Tri-quaternized poly (ether sulfone) anion exchange membranes with improved hydroxide conductivity

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Abstract

A novel anion exchange membrane with tri-quaternized side chain has been developed in the present work. Di-cationic quaternary ammonium salt, 1-(4'-{1"-azonia-4"-azabicyclo [2.2.2] octyl} butyl) azonia-4-azabicyclo [2.2.2] octane (AABAA), is synthesized and used as tri-quaternization reagent. The tri-quaternized side chains enhance ionic interactions, which induce good micro-phase separation and excellent swelling resistance. Better aggregation of ionic clusters is observed in transmission electron microscopy (TEM) image in the tri-quaternized poly (ether sulfone) (tri-QPESOH) membrane compared to that in the mono-quaternized membrane (mono-QPESOH). Tri-QPESOH membranes achieve a well-balanced performance between high hydroxide conductivity and dimensional stability. Especially, the tri-QPESOH membrane with IEC 2.31 mmol g⁻¹ exhibits high hydroxide conductivity of 45.9 mS cm⁻¹ at 25 °C and 130.9 mS cm⁻¹ at 80 °C, and low swelling ratio of 21.5% even at 80 °C. Tri-QPESOH membranes also show improved thermal, mechanical and chemical stabilities. These observations suggest that the tri-cationic side chains provide a promising solution to the electrochemical-mechanical balance of anion exchange membranes.

Keywords: Anion exchange membrane; fuel cells; poly (ether sulfone); micro-phase separation; hydroxide conductivity

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1. Introduction

Intense efforts have been focused on the development of anion exchange membranes (AEMs) used as electrolytes in anion exchange membrane fuel cells (AEMFCs) [1]. Compared to proton exchange membrane fuel cells (PEMFCs), AEMFCs possess outstanding advantages, such as fast kinetics of electrooxidation and non-precious metals as electrocatalysts [2, 3]. However, low mobility and insufficient dissociation of OH^- lead to much lower ionic conductivity in AEMs than that in proton exchange membranes (PEMs). Increasing content of cationic groups usually enhances ionic conductivity, and also may cause excessive swelling and poor mechanical stability [4, 5]. Therefore, the tradeoff between ionic conductivity and dimensional stability is significant [6].

Various strategies have been developed to resist swelling of AEMs, such as covalent and ionic crosslinking [7-9], semi-interpenetrating network [10] and polymer blending [11]. However, hydroxide conductivity of these AEMs is still confined due to the tortuous ionic channels. Hydrophilic-hydrophobic micro-phase separated structure could effectively improve connectivity of ionic channels [12]. As a result, AEMs with good micro-phase separation are promising to achieve high ionic conductivity. Although micro-phase separation could be designed and controlled by block and graft copolymers, preparation procedures usually involve complicated polymerization [13-16]. The most accessible strategy for micro-phase separation is the functionalization of random polymers by attaching with pendent side chains. Since it is difficult for non-fluorinated AEMs to form micro-phase separation due to the less hydrophobic backbones and the weak aggregation ability of the direct linkage of cations on backbones, pendent side chains could enhance flexibility of the functional groups and induce aggregation of both hydrophilic and hydrophobic domains. Different types of pendent side chains reported in the literature are

summarized in Table 1. As seen from No. 1 through 5 in Table 1, despite the fact that the cation is still connected to the polymer backbones, a pendent side chain (either hydrophilic or hydrophobic) could assist in achieving high hydroxide conductivity and low water swelling [5, 17-20]. However, chemical stability of these AEMs is poor, as the cations directly connected to the backbones may induce degradation of the polymer backbones in an alkaline environment. Recent studies have shown that separation of cation from polymer backbones by alkyl or aromatic spacers (seen No. 6 through 9 in Table 1) could improve not only micro-phase separation, but also chemical stability by reducing the influence of cations on the polymer backbones [20-23]. Furthermore, multiple cations have been introduced on side chains to enhance ionic interactions, which promote micro-phase separation and connectivity of ionic channels in AEMs (see No. 10 through 16 in Table 1) [24-28]. From Table 1, it is suggested that different designs of side chains have great influence on the properties of AEMs. Thus, synthetic strategy of functional pendent side chains is to provide a key to achieving high-performance AEMs.

Table 1 AEMs with random polymer backbones and different pendent side chains.

No.	Schematic structure	Polymer matrix	Quaternary reagent	Number of cations ^a	IEC, mmol g ⁻¹	HC ^b , mS cm ⁻¹	Swelling ratio, %	Temperature, °C	Ref.
1 ^c		PSf	TMA	1	1.0	35	8	20	[5]
2 ^d		PSf	TMA	1	1.36	25	-	22	[17]
3		PPO	DMHDA	1	1.92	35	5.6	20	[18]
4		PPO	DMHDA	1	1.65	21	2	20	[19]
5		PPO	DMOA	1	1.4	4.5	-	80	[20]
6		PPO	TMA	1	1.5	43	-	20	[20]
7		PPO	TMA	1	1.5	26	-	20	[21]
8		PPO	TMA	1	1.8	62	-	20	[22]

9		PSf	Cp^*_2Co^+	1	1.20	22	-	R. T.	[23]
10		PSf	TMA	2	1.74	38	4	20	[24]
11		PSf	DQA	2	2.01	31	-	30	[25]
12		PPSU	DQA	2	2.12	33	-	30	[25]
13		PPO	DQA	2	2.23	27.5	-	30	[25]
14		PEEK	DABCO	2	1.22	28.4	25	25	[26]
15		PSf	DHTC	2	1.93	19.5	15	30	[27]
16		PPO	TDAP	3	1.50	39	8.8	30	[28]

Polymer backbone

Cation

Side chain

^aNumber of cations on each side chain; ^bHydroxide conductivity; ^cHydrophobic side chain including 8 non-hydrogen atoms;

^dHydrophilic poly (ethylene glycol) (PEG) side chain; Abbreviations: PSf: polysulfone; TMA: trimethylamine; PPO: poly

(phenylene oxide); PEEK: poly(ether ether ketone), PPSU: polyphenylsulfone; DMHDA: N,N-dimethyl-1-hexadecylamine;

DMOA: N,N-dimethyloctylamine; Cp^*_2Co^+ : permethyl cobaltocenium; R.T.: room temperature; SQA:

1-amino-2-hydroxy-3-trimethylammonium propane chloride; DQA: N, N-di(2-hydroxy-3-trimethylammonium propane chloride)

amine; TDAP: 2,4,6-tri(dimethylaminomethyl)-phenol; DHTC: 1-dimethylamino-2-hydroxy-3-tri-methylammoniumpropane

chloride.

1, 4-diazabicyclo [2.2.2] octane (DABCO) is a bi-functional cyclic diamine, which has good chemical stability against Hofmann degradation due to the rigid cage structure [4]. In our previous work, DABCO was employed as both quaternization and crosslinking reagent to restrict swelling of the poly (ether ether ketone) (PEEK) -based AEMs [29]. Di-quaternized side chain based on DABCO was further developed by quaternizing the unreacted tertiary amine in DABCO mono-quaternized PEEK with iodomethane. Although improved hydroxide conductivity and dimensional stability were achieved due to the strong ionic interactions among the di-cationic side

chains, the two-step quaternization on polymer backbone leads to the decrease of di-quaternization degree (only around 50%) [26], which is also a general concern for the fabrication of AEMs with multi-cationic side chains [25].

In the present work, a novel synthetic route for DABCO-based tri-quaternized side chain has been developed. Di-cationic quaternary ammonium salt, 1-(4'-{1"-azonia-4"-azabicyclo [2.2.2] octyl} butyl) azonia-4-azabicyclo [2.2.2] octane (AABAA), is synthesized and reacts with chloromethylated poly (ether sulfone) (CMPES) to form the third cation on side chain (as shown in Fig. 1). By this way, three cations could be introduced into each side chain, strengthen ionic interactions and enhance micro-phase separation. The obtained tri-quaternized poly (ether sulfone) (tri-QPESOH) AEMs exhibit higher hydroxide conductivity and lower swelling ratio (45.9 mS cm⁻¹ at 25 °C and 21.5% at 80 °C, respectively, for AEM with IEC 2.31 mmol g⁻¹) compared to the DABCO mono- and di-quaternized membranes in our previous works [26]. In view of hydroxide conductivity, the tri-QPESOH membrane is among the best side-chain-type AEMs reported in the literature (as listed in Table 1).

2. Experimental

2.1 Materials

Poly (ether sulfone) (PES, Gafone 3000P, M_w= 62,000–64,000 g mol⁻¹) from Solvay Advanced Polymers was used as the polymer backbone, chloromethyl octyl ether (CMOE) was synthesized according to our previous work [30]. 1, 4-diiodobutane (99% purity) was purchased from Alfa Aesar and used without further purification. 1, 4-diazabicyclo [2.2.2] octane (DABCO, 96% purity), dimethyl sulphoxide (DMSO), dimethylacetamide (DMAc), methanol, acetone,

1-methyl-2-pyrrolidone (NMP), ethyl acetate, ethanol, concentrated sulfuric acid (95% H_2SO_4) and potassium hydroxide (KOH) were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received. These commercial chemicals used in the experiments are of analytical grade. Deionized water was previously boiled to remove CO_2 and used throughout the experiments.

2.2 Synthesis of 1-(4'-{1"-azonia-4"-azabicyclo [2.2.2] octyl} butyl) azonia-4-azabicyclo [2.2.2] octane (AABAA) salt

In the literature, Engel et al. have demonstrated the feasibility of preparing AABAA salt through DABCO and 1, 4-dichlorobutane in acetonitrile [31]. In the present work, AABAA salt was synthesized by using 1, 4-diiodobutane to improve reactivity and ethanol to replace the toxic acetonitrile (as shown in Fig. 1(a)). Specifically, DABCO (10 g) was dissolved in ethanol (22 mL) and 1, 4-diiodobutane (1.2 mL) dissolved in ethanol (15 mL) was added with stirring. Then the mixture was covered with tin foil to avoid exposure to light and stirred for 21 h at room temperature (R. T.). After this time the resultant white precipitate (AABAA salt) was collected by centrifugation, washed with ethanol and ethyl acetate, dried in a vacuum oven at 60 °C for 12 h (83% yield).

2.3 Preparation of DABCO-based mono- and tri- quaternized poly (ether sulfone) membranes

CMOE (4 mL) was added to a round-bottom flask containing a PES solution (1 g PES in 10 mL of 95% concentrated sulfuric acid). The mixture was in an ice water bath and stirred for 0.5 h to 8 h, depending on the desired degree of substitution. Upon completion, the solution was precipitated with water to remove excess reagents. The precipitate was then washed with excess ethanol and collected as a white powder. The powder was dried at room temperature for 48 hours to yield chloromethylated poly (ether sulfone) (CMPES). The degree of chloromethylation was determined by ^1H NMR.

DABCO-based mono-quaternized poly (ether sulfone) materials (mono-QPESCl) were prepared

by mixing a certain amount of DABCO with 0.4 g CMPES in 6 mL DMAc (molar ratio of DABCO to $-\text{CH}_2\text{Cl}$ is about 2.5), stirring at room temperature for 12 h and precipitating with acetone.

Similarly, DABCO-based tri-quaternized poly (ether sulfone) materials (tri-QPESCl) were prepared by mixing CMPES solution (0.2 g CMPES in 2 mL DMSO) with AABAA/DMSO solution (0.05 g mL^{-1} , molar ratio of AABAA to $-\text{CH}_2\text{Cl}$ is also about 2.5). Then the mixture was stirred at room temperature for 12 h and precipitated with methanol at 50°C .

DABCO-based mono- and tri- quaternized poly (ether sulfone) anion exchange membranes (mono-QPESOH, tri-QPESOH) were obtained by dissolving mono-QPESCl and tri-QPESCl materials in NMP to form 5.0 wt% and 2.3 wt% solutions, respectively, casting onto the clean glass plate, drying in an oven at 60°C for 48 h. The obtained membranes were immersed in 1 mol L^{-1} KOH solution for 48 h and washed with deionized water until neutral (as shown in Fig. 1(b)). These membranes are 30-70 μm in thickness.

Fig. 1. Synthetic routes of (a) AABAA salt and (b) mono-QPESOH and tri-QPESOH.

2.4 Membrane characterization

^1H NMR analysis was conducted on a Varian Unity Inova 400 spectrometer at a resonance frequency of 399.73 MHz, using tetramethylsilane as an internal standard and dimethyl sulfoxide- d_6 as solvent.

Thermogravimetric analysis (TGA) was conducted on a Mettler Toledo TGA/SDTA851° TGA analyzer with about 5-10 mg dry samples. Samples were heated from room temperature to 800 °C at a heating rate of 10 °C min⁻¹. A derivative thermogravimetry (DTG) curve was calculated by the first order differential of the TGA curve over temperature.

Transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS) were used to investigate the morphology of membranes. Specifically, the membranes were stained with PdCl₄²⁻ by immersing in a PdCl₂/HCl solution (5 g L⁻¹) for 4 days, then washed with deionized water for several times and dried at room temperature overnight [32]. TEM images were taken on a JEOL JEM-2000EX microscope using an accelerating voltage of 120 kV. Small angle X-ray scattering curves were collected on PANalytical X'Pert Powder X-ray diffraction system with scattering angle 0-5° at a rate of 1° min⁻¹ under vacuum at room temperature. The scattering vector was calculated as following:

$$q = \frac{4\pi \sin \theta}{\lambda} \quad (1)$$

where 2θ is scattering angle and $\lambda = 0.154$ nm is scattering wavelength.

The Bragg spacing was calculated according to:

$$d = \frac{2\pi}{q} \quad (2)$$

Mechanical properties of the fully hydrated membranes were measured using a SANS CMT8102 stretching tester (Xinsansi Co., China) at a stretch rate of 5 mm min⁻¹.

The membranes were immersed in liquid water at different temperature for 12 h, then kept in a vacuum oven at 60 °C for 12 h. The weight and length of the hydrated and dry membranes were recorded. The water uptake and swelling ratio were calculated using equations (3) and (4):

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (3)$$

$$\text{Swelling ratio} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad (4)$$

where W_{dry} and W_{wet} are the weight of the dry and hydrated membranes, L_{dry} and L_{wet} are the average length of the dry and hydrated membranes, respectively. $L_{\text{dry}} = (L_{\text{dry1}}L_{\text{dry2}})^{1/2}$, $L_{\text{wet}} = (L_{\text{wet1}}L_{\text{wet2}})^{1/2}$ [33], L_{dry1} , L_{dry2} and L_{wet1} , L_{wet2} are the length and the width of the dry and hydrated membranes.

The in-plane hydroxide conductivity of the membranes was characterized, using a typical four-electrode AC impedance analyzer (Ivium Technologies A08001). In details, the membranes were sandwiched in a simple home-made four-point cell made from four platinum wires and teflon plates. The cells were compressed by screwing the nuts and placed in liquid water at different temperature for measurement. The testing procedure was conducted in galvanostatic mode with a current amplitude of 0.1 mA over a frequencies range of 1-10⁵ Hz. The ohmic resistance of membranes was then obtained from a Nyquist plot. The hydroxide conductivity was calculated as:

$$\sigma = \frac{L}{AR} \quad (5)$$

where L is the length between the two potential electrodes, A is the cross-sectional area of the membranes, R is the membrane resistance.

The ion exchange capacity (IEC) of the membranes was determined using potentiometric titration [34]. Specifically, the dry membranes were immersed in 50 mL 0.1 mol L⁻¹ NaNO₃ for 48 h to

completely convert Cl^- and I^- to NO_3^- . The content of Cl^- and I^- was measured using 0.01 mol L^{-1} AgNO_3 solution with silver electrode as indicator electrode and double fluid saturated calomel electrode as reference electrode. The IEC was calculated by:

$$IEC_m = \frac{C_{\text{AgNO}_3} \cdot V_{\text{AgNO}_3}}{m_{\text{dry}}} \quad (6)$$

where C_{AgNO_3} is the concentration of AgNO_3 solution, V_{AgNO_3} is the consumed volume of AgNO_3 solution, m_{dry} is the weight of dry membrane (Cl^- form).

Chemical stability was investigated by immersion of the membranes into 4 M NaOH at 25°C for different times, and then washing with deionized water to remove the residual NaOH. Changes of IEC values and hydroxide conductivity were recorded until the values were almost stable.

3. Results and discussion

3.1 Synthesis of AABAA, mono-QPESCl and tri-QPESCl

The present work reports a novel synthetic route for AEMs with tri-quaternized side chain (as shown in Fig. 1), in which AABAA is synthesized as tri-cationic quaternization reagent and then quaternized with CMPES. The ^1H NMR spectrum of AABAA (Fig. 2(a)) reveals all characteristic signals of DABCO and 1, 4-diiodobutane. The signal at 1.85 ppm (H_1 of 1, 4-diiodobutane) slightly shifts upfield to 1.71 ppm (H_1' of $-\text{CH}_2\text{CH}_2-$), while the signal at 2.60 ppm (H_3 and H_4 of DABCO) shifts downfield to 3.04 ppm (H_4' of $-\text{CH}_2\text{N}$) and ~ 3.29 ppm (H_3' of $-\text{CH}_2\text{N}^+$) according to the areal integral and multiplicity of the signals. The chemical shift changes of these characteristic signals are related to the decrease of electron-withdrawing property in the order $\text{I} > \text{N}^+ > \text{N}$, and the electron density of the corresponding adjacent protons decreases in the reverse order $-\text{CH}_2\text{I} < -\text{CH}_2\text{N}^+ < -\text{CH}_2\text{N}$.

^1H NMR spectra of CMPES, mono-QPESCl and tri-QPESCl are presented in Fig. 2(b). The signal at 4.85 ppm is ascribed to the protons in chloromethy (H_3). Since chloromethylation is an electrophilic substitution, it preferentially takes place in H_2 position, which is adjacent to the

electron-donating ether group and has higher electron density. After mono-quaternization with DABCO, the signal at 4.85 ppm (H_3 of $-\text{CH}_2\text{Cl}$) shifts upfield to 4.66 ppm (H_3' of $-\text{CH}_2\text{N}^+$) due to the increased electron density, and the appearance of the signals at 3.05 ppm (H_5) and 3.39 ppm (H_4) identifies the protons in the quaternized DABCO. However, the signal at 4.85 ppm (H_3 of $-\text{CH}_2\text{Cl}$) shifts downfield to 4.97 ppm (H_3'' of $-\text{CH}_2\text{N}^+$) after tri-quaternization with AABAA, as the electron-withdrawing of the di-quaternized DABCO on side chains is stronger than that of the chlorine atom. The characteristic signals of the reacted AABAA appear at 3.98 ppm (H_4'), 3.84 ppm (H_5'), 3.57 ppm (H_6), 1.71 ppm (H_7, H_8), 3.3 ppm (H_9, H_{10}) and 3.05 ppm (H_{11}). These signals are indicative of AABAA onto the polymer backbones.

Fig. 2. ^1H NMR spectra of (a) 1, 4-diiodobutane, DABCO and AABAA and (b) CMPES, mono-QPESCl and tri-QPESCl.

3.2 Morphology of the mono-QPESOH and tri-QPESOH membranes

AEMs are somewhat similar to surfactants, in which ionic functional groups and non-ionic polymer backbones tend to aggregate respectively, forming hydrophilic-hydrophobic micro-phase separation [35]. Hydrophilic ionic clusters provide interconnected ionic channels for hydroxide

transport; meanwhile hydrophobic polymer backbones maintain mechanical properties of AEMs. It is difficult for the mono-QPESOH membranes to form good micro-phase separated structure due to the less hydrophobic PES backbone and the weak aggregation ability of the directly connected mono-quaternized DABCO on the backbone. This is a shared concern for non-fluorinated AEMs. To investigate micro-phase separation of the membranes in this study, TEM and SAXS were taken for the mono-QPESOH (IEC=0.88 mmol g⁻¹) and tri-QPESOH (IEC=0.99 mmol g⁻¹). As shown in Fig. 3(a), ionic clusters (dark areas stained by PdCl₄²⁻) in the mono-QPESOH membrane are very small, indicating narrow and inefficient ionic channels. Comparatively, the tri-QPESOH membrane exhibits much better micro-phase separated structure. As shown in Fig. 3(b), many larger ionic clusters are found to scatter among the smaller ones in the TEM image of the tri-QPESOH membrane, although it has the similar IECs to the mono-QPESOH membrane. To gain a quantification of the ionic clusters, SAXS was also carried out. As shown in Fig. 4, no notable scattering peak is observed for the mono-QPESOH membrane, whereas a broad scattering peak for the tri-QPESOH membrane emerges in the range of 0.47 to 0.75 nm⁻¹, corresponding to Bragg spacing of approximately 8.4-13.4 nm, which indicates the size of ionic clusters [36] and is in good agreement with the results shown in TEM image.

Fig. 3. TEM images of the mono-QPESOH and tri-QPESOH membranes (a. mono-QPESOH, IEC=0.88 mmol g⁻¹; b. tri-QPESOH, IEC=0.99 mmol g⁻¹).

Fig. 4. SAXS patterns of the mono-QPESOH and tri-QPESOH membranes.

Considering the similar IECs, different morphologies between the mono-QPESOH and tri-QPESOH membranes are mainly caused by different ionic density on side chains. Tri-QPESOH membranes possess multi-cationic and flexible side chains, which increase local concentration of cationic groups, enhance interaction among ionic domains and promote aggregation of ionic clusters. Moreover, at a certain IEC, longer intervals of the hydrophobic polymer backbones between the two pendent side chains in tri-QPESOH membranes also enhance the formation of continuous and cohesive hydrophobic domains. With well-defined hydrophilic-hydrophobic micro-phase separation in tri-QPESOH membranes, interconnected ionic conductive channels could be readily built even at low IEC, and contribute to efficient hydroxide conduction.

3.3 Water uptake and swelling ratio

Water sorption behavior of the mono-QPESOH and tri-QPESOH membranes as a function of IEC is presented in Fig. 5. The tri-QPESOH membranes exhibit excellent swelling resistance. Even at IEC as high as 2.31 mmol g⁻¹, water uptake (62.0%) and swelling ratio (21.5%) of the

tri-QPESOH membrane at 80 °C are similar to that of the mono-QPESOH membrane with IEC 0.88 mmol g⁻¹ at 60 °C. In contrast, mono-QPESOH membranes with IEC greater than 0.76 mmol g⁻¹ suffer from poor mechanical stability in 80 °C water because of excessive swelling. The strong electrostatic interactions, not only among cations, but also between the cation and unreacted tertiary amine of AABAA, are believed to be responsible for the low water sorption. They help to aggregate ionic domains and resist water swelling.

Fig. 5. (a) Water uptake and (b) swelling ratio of the mono-QPESOH and tri-QPESOH membranes as a function of IEC.

3.4 Hydroxide conductivity

Fig. 6 shows hydroxide conductivity of the mono-QPESOH and tri-QPESOH membranes as a function of water sorption. The tri-QPESOH membranes exhibit a well-balanced performance between high conductivity and dimensional stability. That is, at a given water uptake or swelling ratio, the tri-QPESOH membranes achieve much higher hydroxide conductivity than the mono-QPESOH ones. Moreover, we also compare the properties of tri-quaternized membranes with that of the di-quaternized membranes developed in our previous work [26]. Conductivity of the di- and tri-quaternized AEMs is about 1.8 and 2.6 fold, respectively, higher than that of the

corresponding mono- quaternized membrane at swelling ratio of around 20%. This indicates that the tri-QPESOH membranes make more effective utilization of water. The well-ordered micro-phase separated structure of the tri-QPESOH membranes effectively restrains water swelling at high IEC. Consequently, high concentration of OH^- has been achieved in the tri-QPESOH membranes, which improves connectivity of ionic channels even at low water uptake and then enhances hydroxide conductivity.

Fig. 6. Hydroxide conductivity of the mono-QPESOH and tri-QPESOH membranes as a function of water sorption at 25 °C (SR: swelling ratio, WU: water uptake).

As shown in Fig. 7, the tri-QPESOH membranes with higher IECs reach very high conductivity. In particular, the tri-QPESOH membrane with IEC 2.31 mmol g⁻¹ exhibits hydroxide conductivity of 45.9 mS cm⁻¹ at 25 °C and 130.9 mS cm⁻¹ at 80 °C, which is among the best side-chain-type AEMs reported in the literature (as already listed in Table 1) and better than the commercialized AEMs, such as Fumasep®FAP-450 (24 mS cm⁻¹, measured under the same condition), Fumapem® FAA (17 mS cm⁻¹), A3 Ver2 (2.6 mS cm⁻¹) and AS-4 (13 mS cm⁻¹) [2]. However, the similar conductivity for the two membranes is observed at IEC ranging from 0.78 to 1.26 mmol g⁻¹, since water uptake and swelling ratio of the mono-QPESOH membranes are higher than that of

tri-QPESOH ones (water uptake: 38-77% vs. 11-23%; swelling ratio: 12-33% vs. 3-7%), which facilitates hydroxide transport. Thus, the advantage of tri-QPESOH membranes is that the membranes could keep low swelling ratio at high IEC, and then reach high hydroxide conductivity. The significant improvement suggests that the strategy of enhancing the number of cationic groups on the side chains is promising to achieve excellent balance between hydroxide conductivity and dimensional stability.

Fig. 7. Hydroxide conductivity of the mono-QPESOH and tri-QPESOH membranes as a function of IEC.

3.5 Thermal, mechanical and chemical stabilities

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) curves of PES, CMPES, mono-QPESOH and tri-QPESOH are displayed in Fig. 8, and thermal decomposition temperatures are listed in Table 2. There is only one weight loss step at around 540 °C for PES due to the degradation of PES backbone [37]. For CMPES, mono-QPESOH and tri-QPESOH samples, roughly three weight loss steps are identified. The first weight loss of CMPES at around 260 °C is suggested to be the release of chlorine compounds (HCl and Cl₂) caused by crosslinking of methyl

chloride and aromatic ring [38]. The onset decomposition temperature (T_{onset1}) of the mono-QPESOH sample (141 °C) caused by the degradation of the quaternized DABCO, though consistent with the values previously reported for DABCO-based AEMs [29, 39], is much lower than that of the tri-QPESOH sample (240 °C), which is owing to the degradation of the quaternized AABAA. It suggests that thermal stability could be greatly improved by the multi-cationic side chain. The second weight loss at around 370 °C (T_{peak2}) is attributed to the further degradation of the residual groups formed in the previous degradations (such as $-\text{CH}_2\text{OH}$ or $-\text{CH}_3$) [40]. The third weight loss above 400 °C (T_{peak3}) is caused by the degradation of the PES backbone, exhibits slightly higher value in the tri-QPESOH sample compared to the mono-QPESOH one.

Fig. 8. (a) TGA and (b) DTG curves of PES, CMPES, mono-QPESOH and tri-QPESOH.

Table 2 Thermal decomposition temperatures of PES, CMPES, mono-QPESOH and tri-QPESOH.

Samples	T_{onset1} (°C)	T_{peak1} (°C)	T_{peak2} (°C)	T_{peak3} (°C)
PES	540	567	-	-
CMPES	260	285	368	434
Tri-QPESOH IEC=1.63	240	311	372	526
Mono-QPESOH IEC=1.26	141	164	368	496

Mechanical properties of the fully hydrated mono-QPESOH and tri-QPESOH membranes are shown in Fig. 9. At similar IECs, elongations at break of the mono-QPESOH and tri-QPESOH membranes are comparable, while the tensile strengths of the tri-QPESOH membranes are about 3 times as high as that of the mono-QPESOH membranes. The tri-QPESOH membrane with IEC 2.31 mmol g⁻¹ exhibits superior hydroxide conductivity and still maintains high mechanical strength (10.3 MPa), which is close to that of Nafion 212 membrane (11.7 MPa) tested in our previous work [41]. This is the contribution of the multi-cationic side chains, which induce aggregation of ionic clusters in the tri-QPESOH membranes, resulting in excellent swelling resistance and mechanical strength even at high IECs.

Fig. 9. Stress–strain curves of the fully hydrated mono-QPESOH and tri-QPESOH membranes.

It is necessary to evaluate the tolerance of AEMs to strong alkaline solutions because AEMs are frequently unstable in an alkaline environment [42]. The chemical stability of the mono-QPESOH (IEC=0.88 mmol g⁻¹) and tri-QPESOH membranes (IEC=1.63 mmol g⁻¹) was assessed by

immersing the membranes in 4 M NaOH at 25 °C for different times and then washing with deionized water. As shown in Fig. 10, although IEC of the mono-QPESOH membrane could be retained 93% of the initial value after alkali treatment for 24 h, hydroxide conductivity could be hardly measured owing to the brittleness of the membrane. It reveals that the mono-quaternized DABCO attached closely to the backbones induces the degradation of PES backbones [25, 43]. Different from the mono-QPESOH membrane, the tri-QPESOH membrane could maintain strength and flexibility after alkaline immersion. IEC and hydroxide conductivity show a fast decline over the first 96 h and then keep almost stable. More than 88% and 70% of their initial IEC and hydroxide conductivity could be reserved after 144 h. It indicates that the tri-QPESOH membranes exhibit much better chemical stability than the mono-QPESOH membrane. It is related to the better aggregated hydrophobic domains and lower swelling ratio, which prevent the attack of OH⁻ to some extent.

Fig.10. Alkaline stability of the mono-QPESOH and tri-QPESOH membranes after 4 M NaOH immersion at 25 °C.

4. Conclusions

A novel synthetic route for AEMs (tri-QPESOH) with multi-cationic side chains is developed in

the present work, using AABAA as tri-quaternization reagent. Strong ionic interactions among tri-cationic side chains promote aggregation of both ionic clusters and hydrophobic domains, as confirmed by well-defined hydrophilic-hydrophobic micro-phase separation shown in the TEM image. Therefore, well balance between hydroxide conductivity and water swelling could be achieved in tri-QPESOH membranes. Hydroxide conductivity of the tri-QPESOH (IEC 2.31 mmol g⁻¹) reaches 45.9 mS cm⁻¹ at 25 °C and 130.9 mS cm⁻¹ at 80 °C, which is among the best side-chain-type AEMs reported in the literature. Meanwhile, swelling ratio is restricted well at around 21.5% at 80 °C. Tri-QPESOH membranes also exhibit better mechanical, thermal and chemical stabilities compared to the mono-QPESOH membranes. All these results indicate that the tri-QPESOH membranes are promising for potential applications in anion exchange membrane fuel cells.

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List of symbols

W_{dry}	weight of the dry membranes (g)
W_{wet}	weight of the hydrated membranes (g)
L_{wet}	average length of the hydrated membranes (cm)
L_{dry}	average length of the dry membranes (cm)
q	scattering vector (nm ⁻¹)
d	the Bragg spacing (nm)
L	length between the two electrodes (cm)

R	membrane resistance (Ω)
A	the cross-sectional area of the membranes
C_{AgNO_3}	molar concentration of the $AgNO_3$ solution ($mol\ L^{-1}$)
V_{AgNO_3}	consumed volume of the $AgNO_3$ solution (mL)
m_{dry}	weight of the dry membrane (Cl^- form, g)
σ	hydroxide conductivity ($S\ cm^{-1}$)
SR	swelling ratio (%)
WU	water uptake (%)

References

- [1] G. Couture, A. Alaaeddine, F. Boschet, B. Ameduri, Polymeric materials as anion-exchange membranes for alkaline fuel cells, *Prog. Polym. Sci.* 36 (2011) 1521-1557.
- [2] S. Gu, R. Cai, T. Luo, Z. Chen, M. Sun, Y. Liu, G. He, Y. Yan, A soluble and highly conductive ionomer for high-performance hydroxide exchange membrane fuel cells, *Angew. Chem. Int. Ed.* 48 (2009) 6499-6502.
- [3] Y. Wang, J. Qiao, R. Baker, J. Zhang, Alkaline polymer electrolyte membranes for fuel cell applications, *Chem. Soc. Rev.* 42 (2013) 5768-5787.
- [4] J. R. Varcoe, P. Atanassov, D. R. Dekel, A. M. Herring, M. A. Hickner, P. A. Kohl, A. R. Kucernak, W. E. Mustain, K. Nijmeijer, K. Scott, T. Xu, L. Zhuang, Anion-exchange membranes in electrochemical energy systems, *Energy Environ. Sci.* 7 (2014) 3135-3191.
- [5] J. Pan, C. Chen, Y. Li, L. Wang, L. Tan, G. Li, X. Tang, L. Xiao, J. Lu, L. Zhuang, Constructing ionic highway in alkaline polymer electrolytes, *Energy Environ. Sci.* 7 (2014) 354-360.
- [6] G. Merle, M. Wessling, K. Nijmeijer, Anion exchange membranes for alkaline fuel cells: a review, *J. Membr. Sci.* 377 (2011) 1-35.
- [7] S. Gu, R. Cai, Y. Yan, Self-crosslinking for dimensionally stable and solvent-resistant quaternary phosphonium based hydroxide exchange membranes, *Chem. Commun.* 47 (2011)

2856-2858.

- [8] J. Han, H. Peng, J. Pan, L. Wei, G. Li, C. Chen, L. Xiao, J. Lu, L. Zhuang, Highly stable alkaline polymer electrolyte based on a poly (ether ether ketone) backbone, *ACS Appl. Mater. Interfaces* 5 (2013) 13405-13411.
- [9] Z. Li, Z. Jiang, H. Tian, S. Wang, B. Zhang, Y. Cao, G. He, Z. Li, H. Wu, Preparing alkaline anion exchange membrane with enhanced hydroxide conductivity via blending imidazolium-functionalized and sulfonated poly(ether ether ketone), *J. Power Sources* 288 (2015) 384-392.
- [10] S. S. He, A. L. Strickler, C. W. Frank, A semi-interpenetrating network approach for dimensionally stabilizing highly-charged anion exchange membranes for alkaline fuel cells, *ChemSusChem* 8 (2015) 1472-1483.
- [11] C. G. Morandi, R. Peach, H. M. Krieg, J. Kerres, Novel imidazolium-functionalized anion-exchange polymer PBI blend membranes, *J. Membr. Sci.* 476 (2015) 256-263.
- [12] E. M. W. Tsang, Z. Zhang, Z. Shi, T. Soboleva, S. Holdcroft, Considerations of macromolecular structure in the design of proton conducting polymer membranes: graft versus diblock polyelectrolytes, *J. Am. Chem. Soc.* 129 (2007) 15106-15107.
- [13] Y. Ye, S. Sharick, E.M. Davis, K.I. Winey, Y.A. Elabd, High hydroxide conductivity in polymerized ionic liquid block copolymers, *ACS Macro Lett.* 2 (2013) 575-580.
- [14] R.A. Mulvenna, J.L. Weidman, B. Jing, J.A. Pople, Y. Zhu, B.W. Boudouris, W.A. Phillip, Tunable nanoporous membranes with chemically-tailored pore walls from triblock polymer templates, *J. Membr. Sci.* 470 (2014) 246-256.
- [15] T.N. Hoheisel, K. Hur, U.B. Wiesner, Block copolymer-nanoparticle hybrid self-assembly, *Prog. Polym. Sci.* 40 (2015) 3-32.
- [16] J. Ding, C. Chuy, S. Holdcroft, Solid Polymer Electrolytes Based on Ionic Graft Polymers: Effect of Graft Chain Length on Nano - Structured, Ionic Networks, *Adv. Funct. Mater.* 12 (2002) 389-394.
- [17] S. S. He, C. W. Frank, Facilitating hydroxide transport in anion exchange membranes via hydrophilic grafts, *J. Mater. Chem. A* 2 (2014) 16489-16497.
- [18] N. Li, T. Yan, Z. Li, T. T. Albrecht, W. H. Binder, Comb-shaped polymers to enhance

- hydroxide transport in anion exchange membranes, *Energy Environ. Sci.* 5 (2012) 7888-7892.
- [19] N. Li, Y. Leng, M. A. Hickner, C. Wang, Highly stable, anion conductive, comb-shaped copolymers for alkaline fuel cells, *J. Am. Chem. Soc.* 135 (2013) 10124-10133.
- [20] H. S. Dang, P. Jannasch, Exploring different cationic alkyl side chain designs for enhanced alkaline stability and hydroxide ion conductivity of anion-exchange membranes, *Macromolecules* 48 (2015) 5742-5751.
- [21] H. S. Dang, E. A. Weiber, P. Jannasch, Poly (phenylene oxide) functionalized with quaternary ammonium groups via flexible alkyl spacers for high-performance anion exchange membranes, *J. Mater. Chem. A* 3 (2015) 5280-5284.
- [22] N. Li, M. D. Guiver, W. Binder, Towards high conductivity in anion-exchange membranes for alkaline fuel cells, *ChemSusChem* 6 (2013) 1376-1383.
- [23] S. Gu, J. Wang, R. B. Kaspar, Q. Fang, B. Zhang, E. B. Coughlin, Y. Yan, Permethyl cobaltocenium (Cp^*Co^+) as an ultra-stable cation for polymer hydroxide-exchange membranes, *Sci. Rep.* 5 (2015) 11668.
- [24] N. Li, Q. Zhang, C. Wang, Y. M. Lee, M. D. Guiver, Phenyltrimethylammonium functionalized polysulfone anion exchange membranes, *Macromolecules* 45 (2012) 2411-2419.
- [25] J. Han, Q. Liu, X. Li, J. Pan, L. Wei, Y. Wu, H. Peng, Y. Wang, G. Li, C. Chen, L. Xiao, J. Lu, L. Zhuang, An effective approach for alleviating cation-induced backbone degradation in aromatic ether-based alkaline polymer electrolytes, *ACS Appl. Mater. Interfaces* 7 (2015) 2809-2816.
- [26] X. Wu, W. Chen, X. Yan, G. He, J. Wang, Y. Zhang, X. Zhu, Enhancement of hydroxide conductivity by the di-quaternization strategy for poly (ether ether ketone) based anion exchange membranes, *J. Mater. Chem. A* 2 (2014) 12222-12231.
- [27] J. Pan, Y. Li, J. Han, G. Li, L. Tan, C. Chen, J. Lu, L. Zhuang, A strategy for disentangling the conductivity-stability dilemma in alkaline polymer electrolytes, *Energy Environ. Sci.* 6 (2013) 2912-2915.
- [28] Q. Li, L. Liu, Q. Miao, B. Jin, R. Bai, A novel poly (2,6-dimethyl-1,4-phenylene oxide) with

- trifunctional ammonium moieties for alkaline anion exchange membranes, *Chem. Commun.* 50 (2014) 2791-2793.
- [29] J. Wang, G. He, X. Wu, X. Yan, Y. Zhang, Y. Wang, L. Du, Crosslinked poly (ether ether ketone) hydroxide exchange membranes with improved conductivity, *J. Membr. Sci.* 459 (2014) 86-95.
- [30] X. Yan, S. Gu, G. He, X. Wu, J. Benziger, Imidazolium-functionalized poly (ether ether ketone) as membrane and electrode ionomer for low-temperature alkaline membrane direct methanol fuel cell, *J. Power Sources* 250 (2014) 90-97.
- [31] R. Engel, J. I. Rizzo, C. Rivera, M. Ramirez, M. L. Huang, D. Montenegro, C. Copodiferro, V. Behaj, M. Thomas, B. Klaritch-vrana, J. F. Engel, Polycations. 18. the synthesis of polycationic lipid materials based on the diamine 1,4-diazabicyclo[2.2.2]octane, *Chem. Phys. Lipids* 158 (2009) 61-69.
- [32] J. Pan, S. Lu, Y. Li, A. Huang, L. Zhuang, J. Lu, High-performance alkaline polymer electrolyte for fuel cell applications, *Adv. Funct. Mater.* 20 (2010) 312-319.
- [33] X. Yan, S. Gu, G. He, X. Wu, W. Zheng, X. Ruan, Quaternary phosphonium-functionalized poly (ether ether ketone) as highly conductive and alkali-stable hydroxide exchange membrane for fuel cells, *J. Membr. Sci.* 466 (2014) 220-228.
- [34] S. Yun, J. Parrondo, V. Ramani, Derivatized cardo-polyetherketone anion exchange membranes for all-vanadium redox flow batteries, *J. Mater. Chem. A* 2 (2014) 6605-6615.
- [35] E. M. W. Tsang, Z. Zhang, A. C. C. Yang, Z. Shi, T. J. Peckham, R. Narimani, B. J. Frisken, S. Holdcroft, Nanostructure, morphology, and properties of fluoruous copolymers bearing ionic grafts, *Macromolecules* 42 (2009) 9467-9480.
- [36] G. Han, P. Xu, K. Zhou, Q. Zhang, A. Zhu, Q. Liu, Fluorene-containing poly (arylene ether sulfone) block copolymers: Synthesis, characterization and application, *J. Membr. Sci.* 464 (2014) 72-79.
- [37] R. Guan, H. Zou, D. Lu, C. Gong, Y. Liu, Polyethersulfone sulfonated by chlorosulfonic acid and its membrane characteristics, *Eur. Polym. J.* 41 (2005) 1554-1560.
- [38] W. Lu, Z. Shao, G. Zhang, Y. Zhao, J. Li, B. Yi, Preparation and characterization of imidazolium-functionalized poly(ether sulfone) as anion exchange membrane and ionomer

- for fuel cell application, *Int. J. Hydrogen Energy* 38 (2013) 9285-9296.
- [39] B. S. Ko, J. Y. Sohn, J. Shin, Radiation-induced synthesis of solid alkaline exchange membranes with quaternized 1,4-diazabicyclo[2,2,2]octane pendant groups for fuel cell application, *Polymer* 53 (2012) 4652-4661.
- [40] X. Yan, G. He, S. Gu, X. Wu, L. Du, H. Zhang, Quaternized poly(ether ether ketone) hydroxide exchange membranes for fuel cells, *J. Membr. Sci.* 375 (2011) 204-211.
- [41] D. Zhang, X. Yan, G. He, L. Zhang, X. Liu, F. Zhang, M. Hu, Y. Dai, S. Peng, An integrally skinned asymmetric architecture design for advanced anion exchange membranes in vanadium flow batteries, *J. Mater. Chem. A* 3 (2015) 16948-16952.
- [42] K. M. Hugar, H. A. Kostalik, G. W. Coates, Imidazolium cations with exceptional alkaline stability: a systematic study of structure–stability relationships, *J. Am. Chem. Soc.* 137 (2015) 8730-8737.
- [43] D. Chen, M. A. Hickner, Degradation of Imidazolium- and Quaternary Ammonium-Functionalized Poly(fluorenyl ether ketone sulfone) Anion Exchange Membranes, *ACS Appl. Mater. Interfaces* 4 (2012) 5775-5781.