5 wt.% solution. The solution was cast onto a glass plate and dried at 60 °C for 24 h. The dried membranes were peeled off from the glass plate and then heated at 80 °C for 4 h. The CPEK-C membranes were soaked in a 30% trimethylamine solution at room temperature for 48 h to prepare the quaternized PEK-C membranes (QPEK-C). The quaternization reaction was performed according to the literature [20]. The QPEK-C membranes were washed with deionized water and immersed in a 2 M KOH solution for 48 h to alkalinize the membranes and convert the membranes from the  $\text{Cl}^-$  form into the  $\text{OH}^-$  form. Finally, the membranes were washed with deionized water and stored in deionized water for further experiments. The reaction sequence for the synthesis of the QPEK-C membranes is shown in Scheme 1.

### 2.4. Structural characterization

$^1\text{H}$  NMR spectra of the chloromethyl PEK-C was recorded, using chloroform-d ( $\text{CDCl}_3$ ) as the solvent and tetramethylsilane (TMS) as an internal standard, on a Bruker AV500 NMR spectrometer. The elemental mapping of the polymer was conducted using an energy-dispersive X-ray spectrometer (EDAX) of ISIS300 (Oxford). X-ray photoelectron spectroscopy (XPS) measurements were performed to analyze the N content and the status of the elements C and O on the surface of the PEK-C and QPEK-C membranes, respectively. Spectra were recorded on a Quantum 2000 Scanning ESCA Microprobe using an Al K X-ray source (1486.60 eV).

Thermo gravimetric (TG) analysis of the membrane samples was carried out using a TG209F1 (NETZSCH, Germany) system. The measurements were conducted by heating from 30 to 900 °C at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere.

### 2.5. Oxidation experiments

The oxidation resistance of the membranes was evaluated by immersing the membrane samples into a 3 wt.% H<sub>2</sub>O<sub>2</sub> solution with stirring at 60 °C for 168 h. The weight loss of the membranes was measured at certain time intervals.

### 2.6. Uptake of water and methanol

The study of uptake of water and methanol in the membranes was carried out by measuring the change in weight of the membranes before and after immersing in deionized water or methanol, respectively. The membranes were immersed in deionized water or methanol at room temperature and equilibrated for more than 48 h. The weight of the wet membrane was determined after removing excess surface water or methanol. Then the wet membranes were dried under vacuum at 60 °C until a constant dry weight was obtained. The percentage of water or methanol content  $W_c$  was calculated using the following relation

$$W_c = \frac{m_h - m_d}{m_d} \times 100\% \quad (1)$$

where  $m_h$  is the mass (g) of a wet membrane and  $m_d$  is the mass (g) of a dry membrane.

### 2.7. Ion-exchange capacity (IEC)

The ion-exchange capacity of the membranes was measured by the classical titration method. A small sample of the QPEK-C membrane in its OH<sup>-</sup> form was equilibrated with 30 mL of 0.01 M HCl solution for 48 h. The IEC values were determined from the reduction in acid measured using a 0.01 M NaOH titration. The IEC values (meq g<sup>-1</sup>) were calculated by

$$\text{IEC (meq} \times \text{g}^{-1}) = \frac{M_{o,\text{HCl}} - M_{e,\text{HCl}}}{m_d} \quad (2)$$

where  $M_{o,\text{HCl}}$  is the milliequivalents (meq) of HCl required before equilibrium,  $M_{e,\text{HCl}}$  is the meq of HCl required after equilibrium, and  $m_d$  is the mass (g) of the dried membrane.

### 2.8. Methanol permeability

The methanol permeability was measured using a diffusion cell comprising two compartments. Magnetic stirrers were used in each compartment to ensure uniform mixing during the experiments. The membrane was clamped between the two compartments. One compartment was loaded with deionized water and the other with a methanol solution with various concentrations in 0.5 M KOH. The concentration of the permeating methanol was measured by gas chromatography (GC-950, Shanghai Haixin Chromatographic Instruments Co., Ltd).

### 2.9. Ionic conductivity

The ionic conductivity of the QPEK-C membrane was measured by two-probe AC impedance spectroscopy [27] with Parstat 263 electrochemical equipment (Princeton Advanced Technology, USA) over the frequency range 0.1–1 MHz. Before testing, the OH<sup>-</sup> form of the membrane was hydrated in deionized water for at least 48 h. The testing device with the membrane was placed in a chamber

with deionized water to keep the relative humidity at 100% during the measurements.

The ionic conductivity  $\sigma$  (S cm<sup>-1</sup>) of a given membrane can be calculated from

$$\sigma = \frac{l}{(RA)} \quad (3)$$

where  $l$  is the distance (cm) between two stainless steel electrodes,  $A$  is the cross-sectional area (cm<sup>2</sup>) of the membrane, obtained from the membrane thickness multiplied by its width, between two electrodes. In our experiment, the value of  $l$  was 0.3 cm and  $A$  was 0.0028 cm<sup>2</sup>.  $R$  is the membrane resistance ( $\Omega$ ) obtained from AC impedance data.

## 3. Results and discussion

### 3.1. Confirmation of the reaction

The chloromethylation reaction was confirmed by <sup>1</sup>H NMR. Fig. 1 shows the <sup>1</sup>H NMR spectra of the PEK-C (a) and CPEK-C (b and c). The protons associated with benzene ring of PEK-C structure appear at 7–8 ppm, which can be found on both the spectra of the PEK-C and CPEK-C. Four new peaks appeared in the <sup>1</sup>H NMR spectrum of the CPEK-C. There is a five-fold multiplet centered at 2.0 ppm, two three-fold multiplets centered at 2.4 and 3.5 ppm, and finally two singlet peaks at 2.2 and 2.8 ppm. There is residual NMP in the chloromethylation products, since NMP was used as the solvent for the PEK-C membranes in the chloromethylation reaction. The peaks at 2.0, 2.4 and 3.5 ppm are attributed to the methylene H of NMP; meanwhile, the peak at 2.8 ppm is attributed to the methyl H of NMP. The peak at 2.2 ppm is attributed to the chloromethyl H of the CPEK-C membrane. The experimental ratio of the peak area (0.09) at 2.2 ppm over those (20.92) corresponding to the protons in the aromatic rings is 0.0043. The theoretical ratio of number of H atoms in the chloromethyl group to those on aromatic rings is 0.1053. Hence, the degree of chloromethylation is 4.1% with the aid of the experimental and theoretical ratios. Since the quaternization reaction is known to have a high efficiency [28], and the content of quaternary ammonium groups equals to the value of IEC.

Table 1 lists the elemental Cl content in the CPEK-C membrane, as measured by EDAX, suggesting that the CPEK-C membrane contains Cl. The <sup>1</sup>H NMR and EDAX results confirm that the desired modification of the PEK-C membrane was successful.

### 3.2. Structural characteristics of the QPEK-C membrane

Fig. 2 shows the C 1s (a) and N 1s (b) core-level XPS spectra for the surface of the PEK-C and QPEK-C membranes, respectively. The single peak at a bonding energy of 284.8 eV for PEK-C and QPEK-C membranes was attributed to the C of the C–H and C–COO groups, respectively, in the structures of these two membranes. The single peak at a bonding energy of about 289 eV was assigned to the C of the COO in the two membranes. Fig. 2 (b) shows an obvious single peak at a bonding energy of about 399.9 eV assigned to the N of the C–N in the QPEK-C membrane; however, there was no corresponding N peak in the XPS spectrum of the PEK-C membrane.

Table 2 lists the theoretical and experimental ratios of the C over O contents, and the N content for the PEK-C and QPEK-C mem-

**Table 2**

Comparison of the C to O atomic ratios between theoretical values and the XPS analysis and N atom% of the PEK-C and QPEK-C membranes.

Items	Theoretical C/O ratio	Experimental C/O ratio	N content%
PEK-C	6.6	4	0
QPEK-C	8.6	5.53	0.81

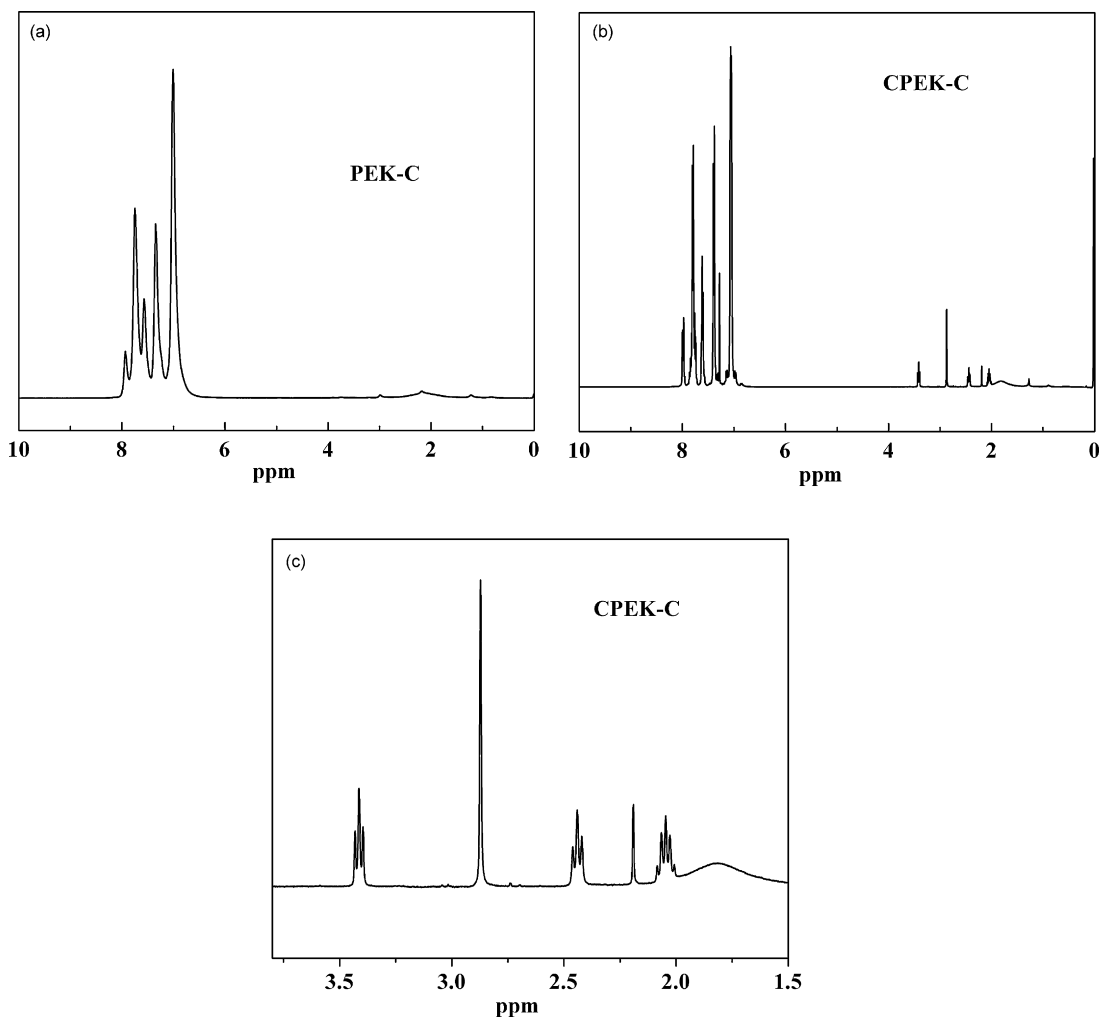


Fig. 1.  $^1\text{H}$  NMR spectra of the PEK-C (a) and CPEK-C (b and c) membranes.

branes, respectively. The ratio of the C over O content of the QPEK-C membrane was greater than that of PEK-C membrane. This may suggest that the  $-\text{CH}_2\text{N}(\text{CH}_3)_3\text{OH}$  group has been introduced into the PEK-C membrane via chloromethylation, quaternization and alkalization. The N content of the QPEK-C membrane is 0.81% compared with that of the PEK-C membrane (content = 0). These results may somewhat show that quaternary ammonium groups have been introduced into the membranes. To some extent, the XPS data may be used in this paper since the membranes produced are homogeneous. Hence, the composition of the surface may somewhat reflect that of the membranes.

### 3.3. Thermal stability

The thermal stability of the PEK-C and QPEK-C membranes was investigated by TG (see the TG diagrams in Fig. 3). The PEK-C material has a good thermal stability and the TG curve conforms to that found in the literature [29]. The weight decrease at  $450^\circ\text{C}$  originates from the splitting off of the phenolphthalein groups in the side-chain.

The chloromethylation and quaternization reaction reduced the thermal stability of the QPEK-C membrane, and its weight loss was greater than that of PEK-C membrane, as can be seen from the TGA curves. The first decrease at  $200^\circ\text{C}$  corresponds to the loss of the  $-\text{CH}_2\text{N}(\text{CH}_3)_3\text{OH}$  groups. In the second weight loss region (at  $450^\circ\text{C}$ ), the polymer residues were further degraded,

which corresponds to the decomposition of the phenolphthalein groups. Compared with other anion exchange membranes, the QPEK-C membrane showed good thermal stability. In the literature [13], the first weight loss of the quaternized PVA is at  $100^\circ\text{C}$ . And the weight loss of the hybrid membrane composed of quaternized PVA and TEOS is about 50% from 200 to  $400^\circ\text{C}$ . Whereas the weight loss of the QPEK-C membrane is about 10% from 200 to  $400^\circ\text{C}$ , which indicates the good thermal stability of the QPEK-C membrane.

### 3.4. Oxidative stability

Fig. 4 shows the change in the weight content of the PEK-C and QPEK-C membranes over time, which indicates the oxidative stability of the two membranes. After immersing for 168 h, there was little weight loss for the two membranes. The weight losses were 3.0 and 2.1% for the PEK-C and QPEK-C membranes, respectively, which were less than those reported for other membranes [30].

The ion conductivities of the QPEK-C membrane, after the oxidation experiment, were  $3.69 \times 10^{-3}$ ,  $4.19 \times 10^{-3}$ ,  $4.86 \times 10^{-3} \text{ S cm}^{-1}$  at 40, 50 and  $60^\circ\text{C}$ , respectively. Compared with those before oxidative experiment ( $2.99 \times 10^{-3}$ ,  $3.86 \times 10^{-3}$  and  $5.06 \times 10^{-3} \text{ S cm}^{-1}$  at 40, 50 and  $60^\circ\text{C}$  respectively), the ion conductivity of the QPEK-C membrane did not decrease, but in contrast increased. This is probably that, during the oxidation experiments, the QPEK-C mem-

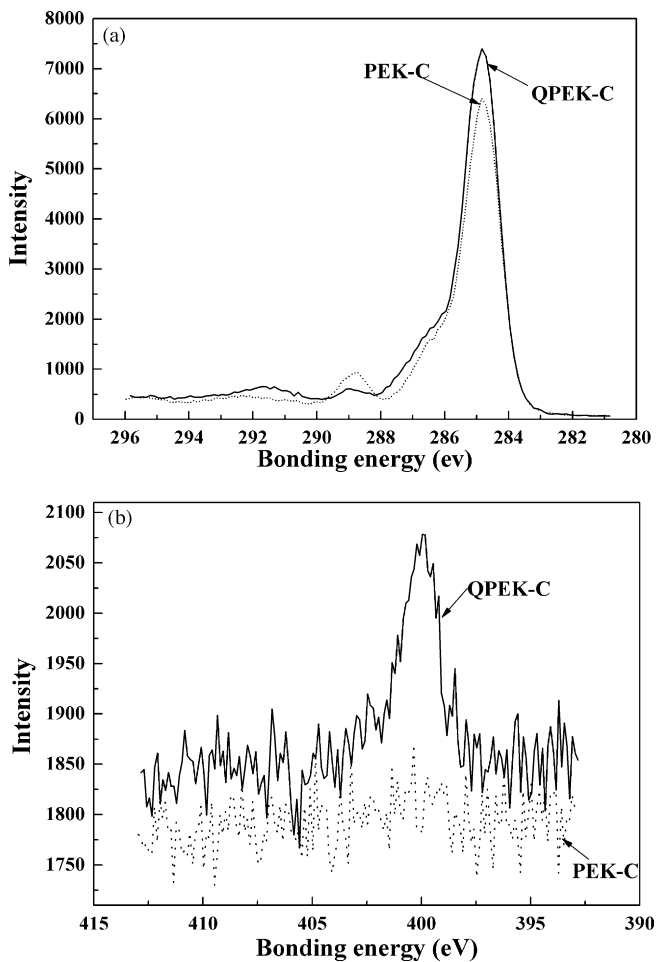


Fig. 2. XPS spectra of C 1s (a) and N 1s (b) for the PEK-C and QPEK-C membranes.

brane had been immersed in 60 °C hot water for one week. Hence it swelled and its water content increased, resulting in an increase in the conductivity of the QPEK-C membrane.

The above results indicate the PEK-C and QPEK-C membranes exhibited good oxidative stability. As for the QPEK-C membranes, the relative amount of introduced quaternary ammonium groups was small, and hence the slight change of structure had little effect on the oxidative stability of the QPEK-C membrane; hence, these

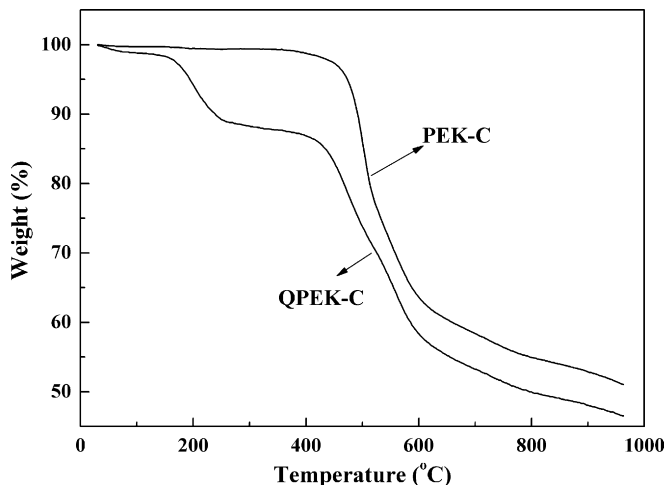


Fig. 3. TGA curves of the PEK-C and QPEK-C membranes.

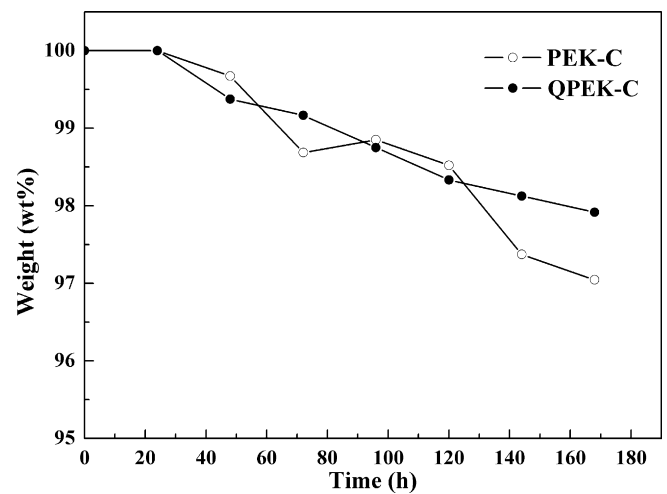


Fig. 4. The oxidative stability of the PEK-C and QPEK-C membranes.

membranes should be able to withstand the oxidative surroundings during the operation of fuel cells.

### 3.5. Water and methanol uptakes and ion-exchange capacity

Table 3 shows the water and methanol uptakes and the IEC of the two membranes. The PEK-C membrane has excellent solvent resistance. The polarity of water is higher than that of methanol, so the methanol uptakes of the two membranes were greater than those of water. Also the water and methanol uptakes of the QPEK-C membranes were both greater than those of the PEK-C membranes, which was attributed to the introduction of the functional groups. Furthermore, the functional groups increased the hydrophilic nature of the QPEK-C membranes. However, this difference between the two membranes was slight, which indicated that the content of functional groups on the QPEK-C membrane was small.

Water molecules offer a transport channel for anions in the ion-exchange membrane. The water uptake of the QPEK-C membrane was less than 5 wt.%, but this still provided sufficient water molecules to transport anions through the membrane. The low water uptake results in a low ion conductivity, which is discussed in the following section on ionic conductivity. The IEC value ( $0.11 \text{ meq g}^{-1}$ ) also agrees with this observation that low water uptake and low IEC result in a small ion conductivity compared with the other membranes containing quaternary ammonium groups, as reported in the literature [6,9].

### 3.6. Ionic conductivity

Fig. 5 shows the relationship between  $\ln \sigma$  ( $\sigma$  represents the ionic conductivity) and  $1000/T$  ( $T$  is the absolute temperature) and the ion transport activation energy  $E_a$  of the QPEK-C membrane. The ionic conductivities of the QPEK-C membrane are  $1.6 \times 10^{-3}$ ,  $2.32 \times 10^{-3}$ ,  $2.99 \times 10^{-3}$ ,  $3.86 \times 10^{-3}$  and  $5.06 \times 10^{-3} \text{ S cm}^{-1}$  at 20, 30, 40, 50 and 60 °C, respectively. This behavior accorded with the recognized free-volume model [14]. The free volume increases with increasing temperature, hence the channel for ion transport expands; mean-

Table 3  
Water and methanol uptakes and the IEC for the PEK-C and QPEK-C membranes.

Membrane	Water uptake (wt.%)	Methanol uptake (wt.%)	IEC ( $\text{meq g}^{-1}$ )
PEK-C	3.23	4.84	0
QPEK-C	3.33	6.67	0.11

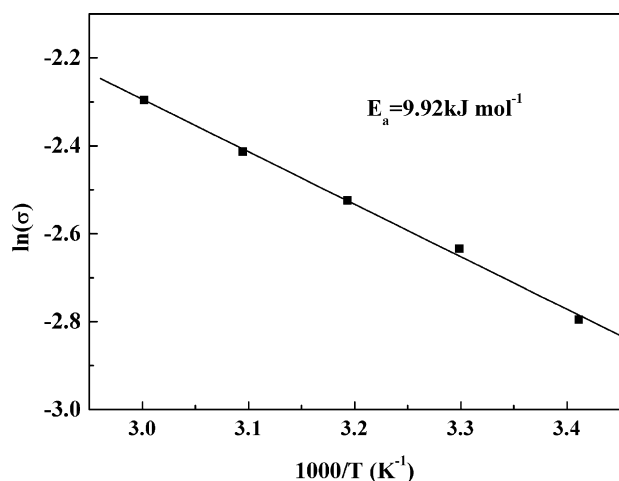


Fig. 5. Temperature dependence of ion conductivity for the QPEK-C membranes.

while, the mobility of ions increases. With these two effects, the ion conductivities of the QPEK-C membrane increase with increasing temperature.

There were no mobile ions in the structure of the PEK-C membrane; however, the introduction of the quaternary ammonium groups added mobile ions into the PEK-C membrane. So the QPEK-C membrane has significant ion conductivity. Many of the same kind of quaternized anion exchange membranes have been reported in the literature, such as quaternized poly(ether-imide) ( $2.3\text{--}3.5 \times 10^{-2} \text{ S cm}^{-1}$  from 25 to 95 °C) [16], quaternized poly(oxyethylene) methacrylates (about  $1.8 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature) [31]. Compared with these anion exchange membranes, the QPEK-C membrane shows an ionic conductivity lower than or comparable to those anion exchange membranes, which is promising at the current stage of development of ADMFCs.

### 3.7. Methanol permeability

The PEK-C material has good solvent resistance, and the QPEK-C membrane also has a good methanol resistance. After placement for 4 h in the two-compartment chamber, with methanol concentrations of 0.5, 1, 2, and 4 M, no methanol could be detected in the other-side compartment. Hence it can be assumed that the methanol permeability of the QPEK-C membrane is less than  $10^{-9} \text{ mol cm}^{-2} \text{ min}^{-1}$ . In former experiments, concerning the methanol permeability of the cross-linked QAPVA membranes in our laboratory, methanol was detected after 30–60 min. Compared with former experiments carried out in our laboratory with cross-linked QAPVA membranes [5,6,13] and the QAPPESK membrane reported in the literature [11], the methanol permeability of the QPEK-C membrane was much lower than that of those anion exchange membranes (cross-linked QAPVA membranes:  $(1.0\text{--}4.1) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , QPES-C membrane:  $10^{-9} \text{ mol cm}^{-2} \text{ min}^{-1}$ , 1 M methanol).

There are two factors that affect methanol permeation: (1) the electro-osmotic drag and (2) diffusion. In the alkaline methanol fuel cell, the ionic current flows from the cathode to the anode, which is the reverse direction of the methanol crossover from anode to cathode. That is one benefit of alkaline direct methanol fuel cells [32]. If the QPEK-C membrane would be used for alkaline methanol fuel cells, the electro-osmotic effect would further decrease the methanol crossover. The low methanol permeability indicates that

the QPEK-C membrane has potential application for methanol fuel cells.

## 4. Conclusions

In this paper, a novel anion exchange membrane, namely quaternized cardo polyetherketone (QPEK-C), was prepared based on polyetherketone (PEK-C). The conductivity of the QPEK-C membrane was  $5.06 \times 10^{-3} \text{ S cm}^{-1}$  at 60 °C. The methanol permeability, being less than  $10^{-9} \text{ mol cm}^{-2} \text{ min}^{-1}$ , suggests that the QPEK-C membrane has excellent methanol resistance. This performance criterion indicates that the QPEK-C membrane has a strong potential for application in alkaline methanol fuel cells.

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## References

- [1] J.S. Spendlow, G.Q. Lu, P.J.A. Kenis, A. Wieckowski, *J. Electroanal. Chem.* 568 (2004) 215–224.
- [2] K. Scott, A.K. Shukla, C.L. Jackson, W.R.A. Meuleman, *J. Power Sources* 126 (2004) 67–75.
- [3] J.R. Varcoe, R.C.T. Slade, Chemistry paper, University of Surrey, 2004.
- [4] Y. Wang, L. Li, L. Hu, L. Zhuang, J.T. Lu, B.Q. Xu, *Electrochem. Commun.* 5 (2003) 662–666.
- [5] Y. Xiong, Q.L. Liu, Q.G. Zhang, A.M. Zhu, *J. Power Sources* 183 (2008) 447–453.
- [6] Y. Xiong, J. Fang, Q.H. Zeng, Q.L. Liu, *J. Membr. Sci.* 311 (2008) 319–325.
- [7] T.N. Danks, R.C.T. Slade, J.R. Varcoe, *J. Mater. Chem.* 13 (2003) 712–721.
- [8] J.R. Varcoe, R.C.T. Slade, *Electrochem. Commun.* 8 (2006) 839–843.
- [9] L. Lei, Y.X. Wang, *J. Membr. Sci.* 262 (2005) 1–4.
- [10] C.C. Yang, S.J. Lin, G.M. Wu, *Mater. Chem. Phys.* 92 (2005) 251–255.
- [11] J. Fang, P.K. Shen, *J. Membr. Sci.* 285 (2006) 317–322.
- [12] Y. Wang, B. Peppley, K.A.M. Creber, V.T. Bui, E. Halliop, *J. Power Sources* 162 (2006) 105–113.
- [13] Y. Xiong, Q.L. Liu, A.M. Zhu, S.M. Huang, Q.H. Zeng, *J. Power Sources* 186 (2009) 328–333.
- [14] J.J. Kang, W.Y. Li, Y. Lin, X.P. Li, X.R. Xiao, S.B. Fang, *Polym. Adv. Technol.* 15 (2004) 61–64.
- [15] J.S. Park, G.G. Park, S.H. Park, Y.G. Yoon, C.S. Kim, W.Y. Lee, *Macromol. Symp.* 249 (2007) 174–182.
- [16] G.G. Wang, Y.M. Weng, D. Chu, D. Xie, R.R. Chen, *J. Membr. Sci.* 326 (2009) 4–8.
- [17] D.S. Shen, *Chem. Res. Appl. (China)* 11 (1999) 229–234.
- [18] Y.H. Huang, C.B. Xiao, *Polymer (China)* 48 (2007) 371–381.
- [19] C. Bieniarz, C. Behme, K. Ramakrishna, *J. Fluorine Chem.* 106 (2000) 99–102.
- [20] L. Wu, T.W. Xu, W.H. Yang, *J. Membr. Sci.* 286 (2006) 185–192.
- [21] G.L. Jing, Z.T. Yu, G.L. Mao, S.Q. Wang, Y. Han, *J. Daqing Pet. Inst. (China)* 24 (2000) 38–42.
- [22] G.C. Li, *Chem. World (China)* 3 (2000) 259–261.
- [23] H.B. Chen, Y.B. Lin, Z.P. Liu, C.Q. Deng, H.C. Li, *Dyestuff Ind. (China)* 38 (2001) 41–42.
- [24] J.H. Chen, Q.L. Liu, Y. Xiong, Q.G. Zhang, A.M. Zhu, *J. Membr. Sci.* 325 (2008) 184–191.
- [25] A. Regina, E. Fontananova, E. Drioli, M. Casciola, M. Sganappa, F. Trotta, *J. Power Sources* 160 (2006) 139–147.
- [26] A. Basile, L. Paturzo, A. Iulianelli, I. Gatto, E. Passalacqua, *J. Membr. Sci.* 281 (2006) 377–385.
- [27] H.N. Deng, L. Xu, Y.X. Wang, *Chem. Online (China)* 68 (2005) 1–6.
- [28] H.W. Zhang, X.F. Liu, X.T. Ma, B.K.Y.Y.X. Zhu, *J. Func. Mater. (China)* 38 (2007) 412–414.
- [29] W.X. Li, *Chem. Ind. Eng. (China)* 19 (2002) 271–273.
- [30] Z.Y. Jiang, X.H. Zheng, H. Wu, F.S. Pan, *J. Power Sources* 185 (2008) 85–94.
- [31] F. Yi, X.P. Yang, Y.J. Li, S.B. Fang, *Polym. Adv. Technol.* 10 (1999) 473–475.
- [32] E.H. Yu, K. Scott, *J. Power Sources* 137 (2004) 248–256.