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PAPER

Cross-linked hydroxide conductive membranes with side chains for direct methanol fuel cell applications

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A series of novel poly(ether ether ketone) copolymers containing methyl groups on the side chain were prepared based on a new monomer (3,4-dimethyl)phenylhydroquinone. Then a series of hydroxide exchange membranes with different IEC values were obtained through bromination and quaternary amination of the copolymers. By adjusting the contents of methyl groups in the copolymers, we could control the final structures of the membranes. The chemical structures of the monomers and copolymers were analyzed by ¹H NMR spectroscopy. After that, for the purpose of enhancing the dimensional stability and methanol resistance of the membrane, we prepared cross-linked membranes through a Friedel–Crafts reaction between bromomethyl groups and aromatic rings. The properties of the membranes related to fuel cell application were evaluated in detail. All the membranes showed good thermal and mechanical stabilities and conductivities. Moreover, the cross-linked membranes exhibit better dimensional stabilities and selectivities. Among those membranes, xPEEK–Q-100 showed a high conductivity (0.036 S cm⁻¹ at 80 °C), a low swelling ratio of 6.6% and a methanol permeation coefficient of 2.9×10^{-7} cm² s⁻¹. The outstanding properties indicated that the application of PEEK–Q-xx membranes in fuel cells was promising.

Introduction

Fuel cells have been regarded as an effective approach to resolve the recent energy crisis and environment problems, because of their high energy density, high conversion efficiency, and low pollution levels.¹⁻⁴ Among the several kinds of fuel cells, proton exchange membrane fuel cells (PEMFCs) have attracted the most attention. The most commercialized PEM, Nafion (DuPont), is a kind of perfluorosulfonic polymer containing pendant sulfonic acid side groups, showing high proton conductivity and excellent chemical, physical, and thermal stabilities. However, some significant deficiencies limit its largescale application, such as the extremely high cost and excessive methanol permeability.⁵ Besides, another major weakness of all the PEMFCs is their essential dependence on the precious metalbased catalysts, such as Pt.^{6,7}

Compared with PEMFCs, hydroxide exchange membrane fuel cells (HEMFCs) show some unique characteristics. The most significant advantage is the inherently faster kinetics of the oxygen reduction reaction, which allows using non-noble and low-cost metal electrocatalysts in the HEMFCs.^{8,9} Furthermore, HEMFCs can offer fuel flexibility (*e.g.*, methanol, ethanol,

ethylene glycol, *etc.*) because of their low over-potential for hydrocarbon fuel oxidation and reduced fuel crossover.¹⁰ To synthesize a HEM material with quaternary ammonium groups, chloromethylation is widely used.^{11–13} The drawbacks of this method are the strong toxicity of the chloromethyl methyl ether reagent and the poor controllability of the chloromethylation position and quantity.¹⁴ Hickner and Yan reported another route to synthesize quaternized polymers by bromination, which was a much safer and more controllable process.¹⁵

Locating the electrolyte groups on the side chain has been proved to be a promising strategy to enhance the separation of the hydrophilic regions and the hydrophobic polymer backbone.^{16,17} However, in the hydroxide exchange membrane, when quaternary ammonium groups are set onto the aliphatic side chains, the degradation of ammonium groups caused by a mechanism of E1 elimination or E2 elimination (Hofmann degradation) will take place easily under the attack of OH⁻ in alkali media, which seriously affects the stability of the membrane.^{18,19}

In our previous work, we synthesized brominated poly(aryl ether sulfone) and related cross-linked membranes for HEMs.²⁰ The results showed that the Br– group could be used for the cross-linking reaction through a Friedel–Crafts mechanism between Br– groups and aromatic rings without any catalysts. Moreover, the cross-linking is a practical method to enhance the performances of the HEMs.²¹⁻²⁴

In this work, we synthesized a novel series of HEMs combining the cross-linked structure and the aromatic side-chain. The

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cross-linking could endow the membrane outstanding dimensional stability and methanol resistance. Meanwhile, the aromatic side-chain quaternary ammonium group could enlarge the space for the motion of hydrophilic groups, could promote the hydroxide conduction and did not aggravate the degradation of quaternary ammonium groups like the aliphatic side chain. The HEMs were obtained based on a series of poly(ether ether ketone) (PEEK) copolymers synthesized from a novel bisphenol monomer with two methyl groups. By adjusting the ratio of the monomer, we could control the methyl contents, the degree of bromomethylation of the polymer and the IEC values of the membranes. Then cross-linked membranes were prepared by the heating method. The monomers and copolymers were characterized in detail. The properties, such as hydroxide conductivity, methanol permeability, swelling ratio and alkaline stability, were evaluated. And the results showed that this method of cross-linking was effective for further research of HEMs.

Experimental

Materials

3,4-Dimethylaniline and hydroquinone (HQ) were purchased from Aladdin Reagent, Shanghai, China. 4,4'-Difluorobenzophenone (DFB), 1,4-benzoquinone, *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.

Synthesis of (3,4-dimethyl)phenylbenzoquinone (Me-BQ)

3,4-Dimethylaniline (6.05 g, 0.05 mol), water (20 mL), hydrochloric acid (17 mL, 0.2 mol), were added into a 500 mL beaker. Then, a water solution (20 mL) of sodium nitrite (3.45 g, 0.05 mol) was added dropwise. The reaction system was stirred at 0-2 °C for 2 h and a brownish-yellow solution was obtained after filtering. The solution was added dropwise into a mixture of 1,4-benzoquinone (4.32 g, 0.04 mol), sodium bicarbonate (12.6 g, 0.15 mol), and deionized water (100 mL). After stirring at 5–8 °C for 4 h, the yellow product was obtained by filtering and washing with deionized water several times. The resulting solid was dried at 80 °C in the vacuum oven for 24 h.

Synthesis of (3,4-dimethyl)phenylhydroquinone (Me-HQ)

(3,4-Dimethyl)phenylbenzoquinone (5.27 g, 0.025 mol), Zn powder (4.875 g, 0.075 mol), and deionized water (35 mL) were added into a 250 mL three-necked flask. When the mixture was heated to boiling, hydrochloric acid (0.075 mol, 6.4 mL) was added dropwise into the flask. Then the mixture was refluxed for another 4 h. Finally the hot mixture was filtered and the obtained precipitate was recrystallized from toluene.

Copolymerization of poly(ether ether ketone)s containing methyl groups

The polymers were named as PEEK–Me-xx, where "xx" represents the percentage of Me-HQ in the copolymers. The content of methyl groups was adjusted by the ratio of Me-HQ to HQ. Here we illustrate the synthesis of (PEEK–Me-80): Me-HQ (3.424 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. Then *N*-methyl-2-pyrrolidone (NMP) (25 mL) and toluene (15 mL) were added into the flask. The reaction mixture was heated at 140 °C for 2 h under nitrogen atmosphere for dehy-dration. After removal of toluene, the reaction temperature was increased to 170 °C. When the viscosity had increased dramatically, the mixture was poured into 2000 mL deionized water slowly. The copolymer was washed with hot water several times and dried under vacuum at 80 °C for 24 h.

Bromination of the poly(ether ether ketone)s

A typical procedure for preparing a bromomethylated copolymer PEEK–Br-80 was as follows: PEEK–Me-80 (2.0 g, the amount of $-CH_3$ was 8.6 mmol) and 40 mL trichloromethane were added to a three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a condenser. After getting a homogeneous solution, NBS (3.05 g, 17.6 mmol) and BPO (0.1 g) were added to the mixture and the reaction was carried out for 24 h at 60 °C. The mixture was then 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.

Preparation of the hydroxide exchange membranes (PEEK-Q-xx)

Brominated polymers (0.6 g) were dissolved in 10 mL NMP. The solutions were filtered and cast on flat glass plates. The membranes were dried at 40 °C for 24 h to remove the solvent. Then the membranes were immersed in a 33% trimethylamine aqueous solution for 48 h to make the membranes quaternary-aminated. After that the membranes were kept in a 1 mol L^{-1} NaOH aqueous solution for 48 h to obtain the OH⁻ form membrane. Finally, the membranes were washed thoroughly and immersed in deionized water for 48 h to remove residual NaOH.

Preparation of cross-linked hydroxide exchange membranes (xPEEK-Q-xx)

We chose PEEK–Br-100 and PEEK–Br-80 to prepare a crosslinked membrane. The cross-linking reaction was performed by heating the brominated membranes at 150 °C for 2 h in a vacuum oven. Then the cross-linked membranes were treated with trimethylamine aqueous solution, 1 mol L⁻¹ NaOH aqueous solution and deionized water as for the preparation of PEEK–Q-xx membranes.

Characterization

Chemical structure of the membranes

To analyse the molecular structures of the monomers and copolymers, ¹H NMR spectra were obtained on a Bruker 510 spectrometer (500 MHz) using deuterated dimethylsulfoxide (DMSO- d_6) or deuterochloroform (CDCl₃) as the solvent and tetramethylsilane (TMS) as the standard.

Gel fraction of the cross-linked membranes

The weights of the cross-linked membranes were measured before and after immersing in *N*-methyl-2-pyrrolidone (NMP) for a long time and the ratio of the residual mass was calculated to evaluate the degree of cross-linking.

Thermal performance

The thermogravimetric analysis (TGA) curves were obtained by a Pyris 1 TGA (Perkin-Elmer) under a nitrogen atmosphere. Each sample was preheated at 110 °C for 10 min to remove the solvent and water completely, and then cooled and reheated from 80 °C to 700 °C at a heating rate of 10 °C min⁻¹.

Mechanical property

The yield tensile strength, elongation at break and Young's modulus of all the membranes were evaluated using a Shimadzu AG-I 1 KN at a test speed of 2 mm min⁻¹. The size of the membrane sample was 15×4 mm². For each testing, at least three samples were measured and the average values were used.

Ion exchange capacity (IEC)

The ion exchange capacity (IEC) was measured using the classical back titration method. Firstly, we obtained the weights of the dried membranes. Then, the 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 that, the solutions were titrated with a standardized NaOH solution using phenolphthalein as an indicator. The IEC was calculated from the formula as follows:

IEC(mequiv. per g) =

$$\frac{\text{consumed NaOH(mL)} \times \text{molarity NaOH(mol mL}^{-1}) \times 1000}{\text{weight of dry membrane(g)}}$$
(1)

Water uptake and swelling ratio

The membranes were vacuum-dried at 80 °C for several days until weights and lengths were constant. Then all the samples were immersed in deionized water at a given temperature for 24 h. We took out and wiped the membranes quickly with tissue paper and measured their weights and lengths as soon as possible. The water uptake and swelling ratio were calculated by the following equations:

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

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

The methanol permeability coefficient $D_{\rm K}$ (cm² s⁻¹) was determined using a cell that contained two reservoirs which has been described in our previous study.²⁵ The two reservoirs were separated by the measured membrane. A 10 M methanol solution was placed on one side of the cell and water was placed on the other side. Magnetic stirrers were used on each compartment. The concentration of methanol was measured by a Shimadzu GC-8A chromatograph. The methanol permeability was calculated as follows:

$$C_{\mathbf{B}(t)} = \frac{A}{V_{\mathrm{B}}} \frac{D_{\mathrm{K}}}{L} C_{\mathrm{A}}(t-t_0) \tag{4}$$

where A (cm²) and L (cm) are the effective area 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 (cm³) is the volume of the diffusion reservoir. D_K (cm² s⁻¹) is the methanol permeability coefficient.

Hydroxide conductivity

The hydroxide conductivity was measured by a four-electrode 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. To remove the ions attached to the membrane surface, membranes in the hydroxide form were initially immersed in deionized water for 24 hours before measurement. The membranes and the electrodes were set in a Teflon cell and the distance between the reference electrodes was 1 cm. The hydroxide ion conductivity was calculated by the following equation:

$$\sigma = \frac{L}{RS} \tag{5}$$

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

Alkaline stability

The alkaline stability of the HEMs was evaluated by two methods: in the first one, the PEEK–Q-xx membrane samples were kept in NaOH solutions (4 M) in test tubes for 7 days at 60 °C, respectively. To check whether the samples had decomposed into pieces, the test tubes were shaken every 8 hours.

In the second method, we immersed one membrane into a moderate alkaline solution (1 M NaOH) at 60 °C for 30 days and measured the conductive performance of the membrane every six days.

Results and discussion

Structure characterization

As shown in Scheme 1, the bisphenol monomer was synthesized by a three-step synthetic process. The structures of Me-BQ and Me-HQ were identified by ¹H NMR spectra in Fig. 1. In Fig. 1(b), the proton peaks at 8.62 and 8.71 ppm were assigned to the protons of hydroxyl groups, which could not be observed in the spectrum of the quinolone form (Fig. 1(a)). And the peak at 2.25 ppm corresponding to the hydrogen atoms of methyl groups is obvious in Fig. 1. This result proved that we have obtained the Me-HQ monomer successfully.

Scheme 2 shows the process to synthesize the copolymers and prepare hydroxide exchange membranes. We also used the ¹H NMR spectrum to analyse the structures of the polymers. Fig. 2 shows the ¹H NMR spectra of PEEK–Me-100 and PEEK–Br-100. It should be noticed that the peaks of bromomethyl groups, which were located at about 4.60 ppm and 4.55 ppm, appeared in the spectrum of the brominated copolymer, and they could not be found in the pristine polymers. The spectra of other copolymers were similar, which proved that we had synthesized the brominated polymers successfully. The degrees of the bromination (DB) of the copolymers are listed in Table 2.

Gel fraction of the cross-linked membranes

After cross-linking treatment, the membranes could not be dissolved in any common solvent. The gel fraction can be considered as an indirect measurement of the cross-linking density. The gel fractions of the two cross-linked brominated membrane were 47.4% (xPEEK–Br-100) and 42.2% (xPEEK–Br-80). The slight difference could be due to the low content of –Br in PEEK–Br-80.

Thermal stability

Fig. 3 shows the thermal performance of the PEEK–XX-100 polymers by the TGA curves. PEEK–Me-100 exhibited the highest 5% weight loss temperature of 502.8 °C, which meant the main chain decomposition. After bromination, the polymers



Scheme 1 Synthesis of the monomer Me-HQ.



Fig. 1 The ¹H NMR spectra of Me-BQ (a) and Me-HQ (b).







Scheme 2 Syntheses of the copolymers.



Fig. 2 The ¹H NMR spectra of PEEK–Me-100 (a) and PEEK–Br-100 (b).

showed an obvious weight loss at about 160 °C, which was associated with the elimination of the –Br groups on the side chains of the macromolecules. The degradation of quaternary ammonium groups started at about 200 °C.²⁶ The weight loss of the cross-linked membranes xPEEK–Br-100 and xPEEK–Q-100 was lagging behind that of PEEK–Br-100 and PEEK–Q-100, respectively. It could be attributed to the consumption of –Br during the cross-linking process (Scheme 3). Because of the same reason, the cross-linked membranes displayed a slightly lower final thermal decomposition than the pristine ones. Table 1 lists the 5% weight loss temperature of the membranes.



Fig. 3 The TGA curves of PEEK–Me-100, PEEK–Br-100, PEEK–Q-100, xPEEK–Br-100, and xPEEK–Q-100.

Mechanical properties

Table 1 lists the yield tensile strength, elongation at break and Young's modulus of all the copolymers. As shown in the table, the uncross-linked quaternized membranes with higher IEC (PEEK–Q-100 and PEEK–Q-80) were much more brittle than PEEK–Q-60, which could be illustrated by the yield tensile strength and the elongation at break values.

After cross-linking, the mechanical properties of the membranes were enhanced significantly. Both the yield tensile strength and the elongation at break values were improved. This meant that the cross-linked membranes had better resistance to deformation or fracture.

IEC, water uptake and swelling ratio

The IEC value is very important for HEMs, it responds to the number of conductive groups in the polymer, and a higher IEC usually leads to a higher conductivity. Table 2 lists the IEC values of the membranes. The IEC values of the uncross-linked membranes showed a decline from 1.43 to 0.90 mequiv. per g with the decrease of the methyl group content. It illustrated that the IEC values of the membranes could be well controlled by our strategy. The cross-linked membranes xPEEK–Q-100 and

xPEEK–Q-80 showed a lower IEC compared with the PEEK–Q-100 and PEEK–Q-80 respectively. We considered that there are three effects on the IEC in a cross-linking process: first, the consumption of bromomethyl groups led to a decreasing introduction of quaternary ammonium groups, which made the IEC decline. Second, the cross-linked structure hindered the quaternization to a certain extent. Third, the elimination of Br atoms (whose atomic weight is 79.90) reduced the average molecular weight of the structure unit, which led to a higher IEC indirectly. And the first two aspects were the main influence in our membranes.

Water uptake affects the conducting performance of intermediate fuel cells to a great extent, but an exorbitant water uptake induces unacceptable dimensional changes and a decrease in the mechanical strength.²⁷ As is shown in Fig. 4, the water uptake of the uncross-linked membranes increased with the IEC and temperature naturally. After cross-linking, the water uptake showed a sharp decline: at 80 °C, the PEEK–Q-100 had a water uptake of 41.7%, and for the xPEEK–Q-100, the value was only 14.2%. The changing rule of the swelling ratio (shown in Fig. 5) was similar to that of water uptake: the xPEEK–Q-80 showed the lowest swelling ratio of 4.7% (20 °C), which was only about onethird of the value of PEEK–Q-80. This result indicated that the cross-linking improved the dimensional stability of the membranes. That is one of the main reasons to do the crosslinking treatment.

Hydroxide conductivity, methanol permeability, and selectivity

The performance of a fuel cell is extremely dependent on the conductivity of the membrane material.²⁸ As shown in Fig. 6, the membranes exhibited hydroxide conductivities in the range from 0.032 S cm^{-1} to 0.041 S cm^{-1} at 80 °C. For the uncross-linked membranes, the conductivity showed a similar trend to the IEC value and water uptake. The cross-linked membranes had lower conductivities compared with the uncross-linked membranes. However, the downward tendency was not as sharp as that of water uptake or swelling ratio. And the hydroxide conductivities were still usable for the HEMFCs. The xPEEK–Q-100 membrane still had a conductivity of 0.036 S cm⁻¹ at 80 °C. Also,



Scheme 3 The mechanism of the cross-linking reaction of the membranes.

Table 1	Mechanical	and thermal	stability of th	e membranes
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Polymers	Yield tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)	<i>T</i> _{d 5%} (°C)
PEEK-Me-100	56.02	5.01	1.42	502.8
PEEK-Me-80	42.69	6.20	1.82	514.6
PEEK-Me-60	60.29	5.09	1.83	515.6
PEEK-Br-100	48.16	3.08	1.51	183.6
PEEK-Br-80	43.06	5.33	1.27	184.0
PEEK-Br-60	46.43	4.40	1.18	181.0
PEEK-Q-100	27.11	2.27	1.39	257.6
PEEK-Q-80	20.87	2.78	1.06	305.9
PEEK-Q-60	76.07	5.84	2.08	264.5
xPEEK-Br-100	61.82	3.52	2.20	197.1
xPEEK-Br-80	55.76	3.27	2.03	200.3
xPEEK-Q-100	48.95	5.72	1.21	262.9
xPEEK-Q-80	49.53	5.18	1.36	286.9

Table 2 DB^a , IEC, water uptake, swelling ratio, hydroxide conductivity, methanol permeability, selectivity, and alkaline stability^b of PEEK–Q-xx/xPEEK–Q-xx membranes

		W C	Water uptake	(%)	Swellir ratio (9	ng %)	σ (mS	cm ⁻¹)			
Polymers	DB (%)	IEC (mequiv. per g)	20 °C	80 °C	20 °C	80 °C	20 °C	80 °C	$D_{\rm K}$ (×10 ⁻⁷ cm ² s ⁻¹)	Selectivity $(\times 10^4 \text{ S s cm}^{-3})$	Time of breaking into pieces (days)
PEEK-Q-100	45.1	1.43	32.1	41.7	15.3	21.2	17	41	6.1	2.7	>7 days
PEEK-Q-80	50.2	1.23	28.9	33.2	13.8	18.8	15	37	5.2	2.9	>7 days
PEEK-Q-60	40.7	0.90	24.6	26.6	11.9	14.7	12	33	4.9	2.4	>7 days
xPEEK-Q-100		1.18	13.5	14.2	6.2	6.6	14	36	2.9	4.8	>7 days
xPEEK-Q-80	_	1.01	8.2	8.6	4.7	5.0	13	32	2.1	6.2	>7 days

^{*a*} The degree of bromination, defined as the percentage of the methyl which converted to bromomethyl during the bromination reaction. It is calculated by the spectra of the ¹H NMR. Considering the consumption of -Br in cross-linking, we did not show the DB of cross-linked membranes. ^{*b*} The alkaline stability was measured by the time of breaking into pieces in 4 M NaOH at 60 °C.



Fig. 4 The water uptakes of the membranes.

the PEEK–Q-80 and xPEEK–Q-100 membranes showed similar IEC values and conductivities. This phenomenon could also be found in the comparison between PEEK–Q-60 and xPEEK–Q-80. We could conclude that the decline was mainly caused by the decrease of IEC after cross-linking. The influence of the limitation from cross-linking bonds was not obvious due to the side-chain-type structure. For fuel cell operation using hydroxide exchange membrane materials, there is a requirement for the hydroxide conductivity to be above 10 mS cm⁻¹.³⁰ All the membranes in this work fulfilled the requirement.



Fig. 5 The swelling ratios of the membranes.

Methanol permeability is another key issue in the application of DMFCs.²⁹ Diffusion or leakage of the fuel from the anode across the membrane to the cathode leads to not only a fuel loss but also some other undesirable consequences, such as complicated water and thermal management, *etc.*³¹ Table 2 lists the methanol permeation coefficients. Each membrane exhibited a coefficient lower than 7×10^{-7} cm² s⁻¹, and the cross-linked membranes showed a significant decrease in methanol permeability. As previously reported, water transportation and methanol permeation take place through the same pathway in the



Fig. 6 The conductivities of the membranes.

membrane.³² So it is easy to understand that the cross-linking results in a more compact membrane structure, which restricts the hydrophilic domains and suppresses the swelling of the membranes, and further effectively resists methanol penetration. The methanol permeation coefficient of the xPEEK–Q-100 membrane was only about one-eighth of that of Nafion $(1.67 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1})$, which meant a good methanol resistance.

Table 3 lists some recent studies of HEMs to compare the hydroxide conductivities and methanol diffusion coefficients of our membranes with those of other HEM materials which were designed for DMFCs. Among these materials, our membranes, especially the xPEEK–Q-100 membrane, exhibited good overall performances.

To evaluate the further performance of each membrane in the fuel cell, we calculated its selectivity, which was defined as the ratio of hydroxide conductivity to the methanol permeability coefficient. The selectivity could reflect the comprehensive properties of a membrane. And a higher selectivity always means better performance in DMFCs.³⁹ As shown in Fig. 7, the two cross-linked membranes showed selectivities of 4.8×10^4 S s cm⁻³ and 6.2×10^4 S s cm⁻³, respectively, which were much higher than those of the uncross-linked membranes (2.4×10^4 S s cm⁻³ to 2.9×10^4 S s cm⁻³). Compared to hydroxide conductivity, the methanol permeability declined more significantly. As a result,

Table 3 Hydroxide conductivity and methanol diffusion coefficient ofHEMs reported

HEMs	$\sigma \ ({\rm mS \ cm^{-1}})$	$D_{\rm K}~({\rm cm}^2~{\rm s}^{-1})$	References
PEEK-Q-100	17 (20 °C)	$\begin{array}{c} 6.1 \times 10^{-7} \ (20 \ ^{\circ}\text{C}) \\ 2.9 \times 10^{-7} \ (20 \ ^{\circ}\text{C}) \\ 1.12 \times 10^{-7} \ (25 \ ^{\circ}\text{C}) \\ 2.6 \times 10^{-7} \ (RT) \\ 6.68 \times 10^{-7} \ (25 \ ^{\circ}\text{C}) \\ 1.92 \times 10^{-9} \ (20 \ ^{\circ}\text{C}) \\ 4.45 \times 10^{-7} \ (30 \ ^{\circ}\text{C}) \\ 7.21 \times 10^{-7} \ (22 \ ^{\circ}\text{C}) \\ 7.5 \times 10^{-8} \ (25 \ ^{\circ}\text{C}) \end{array}$	This work
xPEEK-Q-100	14 (20 °C)		This work
CPPO-40	15.3 (25 °C)		Ref. 33
PBI (alkali doped)	18.4 (RT)		Ref. 34
QPVA	10.6 (30 °C)		Ref. 35
SPES-2OH	18.8 (20 °C)		Ref. 20
QSEBS	5 (30 °C)		Ref. 36
QPPEK-OH	1.2 (22 °C)		Ref. 37
PF2	4.8 (60 °C)		Ref. 38



Fig. 7 The selectivity of the membranes.



Fig. 8 Time courses of hydroxide conductivity of the membrane in 1 M NaOH at 60 °C.

all the selectivity of the cross-linked membranes improved remarkably, which translates to improved overall performance.

Alkaline stability

We evaluated the alkaline stability in two aspects: first, we measured the breaking time of the samples in a strong alkali solution to test the stability of the polymer backbones. As listed in Table 2, all the membranes remained intact during the testing time (7 days). The results illustrate that the copolymers had good tolerance ability in a strong alkaline environment. For the second test, our purpose was to investigate the conductivity performance loss in fuel cell applications. We set a condition of 1 M NaOH at 60 °C to evaluate the stability of quaternary ammonium groups in operating fuel cells. The curve in Fig. 8 is related to the decline of conductivity of the PEEK-Q-100 membrane. We can see that in the testing time, the decrease in hydroxide conductivity was not very serious, and the descending trend got more and more smooth. The conductivity remained at a level of 0.025 S cm⁻¹ after the 12th day. It proved that the aromatic-side-chain type could keep the quaternary ammonium groups with a reasonable stability.

Conclusions

A novel bisphenyl monomer and a series of hydroxide conductive cross-linked poly(ether ether ketone)s containing pendant quaternary ammonium groups with different IEC values were designed and synthesized. By cross-linking, we obtained membranes with outstanding dimensional stability and methanol resistance. And the aromatic side-chain structure gave the membrane a tough tolerance in the alkali environment which simulated a condition of operating HEMFCs. The xPEEK–Q-100 (with an IEC of 1.18 mequiv. per g) showed a conductivity of 0.036 S cm⁻¹ and a swelling ratio of 6.6% at 80 °C, in addition to its excellent mechanical, alkaline stabilities and the methanol resistance, the membrane would exhibit good performance in alkaline fuel cell applications.

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