Synthesis and properties of a novel side-chain-type hydroxide exchange membrane for direct methanol fuel cells (DMFCs)

Shuai Xu[a], Gang Zhang[a], Yang Zhang[b], Chengji Zhao[a], Wenjia Ma[a], Hongcheng Sun[a], Na Zhang[a], Liyuan Zhang[a], Hao Jiang[a], Hui Na[a,b,*]

[a] Alan G MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China
[b] SINOPEC Beijing Research Institute of Chemical Industry, Beijing 100013, People's Republic of China

ARTICLE INFO

ABSTRACT

A series of poly(ether ether ketone) anion exchange membranes with tunable IEC (Ion-exchange capacity) values are polymerized from a novel bisphenol monomer (4-methyl)phenylhydroquinone. These poly(ether ether ketone) copolymers contain methyl groups on the rigid side chain. The degrees of bromination and quaternary amination of the copolymers are controlled by manipulating the contents of methyl groups in the copolymers. Hence, the IEC tunability of the membrane is achieved. The resulting PEEK-Q-xx membranes show good dimensional stability. The highest swelling ratio (PEEK-Q, with an IEC value of 0.90 mequiv. g^{-1}) is only 9.0% at 80 °C, at which temperature, the hydroxide conductivity of PEEK-Q membrane is 0.031 S cm^{-1}. The methanol permeability values of the membranes are all below 1.5×10^{-7} cm^2 s^{-1}, which are much lower than that of Nafion 117. These properties make the membranes good candidate materials for anion exchange membranes for alkaline direct methanol fuel cells.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Among the potential substitutes of fossil fuels, polymer electrolyte fuel cells (PEFCs), have drawn much attention because of their high efficiency and environmental friendliness. As the crucial part of the fuel cells, polymer electrolyte membranes (PEMs), have critical requirements, such as high proton/anion conductivity, low methanol permeability and high mechanical strength [1–3]. Perfluorosulfonic acid polymers, such as Nafion (DuPont), have been models for PEMs materials because of their high proton conductivity and good chemical stability. However, its commercialization has suffered the high cost, high methanol crossover and the low operating temperature [4–6]. In recent years, much effort has been devoted to the development of new PEM materials. Sulfonated aromatic polymers have been studied as candidates for the PEMs. Usually, a non-fluorinated sulfonated aromatic PEM requires a high ion exchange capacity (IEC) to achieve sufficient proton conductivity. However, high IEC results in poor dimensional stability, which leads to the loss of the mechanical properties [7,8]. In addition, the expensive platinum catalyst is a huge obstacle for the application of the proton exchange membrane fuel cells. Compared with the PEMs, the hydroxide exchange polymer membranes (HEMs) have advantages, such as fast kinetics and low cost of metal electrocatalysts in alkaline fuel cell. Therefore, the HEM emerged rapidly as a promising candidate for fuel cell membranes [9–13].

The alkaline fuel cell (AFC) with liquid electrolyte was the first type fuel cell which converted the chemical energy stored in hydrogen directly into electrical power [14]. Then people realized that a polymer membrane could be a more suitable material for electrolyte in AFCs. The application of anion exchange membranes (AEMs) in the HEM fuel cells (HEMFCs) requires necessary conductivity, mechanical strength and chemical stability. Various kinds of polymers have been synthesized as the base materials for HEMs, such as poly(phenylene) [15], poly(styrene)s [16,17], poly(ether sulfone) [18–21], poly(arylene ether)s [22] and poly(ether ether ketone)s (PEEKs) [23].

Some recent reports suggest that locating the sulfonic acid groups on side chains grafted onto the polymer backbones could be a promising approach to enhance the properties of a PEM [24,25]. The side chains separate the hydrophilic sulfonic acid group regions from the hydrophobic polymer main chain [26–28]. In HEMs field, most reported HEM materials contain quaternary ammoniums in the aromatic backbones. Only a few works involve the side-chain-type HEMs.

In this work, we synthesized a new type of polyelectrolyte of which the quaternary ammonium groups are on the side chain, to decrease the steric hindrance of aromatic backbones and promote the separation of hydrophilic and hydrophobic

phases, finally to improve the hydroxide conductivity at a low level of IEC. Here is the strategy to synthesize PEEK with side-chain-type quaternary ammonium groups: a bisphenol monomer (4-methyl)phenylhydroquinone was designed and synthesized and a series of PEEKs containing methyl group side chains (PEEK-Me) were prepared by polycondensation. At last, the resulting copolymers were brominated and quaternized. We controlled the contents of methyl in the copolymers by copolymerization, to prepare membranes with different IEC values. All the monomer and copolymers were characterized and the properties related to HEMs materials for alkaline direct methanol fuel cell were also evaluated in detail.

2. Experimental

2.1. Materials

Hydroquinone (HQ) and 4-methylaniline were purchased from Aladdin Reagent, Shanghai, China. 4,4′-Difluorobenzophenone (DFB), N-bromosuccinimide (NBS), and benzoyl peroxide (BPO) were purchased from Sigma–Aldrich Ltd. Other solvents and reagents were obtained from Beijing Chemical Company and used without further purification.

2.2. Synthesis of monomer

2.2.1. Synthesis of (4-methyl)phenylbenzoquinone

4-Methylaniline (0.05 mol, 5.35 g), water (20 mL), ice (5 g), and hydrochloric acid (0.2 mol, 17 mL), were added into a 500-mL beaker. Then, 20 mL of 2.5 M $NaNO_2$ solution was added dropwise. The reaction mixture was kept in an ice salt bath (0–3 °C) with stirring for 2 h, and then a transparent light yellow solution was obtained after filtration. The filtrate was added dropwise into a suspension of 1,4-benzoquinone (4.32 g, 0.04 mol) in a sodium bicarbonate solution(12.6 g, 0.15 mol). The reaction mixture was stirred at 5–8 °C for 4 h. Finally, yellow solid was obtained by filtering and washing with deionized water several times. The product was dried at 80 °C in a vacuum oven for 24 h.

2.2.2. Synthesis of (4-methyl)phenylhydroquinone

Zn power (4.875 g, 0.075 mol), (4-methyl)phenylbenzoquinone (4.92 g, 0.025 mol), and deionized water (35 mL) were mixed and heated in a 250-mL three-necked flask. When the mixture began to boil, hydrochloric acid (0.075 mol, 6.4 mL) was added dropwise. After 4 h refluxing, the precipitate was collected by filtration and recrystallized from toluene.

2.3. Synthesis of the polymers

2.3.1. Copolymerization of poly(ether ether ketone)s containing methyl group (PEEK-Me-xx)

A typical synthetic procedure, illustrated by the preparation of PEEK-Me-80 copolymer (xx: Me-HQ/HQ = 80/20), is described as follows:

(4-Methyl)phenylhydroquinone (Me-HQ; 3.200 g, 0.016 mol), HQ (0.440 g, 0.004 mol), and 4,4′-difluorobenzophenone (4.36 g, 0.02 mol) with K_2CO_3 (3.32 g, 0.024 mol) were added into a 250-mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a Dean-Stark trap. A mixture of N-methylpyrrolidone (NMP) (25 mL) and toluene (15 mL) was used as the solvent. The reaction mixture was heated at 140 °C for 2 h under a nitrogen atmosphere. After dehydration and removal of toluene, the reaction temperature was increased to 170 °C. The reaction was stopped when viscosity was observed to increase dramatically. The mixture was slowly poured into 1000 mL of deionized water. The resulting fibrous copolymer was washed with hot water several times and dried under vacuum at 80 °C for 24 h.

2.3.2. Synthesis of bromomethylated poly(ether ether ketone)s (PEEK-Br-xx)

A typical procedure for preparing bromomethylated copolymer PEEK-Br-80 was as follows. PEEK-Me-80 (2.0 g, the amount of —CH_3 was 4.4 mmol) and 40 mL of chloroform were added into a three-necked flask equipped with mechanical stirrer, nitrogen inlet and condenser. The mixture was stirred adequately to form homogeneous solution. NBS (1.56 g, 8.8 mmol) and BPO (0.1 g) were then added to the solution. After the reaction had been carried out for 24 h at 60 °C, the mixture was cooled to room temperature and coagulated in acetone. The resulting polymer was washed with acetone several times and dried under vacuum for 24 h at 40 °C.

2.3.3. Preparation of anion exchange membranes

A coating solution was prepared by dissolving 0.6 g of bromomethylated copolymer in 10 mL of NMP. The solution was filtrated and cast onto flat glass plates. The membranes were dried at 80 °C for 24 h to remove the casting solvent. To make the membranes quaternary-aminated, the dry membranes were immersed into a 33% aqueous solution of trimethylamine for 48 h at 30 °C. Then, the membranes were kept in a 1.0 M NaOH solution for 48 h. Finally, the membranes were washed thoroughly and immersed in deionized water for 48 h to remove the residual NaOH. The resulting quaternary-aminated membranes were stored in deionized water before use.

2.4. Characterizations

2.4.1. ^1H NMR spectra

^1H NMR spectra were measured using a Bruker 510 spectrometer (500 MHz). Deuterated dimethylsulfoxide (DMSO-d_6) and deuterochloroform (CDCl$_3$) were employed as the solvents. Tetramethylsilane (TMS) was used as an internal standard.

2.4.2. Thermal properties

The TGA curves were obtained by a Pyris 1 TGA (Perkine-Elmer) under a nitrogen atmosphere. All samples were preheated at 110 °C for 10 min to remove the residual solvents and water completely, and then reheated from 80 °C to 700 °C with a heating rate of 10 °C min^{-1}.

2.4.3. Mechanical properties

Mechanical properties of the membranes was evaluated using SHIMADZU AG-I 1 KN at the test speed of 2 mm min^{-1}. The membrane samples with the sizes of 15 mm × 4 mm were placed between the grips of the testing machine. To obtain statistical results, at least three parallel measurements were carried out for each test.

2.4.4. Ion-exchange capacity (IEC)

The ion exchange capacity (IEC) was measured using a classical back-titration method. Membranes in the OH$^-$ form were immersed in 100 mL of 0.01 M HCl for 48 h to undergo an ionic exchange process. After the ionic exchanging, the solutions were titrated with a standardized NaOH solution using phenolphthalein as an indicator. The IEC was calculated using Eq. (1):

$$IEC = \frac{consumed\ NAOH\,(mL) \times molarity\ NAOH\,(mol\ mL^{-1}) \times 1000}{weight\ of\ dry\ membrane\,(g)} (mequiv\ g^{-1})$$

(1)
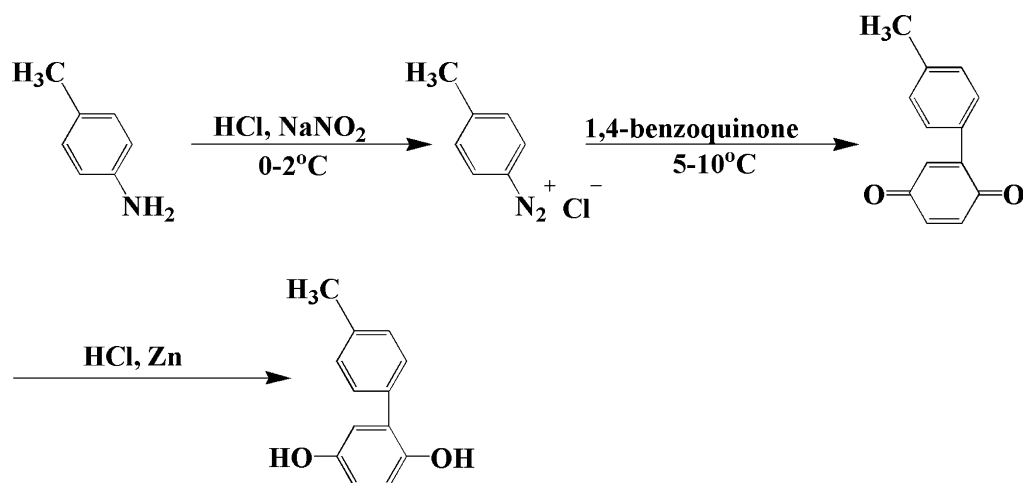
Scheme 1. The synthesis of (4-methyl)phenylhydroquinone.

2.4.5. Water uptake and swelling ratio

The membranes were vacuum-dried at 80 °C for several days until the weights and lengths stayed constant. Then all the samples were immersed into deionized water at given temperatures for 24 h. The water-saturated membranes were taken out, wiped quickly with tissue paper. The weights and lengths were measured as soon as possible. The water uptake and swelling ratio were calculated by the following equations:

$$WU\,(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \qquad (2)$$

$$SW\,(\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \qquad (3)$$

where W_{wet} and W_{dry} are the weights of wet and dry samples, respectively; L_{wet} and L_{dry} are the lengths of the wet and dry membranes, respectively.

2.4.6. Methanol permeability

Methanol permeability coefficient DK ($cm^2\,s^{-1}$) was determined by using a glass diffusion cell, which has been described in the literature [29]. Two reservoirs were separated by the membrane under test. A 10 M methanol solution was added into one side of the cell and water was added into another side. Magnetic stirrers were used on both compartments to ensure uniformity. The change of methanol concentration was measured by SHIMADZU GC-8A chromatograph. The methanol permeability was calculated as follows:

$$C_{B(t)} = \frac{A}{V_B} \frac{D_K}{L} C_A (t - t_0) \qquad (4)$$

where A (cm^2) and L (cm) are the effective areas and the thickness of the membrane, respectively. C_A and C_B are the methanol concentrations in methanol reservoir and water reservoir, respectively. V_B (cm^3) is the volume of diffusion reservoir. D_K ($cm^2\,s^{-1}$) is the methanol permeability.

2.4.7. Hydroxide ion conductivity

The hydroxide ion conductivity of each membrane was measured by a four-point probe alternating current impedance spectroscopy using a Princeton Applied Research Model 2273 potentiostat/galvanostat/FRA. Membranes in the hydroxide form were immersing in deionized water at room temperature for 24 h before measurement. The membranes and the electrodes were set in a Teflon cell, where the probes were directly attached to membranes, and the resistance of the membranes was measured in

deionized water. The hydroxide ion conductivity was calculated by using the following equation:

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

where L is the distance between the two electrodes, R is the resistance of the membrane, and S is the area.

2.4.8. Alkaline stability

For alkaline stability, the PEEK-Q-xx membrane samples were kept in NaOH solutions (4 M) in test tubes for 7 days at room temperature and 80 °C, respectively. To check whether the samples had decomposed into pieces, the test tubes were shaken every 8 h.

3. Results and discussion

3.1. Synthesis and characterization of monomer and copolymers

As shown in Scheme 1, the bisphenol monomer was synthesized in a three-step synthetic process. The structure of the (4-methyl)phenylbenzoquinone and (4-methyl)phenylhydroquinone were identified by ^{1}H NMR spectroscopy. As shown in Fig. 1, the shift at 8.70 ppm was assigned to the protons of hydroxyl groups, which could not be observed in the spectrum of the corresponding quinolone, and the shift at 2.32 ppm corresponded to the hydrogen atoms of methyl groups was obvious in Fig. 1. This result proved that the (4-methyl)phenylhydroquinone monomer had been synthesized successfully.

Scheme 2 shows the routes to synthesize the copolymers PEEK-Q-xx. Figs. 2 and 3 show the ^{1}H NMR spectra of the pristine and bromomethylated copolymers named PEEK-Me, PEEK-Br, PEEK-Me-80 and PEEK-Br-80, respectively. It should be noticed that in these two figures, the shifts of —CH$_2$Br and —CHBr$_2$ could be found at about 4.44 ppm and 6.60 ppm, which suggested that the benzyl groups on the side chains had been brominated.

3.2. Thermal stability

The thermal stability of the membranes was studied by TGA technique under a nitrogen atmosphere. Fig. 4 shows that the TGA curves of PEEK-80s. A slight weight loss was observed below 180 °C, corresponding to the evaporation of the residual water and solvents. The first obvious weight loss of PEEK-Q-80 could be found around 210 °C, which precisely correlated with the degradation of quaternary ammonium groups [23]. For the copolymer PEEK-Br-80, the first stage (290–390 °C) was associated to the elimination
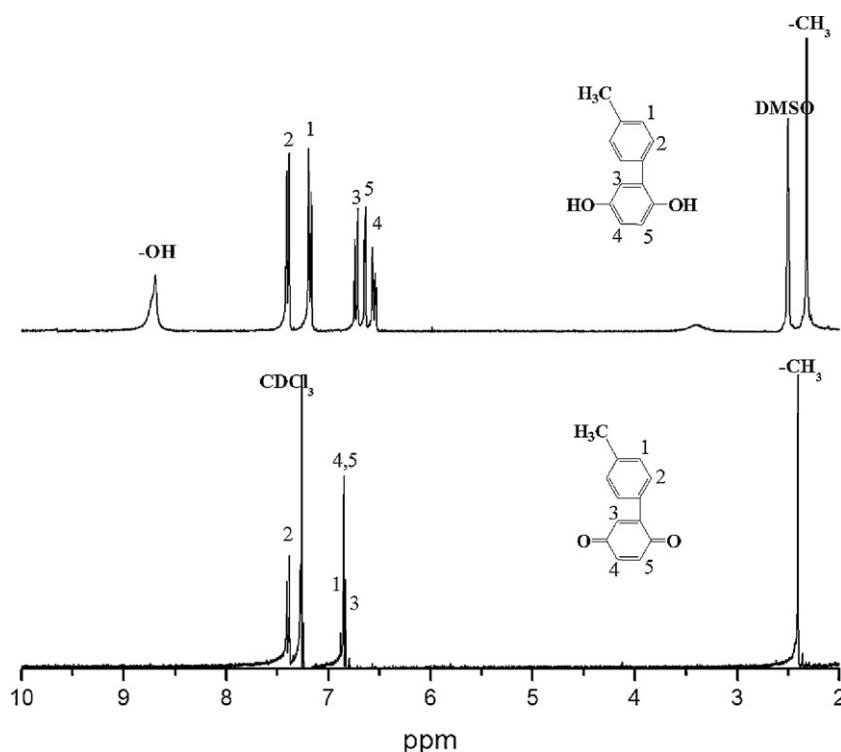
Fig. 1. The ^{1}H NMR spectra of (4-methyl)phenylbenzoquinone and (4-methyl)phenylhydroquinone.

of the bromine atom on the side chains. All the copolymers had dramatic weight loss when the temperatures rose to 480 °C, which indicated the main-chain decompositions [30]. Similar processes of other copolymers could be found in Table 1, which shows the 5% weight-loss temperatures of all the polymers in this study.

3.3. Mechanical properties

It is essential for HEMs to maintain adequate mechanical strength to withstand fabrication of the membrane electrode assembly (MEA) [31]. The mechanical properties of all the membranes were evaluated and listed in Table 1. It can be seen that the PEEK-Q-xx membranes present lower tensile strength and Young's modulus but higher maximum elongation values than the PEEK-Br-xx and PEEK-Me-xx polymers. The decline of the tensile strength in PEEK-Q-xx could attribute to the introduction of strong polar quaternary ammonium groups in side chains, which changed the ordering of aggregative state. However, the polar groups enhanced the molecular interaction and led to the increase of the maximum elongations. The PEEK-Q-xx membranes showed good toughness and strength, which could fulfill the requirements of mechanical properties in HEM fuel cells.

3.4. IEC, water uptake and swelling ratio

The IEC value reflects the density of quaternary ammonium groups in membranes and determines the water uptake and hydroxide conductivity directly [32]. As is shown in Table 2, the IEC values of PEEK-Q-xx increased from 0.62 mequiv. g^{-1} to 0.90 mequiv. g^{-1} with the contents of methyl groups in the original copolymers mount up. It indicates that the introduction of the ammonium groups to the polymer could be controlled to a certain extent by our strategy.

Water uptake of the membrane is particularly important because swelling affects mechanical integrity of the electrode-membrane structure and conductivity of the membrane itself [33]. Excessively high levels of water in the membrane can result in excessive swelling, finally leads to the loss of mechanical properties. As expected, water uptake and swelling ratio rose with the increase of temperature and IEC value (Figs. 5 and 6). Overall, the membranes showed limited swelling ratio, the PEEK-Q membrane with the highest IEC value (0.90 mequiv. g^{-1}) showed a water uptake of 30.1% and a swelling ratio of 9% at 80 °C. It indicates that the serialized copolymers have a reliable dimensional stability.

Table 1
The mechanical properties of membranes.

Polymers	5% weight loss temperature (°C)	Tensile strength (MPa)	Maximum elongation (%)	Young's modulus (GPa)
PEEK-Me	488.2	54.38	7.19	1.35
PEEK-Me-80	481.3	53.75	8.95	1.36
PEEK-Me-60	494.4	53.78	9.28	1.40
PEEK-Br	331.9	64.17	6.18	1.83
PEEK-Br-80	332.7	55.79	6.07	1.42
PEEK-Br-60	325.4	63.02	8.35	1.61
PEEK-Q	284.6	47.97	23.58	1.05
PEEK-Q-80	278.5	50.68	17.18	1.17
PEEK-Q-60	290.1	51.98	19.96	1.31
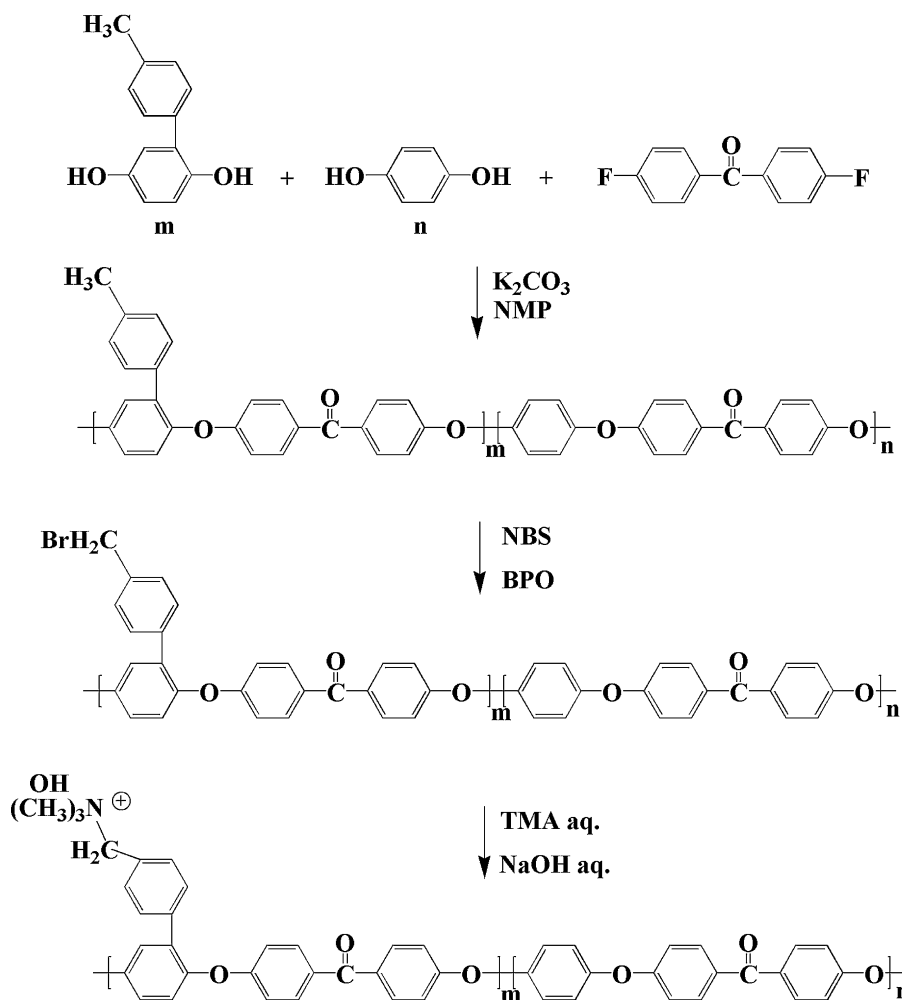
Scheme 2. The copolymerization of poly(ether ether ketone)s bearing pendant quaternary ammonium groups (PEEK-Q-xx).

3.5. Hydroxide conductivity and methanol permeability

Fig. 7 shows the hydroxide conductivities of the PEEK-Q membranes as a function of temperature. The hydroxide conductivities of all the membranes increased with temperatures. The PEEK-Q had the highest conductivity of 0.031 S cm^{-1} at 80 °C. Considering its low IEC value (0.90 mequiv. g^{-1}) and swelling ratio (9.0%), The PEEK-Q showed a relatively good performance and could be satisfactory for the operation of alkaline fuel cell. Compared with some other main-chain type quaternary-aminated polymers for AEM materials with similar IEC values, the PEEK-Q-xx membranes showed higher conductivities [18,21]. Since these copolymers have similar main-chain structures, we believe that the difference of their conductivity may be resulted from the position of the alkaline groups in the PEEK-Q-xx polymers. The performances of anion conductivity prove that the introduction of the side-chain-type alkaline groups could decrease the steric hindrance of aromatic backbones, form an ionic network more readily and enhance the anion conductivity.

The methanol permeability was listed in Table 2. As shown, each membrane had an excellent methanol resistance. The methanol permeability increased dramatically as the increase of IEC. The membrane PEEK-Q with the highest conductivity showed a methanol diffusion of 1.427×10^{-7} cm^2 s^{-1}, which was only about one ninth of Nafion® (1.32×10^{-6} cm^2 s^{-1} at room temperature). To evaluate the further performance of each membrane on direct methanol fuel cell, the selectivity was calculated, which was defined as the ratio of ion conductivity to methanol permeability. Fig. 8 shows the selectivity of each membrane. All the PEEK-Q-xx had much higher selectivities than Nafion (3.19×10^4 S cm^{-3} s).

Table 2
The IEC, water uptake, swelling ratio, hydroxide conductivity, methanol permeability, selectivity, and alkaline stability of membranes.

| Membranes	IEC (mequiv. g^{-1})	Water uptake (wt%)		Swelling ratio (%)		Hydroxide ion conductivity (S cm^{-1})		Methanol permeability ($\times 10^{-7}$ cm^2 s^{-1})	Selectivity ($\times 10^4$ S cm^{-3} s)	Time of breaking into pieces in 4 M NaOH(aq)	
		20 °C	80 °C	20 °C	80 °C	20 °C	80 °C	20 °C	20 °C	20 °C	80 °C
PEEK-Q	0.90	11.9	30.1	5.0	9.0	0.011	0.031	1.427	7.91	>7 days	>7 days
PEEK-Q-80	0.80	6.4	13.9	2.5	6.5	0.007	0.022	0.318	22.01	>7 days	>7 days
PEEK-Q-60	0.62	5.3	7.0	2.4	4.1	0.005	0.018	0.223	22.42	>7 days	>7 days
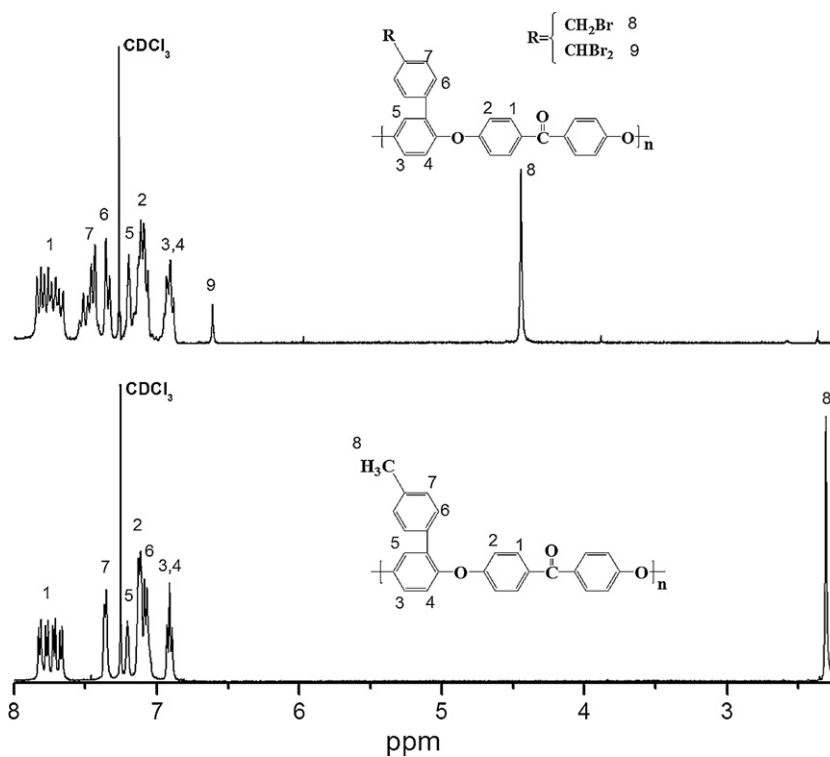
Fig. 2. The ^{1}H NMR spectra of PEEK-Me and PEEK-Br.

Among them, PEEK-Q, which had the highest conductivity (0.031 S cm^{-1}), showed a selectivity of 7.91×10^4 S cm^{-3} s, and the two membranes obtained by copolymerization with HQ have much higher selectivity (about 22.0×10^4 S cm^{-3} s). With outstanding methanol resistance, the application of PEEK-Q-xx membranes in fuel cells is promising.

3.6. Alkaline stability

Besides the good conductivity and selectivity, these membranes had outstanding stability in strong alkaline solutions. Just as Table 2 showed, the PEEK-Q-xx membranes maintained their flexibility and toughness even after being immerged in a 4 M NaOH solution
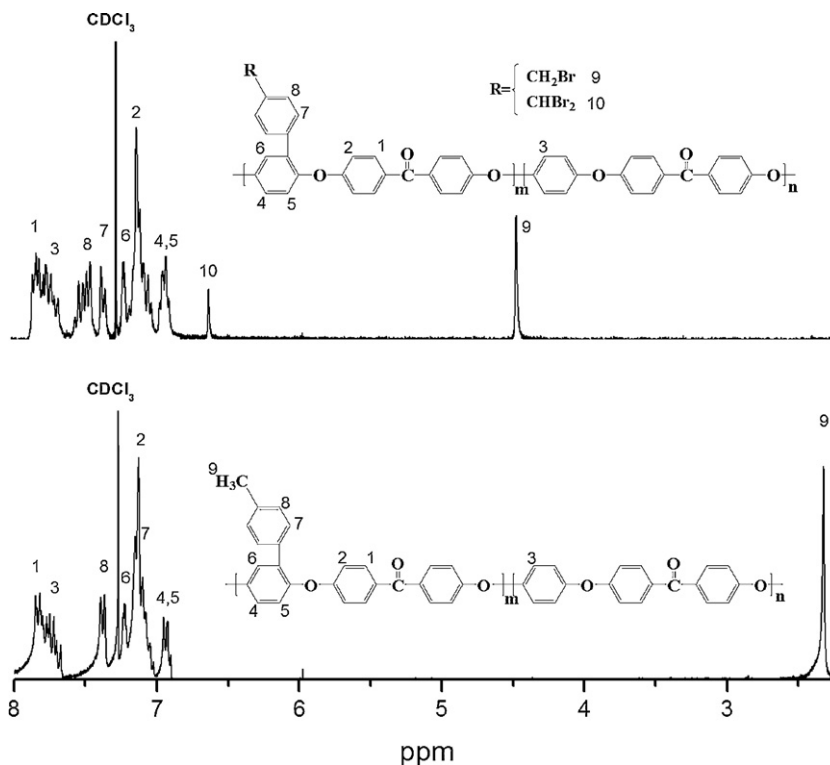
Fig. 3. The ^{1}H NMR spectra of PEEK-Me-80 and PEEK-Br-80.
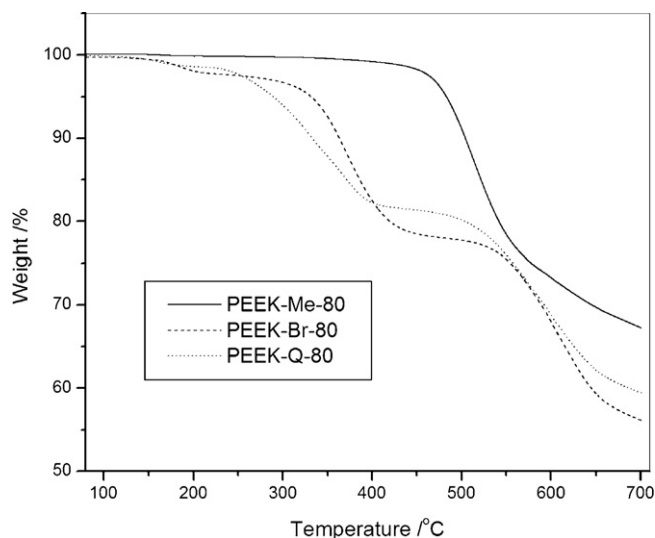
Fig. 4. The TGA curves of the membranes of PEEK-R-80.
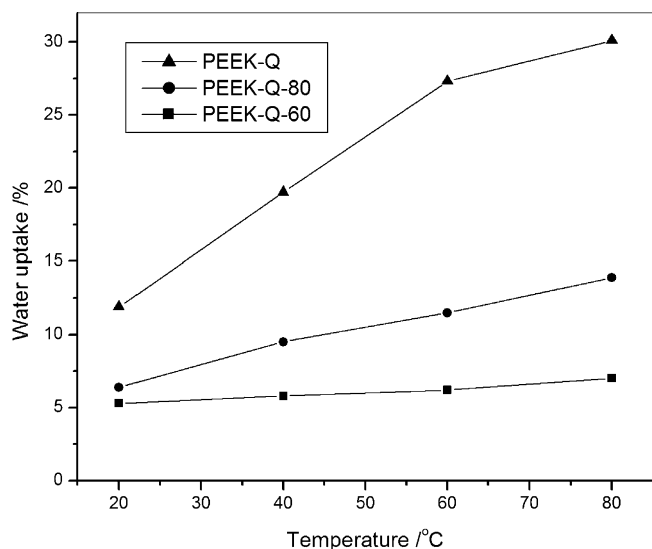

Fig. 5. The water uptakes of membranes at different temperatures.
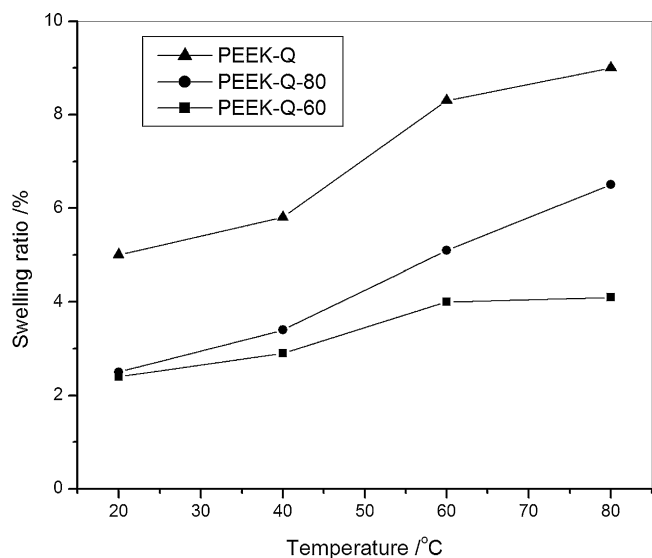

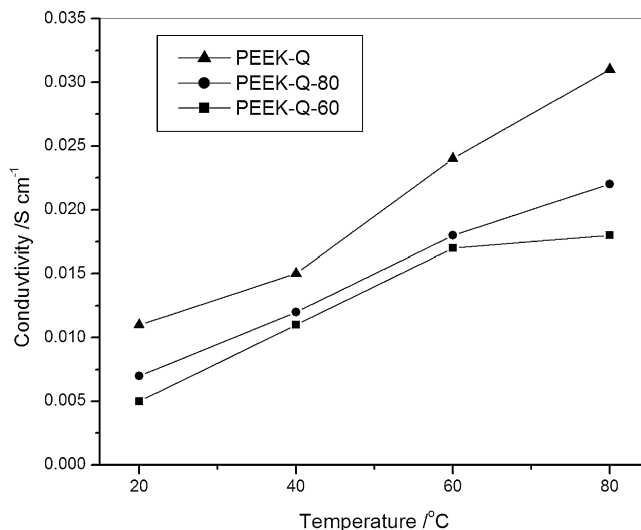**Fig. 6.** The swelling ratios of membranes at different temperatures.

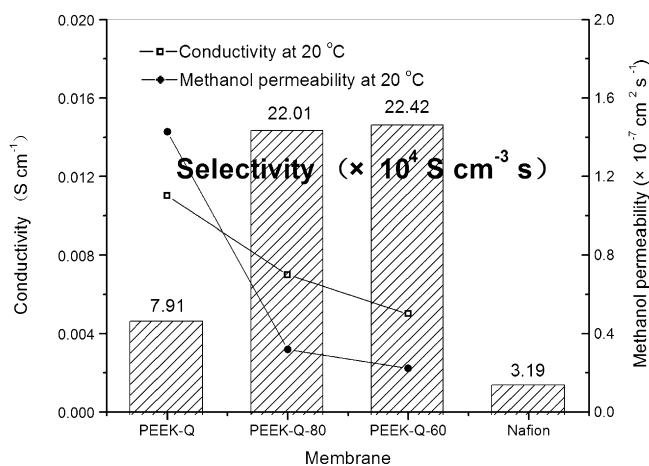**Fig. 7.** The hydroxide conductivities of the PEEK-Q-xx membranes.

Fig. 8. conductivities, methanol permeabilities and selectivities of the membranes at 20 °C.

at 80 °C (which is higher than the operating temperatures of HEM-FCs) for 7 days. It illustrated that the PEEK-Q-xx could withstand corrosion in strong alkalis.

4. Conclusion

In summary, a novel series of poly(ether ether ketone) copolymers bearing pendant quaternary ammonium groups (PEEK-Q-xx) have been prepared as hydroxide exchange membranes for direct methanol fuel cells (DMFCs). The IEC values of the membranes were well controlled through adjusting the content of methyl on the pristine polymer. All the membranes showed good thermal and mechanical stabilities. The PEEK-Q membrane has an appropriate conductivity of 0.031 S cm^{-2}, with a relatively low IEC (0.90 mequiv. g^{-1}), and the swelling ratio of the PEEK-Q membrane was only 9.0% at 80 °C. The methanol permeability was very low and the selectivity was much higher than Nafion 117. The alkaline stabilities of the membranes meet the requirements of the operation of fuel cells. All the parameters indicate that these membranes exhibited good potential in DMFCs application.

Acknowledgements

References

[1] S. Bose, T. Kuila, T.X.H. Nguyen, N.H. Kim, K. Lau, J.H. Lee, Prog. Polym. Sci. 36 (2011) 813–843.
[2] K. Nakabayashi, T. Higashihara, M. Ueda, Macromolecules 43 (2010) 5756–5761.
[3] X.F. Li, G. Zhang, D. Xu, C.J. Zhao, H. Na, J. Power Sources 165 (2007) 701–707.
[4] Z. Wang, X.F. Li, C.J. Zhao, H.Z. Ni, H. Na, J. Power Sources 160 (2006) 969–976.
[5] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Chem. Rev. 104 (2004) 4587–4611.
[6] L. Wu, G.F. Zhou, X. Liu, Z.H. Zhang, C.R. Li, T.W. Xu, J. Membr. Sci. 371 (2011) 155–162.
[7] J. Kerres, A. Ullrich, Sep. Purif. Technol. 22–23 (2001) 1–15.
[8] Y. Zhang, G. Zhang, Y. Wan, C.J. Zhao, K. Shao, H.T. Li, M.M. Han, J. Zhu, S. Xu, Z.G. Liu, H. NA, J. Polym. Sci. A: Polym. Chem. 48 (2010) 5824–5832.
[9] Q. Zhang, S.H. Li, S.B. Zhang, Chem. Commun. 46 (2010) 7495–7497.
[10] S. Gu, R. Cai, T. Luo, Z.W. Chen, M.W. Sun, Y. Liu, G.H. He, Y.S. Yan, Angew. Chem. Int. Ed. 48 (2009) 6499–6502.
[11] B.C. Lin, L.H. Qiu, J.M. Lu, F. Yan, Chem. Mater. 22 (2010) 6718–6725.
[12] G. Wang, Y. Weng, D. Chu, R. Chen, D. Xie, J. Membr. Sci. 332 (2009) 63–68.
[13] J.H. Wang, S.H. Li, S.B. Zhang, Macromolecules 43 (2010) 3890–3896.
[14] T. Mikami, K. Miyatake, M. Watanabe, Appl. Mater. Interface 2 (2010) 1714–1721.
[15] M.R. Hibbs, C.H. Fujimoto, C.J. Cornelius, Macromolecules 42 (2009) 8316–8321.
[16] J.R. Varcoe, R.C.T. Slade, E.L.H. Yee, Chem. Commun. 13 (2006) 1428–1429.
[17] H. Liu, S.H. Yang, S.L. Wang, J. Fang, L.H. Jiang, G.Q. Sun, J. Membr. Sci. 369 (2011) 277–283.
[18] L. Li, Y.X Wang, J. Membr. Sci. 262 (2005) 1–4.
[19] J. Pan, S.F. Lu, Y. Li, A.B. Huang, L. Zhuang, J.T. Lu, Adv. Funct. Mater. 20 (2010) 312–319.
[20] T. Sata, M. Tsujimoto, T. Yamaguchi, K. Matsusaki, J. Membr. Sci. 112 (1996) 161–170.
[21] Z. Zhao, J.H. Wang, S.H. Li, S.B. Zhang, J. Power Sources 196 (2011) 4445–4450.
[22] M. Tanaka, K. Fukasawa, E. Nishino, S. Yamaguchi, K. Yamada, H. Tanaka, B. Bae, K. Miyatake, M. Watanabe, J. Am. Chem. Soc. 133 (2011) 10646–10654.
[23] W.J. Ma, C.J. Zhao, H.D. Lin, G. Zhang, H. Na, J. Appl. Polym. Sci. 120 (2011) 3477–3483.
[24] J.C. Tsai, C.K. Lin, J. Power Sources 196 (2011) 9308–9316.
[25] Y.Q. Zhu, A. Manthiram, J. Power Sources 196 (2011) 7481–7487.
[26] B. Lafitte, P. Jannasch, Adv. Funct. Mater. 17 (2007) 2823–2834.
[27] Y. Yin, O. Yamada, Y. Suto, T. Mishima, K. Tanaka, H. Kita, K. Okamoto, J. Polym. Sci. A: Polym. Chem. 43 (2005) 1545–1553.
[28] N. Asano, M. Aoki, S. Suzuki, K. Miyatake, H. Uchida, M. Watanabe, J. Am. Chem. Soc. 128 (2006) 1762–1769.
[29] X.F Li, Z. Wang, H. Lu, C.J. Zhao, H. Na, C. Zhao, J. Membr. Sci. 254 (2005) 147–155.
[30] J. Wang, C.J. Zhao, H.D. Lin, G. Gang, Y. Zhang, J. Ni, W.J. Ma, H. Na, J. Power Sources 196 (2011) 5432–5437.
[31] T.Z. Fu, Z.M. Cui, S.L. Zhong, Y.H. Shi, C.J. Zhao, G. Zhang, K. Shao, H. Na, W. Xing, J. Power Sources 185 (2008) 32–39.
[32] M. Tanaka, M. Koike, K. Miyatake, M. Watanabe, Polym. Chem. 2 (2011) 99–106.
[33] J.F Zhou, M. Ünlü, I. Anestis-Richard, H. Kim, P. Kohl, J. Power Sources 196 (2011) 7924–7930.