Anion exchange membranes with well-developed conductive channels: Effect of the functional groups

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Flexible alkyl spacers
Cationic groups
Alkaline fuel cells

A B S T R A C T

To explore the alkaline stability of cationic groups, several investigations have been reported via small molecule model compounds, theoretical calculations or grafting cations to the benzyl positions of the polymer backbones. In this work, anion exchange membranes (AEMs) with various head groups of trimethylammonium (TMA), 1-methylpyrrolidinium (MPY), 1-methylpiperidinium (MPRD), 1-methylimidazolium (Im1) and 1,2-di-methylimidazolium (Im1,2) flexibly linked to poly(ether sulfone) (PES) backbones are prepared to explore the effect of pendent functional groups. The AEMs tethering MPRD groups are found to exhibit the highest Br\(^{-}\) conductivity of 60.4 ± 2.1 mS cm\(^{-1}\) at 80 °C. PES-MPY exhibits the best relative stability and maintains 90.7% and 83.1% of the original ionic exchange capacity (IEC) and conductivity, respectively, after immersed into 2 M NaOH at 60 °C for 672 h. Meanwhile, the alkaline stability is in the order of PES-MPY > PES-MPRD > PES-TMA > PES-Im1,2 > PES-Im1. The maximum power density of a H\(_2\)/O\(_2\) fuel cell using PES-MPRD (109.0 mW cm\(^{-2}\)) and PES-MPY (106.5 mW cm\(^{-2}\)) is larger than that using PES-Im1 (65.1 mW cm\(^{-2}\)). The results provide a guidance for designing high-performance AEMs.

1. Introduction

With the industrialization and population explosion, the world suffers from energy crisis and resources shortage. Burning fossil fuel not only has inefficient conversion of chemical energy into electric energy, but also pollutes the environment [1,2]. Hence, the development of new energy technology, especially fuel cells, as one of the promising clean energies, has already attracted increasing attentions [3–5]. As a critical component of fuel cells, polyelectrolyte membranes that were employed to separate the anode and cathode and to transport ions can be divided into two kinds, namely, proton exchange membranes (PEMs) and anion exchange membranes (AEMs). Few decades ago, attentions have been drawn to PEMs; the commercialized Nafion membrane is a representative. Nevertheless, PEM fuel cells have been facing some dilemmas, such as high fuel permeability and high cost because of using expensive metal catalysts (such as Pt) [5–7]. Currently, alkaline fuel cells (AFCs) attract the researchers’ much attention because AFCs using AEMs enable the utilization of low-cost non-noble metal catalysts (e.g. Ni, Ag, Co), and show much faster kinetics of electrode reaction and lower fuel permeation [8–10]. However, the poor chemical stability and low ion conductivity of the AEMs are still challenges in developing superior performance membrane materials [11,12]. Nowadays, polymer backbones including poly(phenylene oxide) [5,11–14], polybenzimidazole [15,16], poly(ether sulfone) [17,18], polyphenylene [19] and poly(ether imide) [20] have been used to make AEMs. To explore highly alkaline stable cations, numerous studies have been focused on quaternary ammonium (QA) [3,8,13,21], imidazoliums [22,23], spiro-ammonium [9,24], guanidinium [25,26], pyrroldinum [19,27], piperidinium [5,28], phosphonium [14] and metal cations [29]. Density functional theory calculations were employed to study the alkaline stability of various ions [30]. In addition, a number of small molecule studies were reported for evaluating the stability of cationic groups in alkaline media [31–34]. Mohanty et al. evaluated the alkaline stability of various cations linked to small molecule model compounds via the hexyl methylene spacer or short linkages [32]. They concluded that the chemical stability of functional groups connected to the benzene ring via the hexyl alkyl spacer is greatly improved and the heterocyclic QA demonstrates optimized stability at the identical test condition. Marino et al. found that N-methylpiperidinium shows 1.5-fold the half-time of trimethylammonium, 10-fold the half-time of benzyl-N-methylpiperidinium in a 6 M NaOH solution at 160 °C [33]. The steric shielding of cycloaliphatic QA is likely to render robust alkaline stability in alkaline media [28,32,35]. Olsson et al. concluded that the high base-stable ring structure was attributed to the low ring...
strain and conformational restrictions imposed by the cyclic structure [36]. Although plenty of works have been done on small molecule studies, the chemical stability of cationic groups will change when they are linked to the polymer chains [19].

Recently, some researchers have started to compare the chemical stability of various cations in the benzylic position of different polymer main chains. Ponce-Gonzalez et al. investigated the aliphatic-heterocyclic benzyl-QA by radiation-grafting and concluded that the AEM with N-methylpyrrolidinium exhibited a higher conductivity and chemical stability (18% loss in IEC) in a 1 M KOH solution at 80 °C for 28 days [37]. Zhu et al. investigated the effect of benzyltrimethylammonium on the alkaline stability of the AEMs, and found that 1,2,4,5-tetramethylimidazolium-functionalized AEMs exhibited the highest alkaline stability [38]. Dang et al. and Wang et al. also noted that the alkaline stability of cationic group in the benzylic position is different from that tethered to the hydrophobic backbone through flexible spacers (longer than -CH2-) [8,39]. Long et al. demonstrated the degradation pathways from the OH- attack via density functional theory, and found that Hofmann elimination reaction is dominant [40]. Our previous report also showed that the Hofmann elimination reaction of the cations was retarded when the length of alkyl chains between the cations and polymer chains are longer than -O(CH2)6- [17]. Introducing flexible alkyl spacers to the polymer main chains not only improves the stability of both the functional groups and backbones, but also is beneficial to increase the hydrophilic/hydrophobic phase separation to facilitate local ion mobility [8,28,41]. The performance of AEMs with QA in the benzylic positions and in the end of heptyl spacers on the poly(ether sulfone)s backbone via long alkyl chains are longer than -O(CH2)6- [17]. Furthermore, the flexible spacers have an effect on the conductivity of the AEMs. Extending the length of flexible spacer results in a higher conductivity when the flexible spacer is in the range from -O(CH2)6- to -O(CH2)8-, while the conductivity will decrease when the alkyl chains are longer than -O(CH2)8- [17]. Introducing flexible alkyl spacers to the polymer main chains not only improves the stability of both the functional groups and backbones, but also is beneficial to increase the hydrophilic/hydrophobic phase separation to facilitate local ion mobility [8,28,41]. The performance of AEMs with QA in the benzylic positions and in the end of heptyl spacers on the poly(ether sulfone)s backbone via long alkyl chains are longer than -O(CH2)6- [17]. Furthermore, the flexible spacers have an effect on the conductivity of the AEMs. Extending the length of flexible spacer results in a higher conductivity when the flexible spacer is in the range from -O(CH2)6- to -O(CH2)8-, while the conductivity will decrease when the alkyl chains are longer than -O(CH2)8- [17]. Introducing flexible alkyl spacers to the polymer main chains not only improves the stability of both the functional groups and backbones, but also is beneficial to increase the hydrophilic/hydrophobic phase separation to facilitate local ion mobility [8,28,41]. The performance of AEMs with QA in the benzylic positions and in the end of heptyl spacers on the poly(ether sulfone)s backbone via long alkyl chains are longer than -O(CH2)6- [17]. Furthermore, the flexible spacers have an effect on the conductivity of the AEMs. Extending the length of flexible spacer results in a higher conductivity when the flexible spacer is in the range from -O(CH2)6- to -O(CH2)8-, while the conductivity will decrease when the alkyl chains are longer than -O(CH2)8- [17]. Introducing flexible alkyl spacers to the polymer main chains not only improves the stability of both the functional groups and backbones, but also is beneficial to increase the hydrophilic/hydrophobic phase separation to facilitate local ion mobility [8,28,41]. The performance of AEMs with QA in the benzylic positions and in the end of heptyl spacers on the poly(ether sulfone)s backbone via long alkyl chains are longer than -O(CH2)6- [17]. Furthermore, the flexible spacers have an effect on the conductivity of the AEMs. Extending the length of flexible spacer results in a higher conductivity when the flexible spacer is in the range from -O(CH2)6- to -O(CH2)8-, while the conductivity will decrease when the alkyl chains are longer than -O(CH2)8- [17]. Introducing flexible alkyl spacers to the polymer main chains not only improves the stability of both the functional groups and backbones, but also is beneficial to increase the hydrophilic/hydrophobic phase separation to facilitate local ion mobility [8,28,41].

2. Experimental

2.1. Materials

Methoxyhydroquinone (98.0%) and bis(4-fluorophenyl) sulfone (99.0%) were supplied by Tokyo Chemical Industry Co. Ltd. 4,4′-(Hexafluorosopropylidenediphenol (98%), dimethyl sulfoxide (DMSO) (AR), N,N-dimethylacetamide (DMAc) (AR), dimethyl formamide (DMF) (AR) 1-methylimidazolide (Im1) (99%), 1,2-dimethylimidazolide (Im1,2), 1-methylpyrrolidinium (MPY) (98%), 1-methylpyperidine (MPRD) (97%), 1,6-dibromohexane and boron tribromide (BBr3) (99.9%) were provided from Aladdin Chemistry Co. Ltd. and used as received. Trimethylamine solution (TMA) (30 wt% in H2O) was purchased from Macklin Biochemical Co. Ltd. Potassium carbonate (K2CO3, 99%) was vacuum dried at 80 °C for 12 h. Toluene (AR), tetrahydrofuran (AR) and acetonitrile were purchased from Sinopharm Chemical Reagent Co. Ltd.

2.2. Preparation of anion exchange membranes

2.2.1. Synthesis of ionic liquids

1-(6-Bromohexyl)trimethylammonium bromide (Br-6-TMA, 6 is the number of -CH2- group) was made by the report [43]. 1-(6-Bromohexyl)-3-methylimidazolium bromide (Br-6-Im1) was synthesized as noted in the literature [4]. 3-(6-Bromohexyl)-1,2-dimethylimidazolium bromide (Br-6-Im1,2) was made according to the literature [44]. The specific reaction route is displayed in Scheme S1 (Supporting information). A mixture of 1,6-dibromohexane (294 mmol, 71.727 g) and acetonitrile (60 mL) was put into a 200 mL flask. Next, a mixture of 1,2-dimethylimidazolide (42 mmol, 4.037 g) and acetonitrile (4 mL) was put in a constant pressure dropping funnel, and was further added dropwise into the flask. The mixture was heated and stirred to 60 °C for 12 h. A crude product was obtained by filtration to remove the precipitate. The crude product was further rotovaporated to remove excess acetonitrile before extraction with ethyl ether and ethyl acetate several times, and vacuum dried at 80 °C overnight. A brown viscous liquid was obtained.

1-(6-Bromohexyl)-1-methylpyrrolidinium bromide (Br-6-MPY) was made by the previous report [45]. 1,6-Bibromohexane (200 mmol, 48.769 g) was mixed with acetonitrile (100 mL) in a 200 mL flask. The mixture of 1-methylpyrrolidone (20 mmol, 1.703 g) and acetonitrile (10 mL) was added dropwise into 1,6-dibromohexane under strong stirring at 60 °C. After 24 h, the mixture was poured into a large excess of ethyl ether (300 mL) to precipitate the crude product, which was washed with ethyl ether for several times, followed by vacuum drying at room temperature (RT) for 24 h. The synthesis of 1-(6-bromohexyl)-1-methylpyrrolidinium bromide (Br-6-MPRD) is as follows. A mixture of 1, 6-bibromohexane (400 mmol, 97.600 g) and acetonitrile (200 mL) was added to a 250 mL flask under violent magnetic stirring. A solution made up of 1-methylpyrrolidone (40 mmol, 3.966 g) and 10 mL of acetonitrile was then added dropwise into the flask by a dropping funnel to take reaction at 60 °C for 24 h. A precipitate was obtained by pouring the mixture into ethyl ether, a sticky white product was obtained after removing the filtrate and flask white precipitate. After washing with ethyl ether for several times and vacuum drying at RT for 24 h, we yield the product.

2.2.2. Synthesis of methoxyl-contained poly(ether sulfone) (PES-OCH3)

Methoxyl-contained PES was synthesized by the report [17]. The synthesis of copolymer via a nucleophilic polycondensation reaction is described in Scheme 1 (x = 0.85).

2.2.3. Synthesis of poly(ether sulfone)s containing hydroxyl groups (PES-OH)

PES-OH can be obtained via demethylation reaction. Chloroform (100 mL) was used to dissolve the PES-OCH3 (5.5 g) at RT with stirring. BBr3 (5 mL) was added into the above solution. After 12 h, a small amount of methanol was added to quench, followed by washing with excess methanol for three times to yield a solid product. Finally, a vacuum oven was used to dry the solid at 60 °C overnight.

2.2.4. Preparation of functionalized copolymers (PES-R, R = Im1, Im1,2, MPY, TMA and MPRD)

DMSO (20 mL) was used to dissolve PES-OH (n(OH) = 2.286 mmol, 1 g) in a 50 mL three-necked flask with a condenser, a magnetic stirrer and N2 flow. Then, K2CO3 (4.5716 mmol, 0.632 g) and KI (0.2283 mmol, 0.038 g) were added into the flask. Ionic liquids (3.429 mmol) were dissolved in 2 mL of DMSO and then added dropwise into the flask. The reaction was conducted in a 90 °C oil bath for 24 h. The reaction solution was precipitated, washed with acetone and dried, and washed again with deionized water and dried at 60 °C for
2.2.5. Membrane formation

A 5 wt% solution was made by dissolving PES-MPRD in DMSO (10 mL). After filtrating through a 0.45 µm PTFE membrane, the filtration was poured onto glass plates and placed in a vacuum oven at 60 °C for 24 h. The transparent membranes in Br\(^-\) form were peeled off with the aid of deionized water. The preparation of other kinds of membranes is the same as that of PES-MPRD.

2.3. Characterization

The chemical structure was confirmed via \(^1\)H NMR spectra recorded on an AV500 MHz spectrometer (Bruker, Switzerland). Deuterium oxide (D\(_2\)O) or deuterated dimethyl sulfoxide (DMSO-d\(_6\)) was used as the solvent and tetramethylsilane (TMS) as the internal standard. The molecular weight of the as-synthesized copolymer was determined by gel permeation chromatography (GPC, Waters, USA) using tetrahydrofuran (THF) as the eluent under a flow rate of 1.0 mL min\(^{-1}\). The molecular weight was calibrated by polystyrene standard. Cross polarization/magic angle spinning \(^{13}\)C NMR solid state spectra were recorded on a Bruker Advance III 400 spectrometer.

2.3.1. Small-angle X-ray scattering (SAXS) analysis and atomic force microscopy (AFM)

SAXS was used to study the microphase separated structure of AEMs in Br\(^-\) form and to calculate the size of ionic cluster from the aggregation of hydrophilic moieties via a SAXSessMC2 X-ray diffractometer (Anton paar, Austria). The characteristic separation distance (d) is calculated by the Bragg’s law

\[
d = \frac{2\pi}{q}
\]

where q is the scattering vector.

The surface morphology of the samples in Br\(^-\) form was observed by AFM in a tapping mode. All the samples with 60% relative humidity were characterized at ambient temperature.

2.3.2. Ionic exchange capacity (IEC)

The IEC of the AEMs in Br\(^-\) form was obtained using the Mohr’s titration method. To measure the mass of dry membranes, the samples were vacuum dried at 100 °C for 12 h and weighted. Then, these samples were soaked in a 0.5 M NaNO\(_3\) solution (40 mL) at RT for 48 h. A 0.02 M standard aqueous AgNO\(_3\) solution was used to titrate the resulting solution and 0.1 M K\(_2\)CrO\(_4\) as the color indicator. The IEC is calculated by

\[
\text{IEC} = \frac{V_{\text{AgNO}_3} \cdot C_{\text{AgNO}_3}}{m_{\text{dry}}} \cdot \frac{1}{3}
\]

where \(m_{\text{dry}}\) (g) denotes the mass of dry membranes, \(V_{\text{AgNO}_3}\) (mL) denotes the volume and \(C_{\text{AgNO}_3}\) (mol L\(^{-1}\)) the concentration of the aqueous AgNO\(_3\).

2.3.3. Water uptake (WU) and swelling ratio (SR)

After the length (\(L_d\)) and weight (\(W_d\)) of the dry oblong shape samples being measured, the samples were placed in deionized water at 30 and 60 °C for 24 h, successively. After wiped the surface water, the length (\(L_w\)) and weight (\(W_w\)) of the wet samples can both be determined. The WU can be calculated by

\[
\text{WU} = \frac{W_w - W_d}{W_d} \times 100\%
\]

The SR is estimated as follows

\[
\text{SR} = \frac{L_w - L_d}{L_d} \times 100\%
\]

The hydration number (\(\lambda\)), which is defined as the number of water molecules per ion exchange group, is estimated from
2.3.4. Ionic conductivity

Each sample was placed in deionized water at ambient temperature for 24 h before measurement. The membrane resistance was measured via an electrochemical workstation (VersaSTAT 4, USA). The temperature was elevated from 30 to 80 °C and maintained constant for half an hour at every 10 °C during measurement. The $Br^-$ conductivity can be estimated by

$$\lambda = \frac{WU}{IEC \times 18} \times 1000$$

2.3.5. Thermal stability

Prior to measurements, the sample was dried at 100 °C overnight. The thermal decomposition of the AEMs was examined via a thermogravimetric analyzer (TG-209F1, TA, USA) at a heating rate of 10 °C/min under N$_2$ protection.

2.3.6. Mechanical property

A universal testing machine (Instron 3343) was employed to determine the tensile strength and elongation at break at a tensile speed of 0.25 mm/s at ambient temperature. Before test, the dog-bone-shape membrane in Br$^-$ form was immersed in deionized water at RT for 24 h.

2.3.7. Alkaline stability

The alkaline stability of the sample is tested by soaking the sample into a 2 M aqueous NaOH at 60 °C for 672 h. Degassed deionized water was used to wash the membrane at RT for 48 h and changed every 12 h to remove the surplus sodium hydroxide solution thoroughly. The membrane degradation was monitored by determining the remaining hydroxide conductivity and IEC. The change in chemical structure is characterized via $^1$H NMR and/or $^{13}$C NMR before and after the test.

2.3.8. Single cell performance

Pt/C catalyst (0.8 g, 40%, Johnson Matthey), deionized water (3.300 g), ethanol (4.300 g), ionomer (0.250 g) and DMF (6 mL) were mixed to prepare a catalyst ink. The mixture was sonicated and stirred overnight. The catalyst-coated membranes (CCM) was made by spraying the ink onto two sides of the membrane. The catalyst loading is 0.5 mg cm$^{-2}$ in each membrane, and the effective area of the electrodes is 4 cm$^2$. Before assembling the CCM was immersed in 1 M NaOH for 24 h and then placed in deionized water for another 24 h. To prepare the membrane electrode assembly, the final CCM was placed between two pieces of Toray-treated carbon paper.

Single cell was examined using a TE201 fuel cell test station (Kunshan Sunlaite, China) at 60 °C. The H$_2$ and O$_2$ with 100% humidity were conducted at a flow rate of 100 mL min$^{-1}$. The single cell using PES-MPRD, PES-MPY and PES-Im1 AEMs was studied.

3. Results and discussion

3.1. Synthesis and characterization of various ionic liquids and copolymer

Taking Br-6-MPRD as an example, the synthesis is shown in Scheme S1. $^1$H NMR was adopted to characterize the structure of Br-6-MPRD using D$_2$O. As depicted in Fig. S1, the signal at 2.97 ppm is assignable to methyl on the piperidine ring, the signals from 3.25 to 3.29 ppm are assigned to methylene in the aliphatic chain close to the Br atom. The signals ranging from 1.81 to 1.83 ppm are ascribed to other -CH$_2$- groups on the ring. The signals at 1.36, 1.46, 1.61 and 1.73 ppm are related to the methylene of the alkyl spacer. The integration ratio of H10 to H1 is approximately 1:1.5. This suggests that Br-6-MPRD is successfully synthesized without by-product. The $^1$H NMR spectra of other ionic liquids are shown in Fig. S1, indicating the successful synthesis of ionic liquids.

PES-OCH$_3$ ($M_w = 41$ kg mol$^{-1}$ and $M_{ow} = 54$ kg mol$^{-1}$) is successfully synthesized. As shown in Fig. S2, the peak at 3.63 ppm ascribed to proton on the -OCH$_3$ disappeared. Meanwhile, a new signal at 10.13 ppm assignable to the phenolic hydroxyl proton was observed after the demethylation reaction, implying that the methoxyl group is substituted for phenolic hydroxyl completely. Moreover, the integration ratio of H4 to H6 is approximate to the theoretical value.

The synthesis of PES-MPRD is taken as example, excess Br-6-MPRD was grafted to the polymer backbone via a Williamson reaction. As described in Fig. S3, the appearance of a new signal at 2.98 ppm is assignable to methyl on the piperidine ring. The new signals at 3.92, 3.22–3.28, 1.77, 1.46–1.53, and 0.98–1.11 ppm are assignable to the -CH$_2$- of the alkyl spacer and piperidine ring. The signal associated with the phenolic hydroxyl proton at 10.13 ppm disappeared. This suggests successful synthesis of PES-MPRD. The integration ratio of H3–H8 is approximately to 1:2, indicating that the ionic liquids were grafted completely. The analysis for other PES membranes is shown in Fig. S3.

3.2. Membrane morphology

SAXS can be employed to study the microphase separated morphology that can be attributed to incompatibility between the hydrophobic segments and the hydrophilic groups [6,46,47]. As we know, ion migration will be improved by introducing long chain that plays a positive role in the aggregation of ionic clusters. Fig. 1 shows the SAXS profiles of PES AEMs. The maximum scatterings ($q_{max}$) of 1.62, 1.83, 1.83,1.88 and 1.88 nm$^{-1}$ correspond to an average separation distance.
Mechanical stability and even a decline in ionic conductivity. The water as media facilitates ion transport, excess water will cause a loss of ionic stability, ion mobility, and ionic conductivity. Although the grafting ratio approximates the monomer ratio.

As a key parameter, IEC plays a critical role in WU, SR and conductivity of AEMs to some extent. As listed in Table 1, the IEC is in the range 1.36–1.47 mmol g\(^{-1}\), indicating that the IEC calculated from the feed ratio is similar to that from the Mohr's titration, revealing that the grafting ratio approximates the monomer ratio.

The water content has a great influence on the swelling, dimensional stability, ion mobility, and ionic conductivity. Although the water as media facilitates ion transport, excess water will cause a loss of mechanical stability and even a decline in ionic conductivity. The WU and SR at 30 and 60 °C, IEC and \(\lambda\) (hydrated number) are listed in Table 1. An obvious distinction in IEC can be observed for various cationic groups, though the polymer backbone and degree of functionalization are identical. The difference in molecular weight of different functional groups can be used as an interpretation. As shown in Table 1, similar to WU, SR strongly depends on temperature. WU and SR increased at elevated temperature because the channel will be broadened with increasing temperature. Additional free volume can be created by the increased mobility of the PES chains with increasing temperature. As a consequence, more water entering into the membranes increases the swelling and facilitates the migration of ions to improve the conductivity.

As listed in Table 1, grafting different ion conducting groups onto the side-chain has a significant influence on the WU and SR of AEMs. The water content and swelling of PES-MPRD (WU = 36.5%, SR = 17.2%) are higher than those of PES-Im1 (WU = 19.3%, SR = 7.2%) at 30 °C, probably because the larger piperidine moiety formed a bigger ionic cluster. PES-MPY has a similar WU with PES-TMA at 30 °C, but the former has a larger \(\lambda\) (9.95) than the latter (8.09). This agrees with that reported in the literature [47]. The AEM whose C2 position of imidazolium ring was substituted with a methyl substituent absorbs more water than the unsubstituted counterpart, and this result is in accordance with the report [51].

Noticeably, all kinds of membranes have low swelling. The flexible hydrophobic alkyl chains may restrict the swelling [17,28,42]. The PES-MPY shows the lowest swelling, indicating that the AEMs have desirable dimensional stability.

### 3.3. Ionic exchange capacity, water uptake and swelling ratio

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### 3.4. Ionic conductivity

The conductivity of the AEMs is a critical property and has an influence on the development of fuel cells. The conductivity of membranes is required to exceed 10 mS cm\(^{-1}\) at RT when the AEM materials are applied for fuel cells [49]. The temperature dependence of conductivity of the PES membranes is plotted in Fig. 3(a). The conductivity is measured in bromide form rather than hydroxide form because some cationic groups (e.g. Im1 and Im1,2) are vulnerable to degrade in hydroxide form whereas the bright regions consist of hydrophilic side chain and water, whereas the bright regions consist of hydrophobic polymer backbones. Well-defined hydrophilic-hydrophobic phase-separated structure is observed for all the AEMs. The existence of phase separation is beneficial to construct well-developed conductive channels [49]. The PES-MPRD exhibited the most pronounced ionic domains but the PES-Im1 exhibited the least, which is in line with the SAXS result.

### Table 1

<table>
<thead>
<tr>
<th>Membranes</th>
<th>IEC (meq g(^{-1}))</th>
<th>WU (%)</th>
<th>SR (%)</th>
<th>(\lambda)</th>
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<tr>
<td></td>
<td>Theor.(^a)</td>
<td>Exp.(^b)</td>
<td>30 °C</td>
<td>60 °C</td>
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<tr>
<td>PES-Im1</td>
<td>1.46</td>
<td>1.40 ± 0.03</td>
<td>19.3 ± 0.2</td>
<td>34.6 ± 0.1</td>
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<tr>
<td>PES-Im1,2</td>
<td>1.43</td>
<td>1.36 ± 0.02</td>
<td>33.2 ± 0.2</td>
<td>43.1 ± 0.2</td>
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<tr>
<td>PES-MPY</td>
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<td>1.44 ± 0.02</td>
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<td>36.1 ± 0.1</td>
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<td>PES-TMA</td>
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<td>21.4 ± 0.3</td>
<td>33.8 ± 0.3</td>
</tr>
<tr>
<td>PES-MPRD</td>
<td>1.43</td>
<td>1.42 ± 0.03</td>
<td>36.5 ± 0.1</td>
<td>48.9 ± 0.5</td>
</tr>
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\(^a\) Calculated from the monomer ratio.

\(^b\) Measured by Mohr's titration.
promote ionic assembling and bring wide ion conducting channels [8].

Likewise, the Br$^-$ conductivity of the as-prepared PES AEMs follows an approximate Arrhenius law, as described in Fig. 3(b). The activation energies ($E_a$) for Br$^-$ transport are acquired from the slopes to be 25.0, 22.6, 22.5, 22.8 and 20.7 kJ mol$^{-1}$ for PES-Im1, PES-Im1,2, PES-MPY, PES-TMA and PES-MPRD, respectively. This indicates that the cationic groups share a similar ion conducting mechanism. However, the higher $E_a$ for AEMs, the more energy is required for ion transport across the membranes. Bromide ions are easiest to transport through the ion conducting channels in PES-MPRD. Fig. 4 shows the Br$^-$ conductivity of various cations at 30, 60 and 80 °C. The PES-MPRD with the highest WU displays the highest Br$^-$ conductivity (60.4 ± 2.1 mS cm$^{-1}$, IEC = 1.42 mmol g$^{-1}$) at 80 °C. The Br$^-$ conductivity is ranging from 51.3 ± 1.7–60.4 ± 2.1 mS cm$^{-1}$ for various AEMs at 80 °C and shares a similar tendency with water uptake. The conductivity is in the order as noted in Fig. 4.

3.5. Thermal stability

The thermal property of the five membranes in Br$^-$ form was evaluated via thermal gravimetric analysis (TGA) from 30 to 800 °C under a N$_2$ atmosphere. The thermal stability curves are plotted in Fig. 5. A slight degradation (weight loss ≤ 3.5%) below 200 °C is associated with the evaporation of DMSO and water although all AEMs were vacuum dried at 100 °C for 12 h before test. The losing weight of PES-MPRD and PES-Im1,2 is around 4.5%, indicating that they absorb water more easily in the air. The degradation starting from 200 to 350 °C is attributed to the decomposition of the functional groups. From those curves, the imidazolium groups have a good thermal stability.

Table 2

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>After</td>
<td>Before</td>
</tr>
<tr>
<td>PES-Im1</td>
<td>36.5 ± 1.1</td>
<td>53.7 ± 1.6</td>
</tr>
<tr>
<td>PES-Im1,2</td>
<td>22.1 ± 2.2</td>
<td>11.32 ± 1.0</td>
</tr>
<tr>
<td>PES-MPY</td>
<td>41.3 ± 1.3</td>
<td>36.97 ± 2.3</td>
</tr>
<tr>
<td>PES-TMA</td>
<td>27.6 ± 2.5</td>
<td>19.29 ± 1.2</td>
</tr>
<tr>
<td>PES-MPRD</td>
<td>28.8 ± 1.1</td>
<td>23.72 ± 2.0</td>
</tr>
</tbody>
</table>

This agrees with the result in other report [52]. The weight loss above 350 °C could be ascribed to the decomposition of hydrophobic backbone. This result indicates that the five membranes can meet the requirement for fuel cells in terms of thermal stability.

3.6. Mechanical property

As an important factor, the mechanical properties are pertinent to long-term service of fuel cells. As noted in Table 2, the tensile strength of the AEMs is in the range of 22.1–41.3 MPa and elongation at break is from 5.0% to 7.9%. It is clear that the tensile strength deceased with increasing swelling ratio. Of those membranes, PES-MPY has the...
The change in IEC and conductivity was monitored to assess the alkaline tolerance during the test. The remaining IEC and conductivity after 672 h are shown in Figs. 6 and 7, respectively. As shown in Figs. 6 and 7, the remaining IEC and conductivity after 672 h are 26.0% and 23.1%, 66.4% and 65.3%, 90.7% and 83.1%, 74.8% and 71.0%, and 85.6% and 79.1% for PES-Im1, PES-Im1,2, PES-MPY, PES-TMA, and PES-MPRD, respectively. This suggests that imidazolium-based AEMs degraded much faster than QA-based AEMs under basic condition [10,52,53]. Particularly, PES-MPY exhibits the highest alkaline stability at the same condition, followed by PES-MPRD. The chemical stability of the AEMs is in the order as noted in Figs. 6 and 7 in terms of decline in IEC and conductivity, respectively. The change of mechanical properties of the PES samples is listed in Table 2 after the alkaline test. The samples except for PES-Im1 showed a decline in the mechanical strength after the test which were associated with the degradation of the polymer chain and the cationic groups. However, the tensile strength of PES-Im1 showed an obvious increase after the test, which may be due to the crosslinkage.

3.7. Alkaline stability

The AEMs were exposed to 2 M aqueous NaOH at 60 °C for 672 h to examine their stability. As we know, cationic groups are quite susceptible to a basic environment due to the attack of OH− on the cationic groups via Hofmann elimination and nucleophilic substitution [3,37,46]. The change in IEC and conductivity was monitored to assess the alkaline tolerance during the test. The remaining IEC and conductivity are shown in Figs. 6 and 7, respectively. As shown in Figs. 6 and 7, the remaining IEC and conductivity after 672 h are 26.0% and 23.1%, 66.4% and 65.3%, 90.7% and 83.1%, 74.8% and 71.0%, and 85.6% and 79.1% for PES-Im1, PES-Im1,2, PES-MPY, PES-TMA, and PES-MPRD, respectively. This suggests that imidazolium-based AEMs degraded much faster than QA-based AEMs under basic condition [10,52,53]. Particularly, PES-MPY exhibits the highest alkaline stability at the same condition, followed by PES-MPRD. The chemical stability of the AEMs is in the order as noted in Figs. 6 and 7 in terms of decline in IEC and conductivity, respectively. The change of mechanical properties of the PES samples is listed in Table 2 after the alkaline test. The samples except for PES-Im1 showed a decline in the mechanical strength after the test which were associated with the degradation of the polymer chain and the cationic groups. However, the tensile strength of PES-Im1 showed an obvious increase after the test, which may be due to the crosslinkage.

1H NMR spectra are used to further observe the structure changes of the copolymers before and after the alkaline treatment and to identify the degradation mechanisms. However, the degree of degradation cannot be quantified from the 1H NMR signals because of the complexity of degradation processes. Take PES-TMA as an example, there are two possible degradation mechanism of QA groups during alkaline stability test (Scheme S2), however, we do not know the ratio of each degradation route via 1H NMR signals. Furthermore, some degradation products such as trimethylamine (gas) is hard to capture. Thus, it is impossible to quantify the degree of degradation from the 1H NMR signals of the degradation products from the head group. Fig. 8 shows the 1H NMR spectra of the polymers containing various cationic groups except Im1 group because PES-Im1 is insoluble in organic solvents after treatment. The insolubility of the PES-Im1 is likely due to crosslinking during the alkaline test, and agrees with the reports [32,34,55]. The degradation mechanism of Im1 groups is shown in Scheme S2(a). Crosslinkages are formed via the reaction between the highly active -CHO groups and -NH-CH3 groups which are generated from the ring opening reaction. Moreover, 13C NMR solid state spectra of PES-Im1 before and after the treatment were recorded to further analyze the crosslinking mechanism. As observed in Fig. S4, a new peak around 78 ppm is ascribed to the carbon from -NH-CH(OH)-NH- of the product from the first degradation step. The increased intensity at 86 ppm is ascribed to the carbon from -NH-C= C-N(CH3)- of the crosslinked network. A new peak around 147 ppm is assignable to the carbon of the crosslinked groups (-NH-CO-N(CH3)2) that are the product of the crosslinking reaction during degradation. The peak intensity at 163 ppm assignable to the -CHO carbon decreased after treatment. As reported in the literature [39], the proposed degradation mechanism of Im1,2 groups in PES-Im1,2 is shown in Scheme S2(b). Fig. 8(a) shows the 1H NMR of PES-Im1,2. The lower signal intensity at 2.57 ppm (H10) is assignable to the methyl protons adjacent the nitrogen cation. An obvious new chemical shift at 1.98–2.03 ppm (H10′, H10′′) appeared, illustrating that the opening reaction of the imidazole ring occurred at the C2 position via nucleophilic attack of hydroxide ions. Fig. 8(b) shows the 1H NMR of PES-TMA. The signal intensity at 3.91 (H1) and 3.05 ppm (H7) decreased and two new signals at 2.02 (H7′) and 3.82 ppm (H6′) are attributed to the degradation product of TMA groups. The change in the signals reveals that the main degradation pathway by OH− attack is nucleophilic substitution. As noted, the degradation pathway of TMA groups is shown in Scheme S2(c) [17]. There are not any new peaks in PES-MPY after alkaline treatment (Fig. 8(c)), whereas the signal intensity of methyl protons adjacent the nitrogen cation decreased, presumably methyl substitution occurred by Sn2 attack of OH−. The proposed degradation mechanism of MPY group in this work is shown in Scheme S2(d) [32,37]. In Fig. 8(d), a new peak at 4.07 ppm (H7′) in the spectra of PES-MPRD is assigned to the by-product from the ring opening reaction of 6-member ring because of OH− attack. The signal at 2.97 ppm (H10) attributed to methyl on the piperidine ring became smaller after test. These indicate that both methyl substitution and ring opening reaction occurred during the alkaline stability test, as shown in Scheme S2(e). Nevertheless, no new proton resonance signal of -CH= CH2 was observed in the 1H NMR spectra.
spectra. This implies that the attack of hydroxide ions on β-hydrogens via Hofmann elimination is inhibited when the cationic groups are separated from the polymer backbone by flexible alkyl chains [17,28]. It is known that the PES main chain will degrade slightly when the length of the alkyl spacers between the hydrophobic backbone and the cationic groups is larger than 4 (> -(CH2)4-) [17]. As shown in Fig. 8(a-d), the new signals at 1.0–1.5 ppm are assigned to the degradation of corresponding ionic groups and the small peaks at 7.6–7.8 ppm are probably attributed to the by-products from the PES backbone degradation [56]. Hence, the decomposition of cationic groups is the dominant degradation pathway that cause a decrease in IEC and conductivity.

With comparison, it is obviously that QA-based AEMs show higher alkaline tolerance than the imidazolium-based AEMs, and is in line with the reports [53,54]. According to the retention of IEC and conductivity of PES-Im1 and PES-Im1,2, the AEM with a methyl substituent at the C2 position of imidazolium ring demonstrates higher chemical stability than the unsubstituted analogue. The degradation of PES-Im1,2 needs much more energy because the presence of methyl groups has steric protection against hydroxide ions attack [22,30]. PES-MPY and PES-MPRD have the highest stability due to the conformational restrictions imposed by the cyclic structure [36]. The former exhibits even more robust alkaline tolerance (remaining 90.7% IEC) than the latter (remaining 85.6% IEC). The reason is that PES-MPY only undertakes substitution but no ring opening reaction while PES-MPRD would take both methyl substitution and ring opening reaction. Above all, PES-MPY and PES-MPRD are the most promising candidates in terms of alkaline tolerance.

3.8. Single cell performance

PES-MPY and PES-MPRD with higher conductivity and robust alkaline stability were employed to assess the H2/O2 single cell performance. PES-Im1 was used as a blank because of its lowest conductivity and poorest chemical stability. Fig. 9 exhibits the polarization curves of single cells using PES-MPY, PES-MPRD and PES-Im1 at 60 °C. The open circuit voltage is in the range of 1.01–1.07 V, indicating a low gas permeability of these membranes. Furthermore, as displayed in Fig. S5, the high frequency resistances of single cell using PES-MPY and PES-MPRD are nearly a constant value (0.38 and 0.36 Ω cm2) and are both lower than that using PES-Im1 (0.62 Ω cm2). This indicates that the high frequency resistance of fuel cell is related to the conductivity. As shown in Fig. 9, the cell using PES-MPRD achieved a power density (109.0 mW cm−2) at a current density of 250 mA cm−2 which is close to the value with that using PES-MPY (106.5 mW cm−2). These results were much larger than that using PES-Im1 (65.1 mW cm−2 at a current density of 130 mA cm−2). Therefore, the researches of 5- or 6-member ring structure based ammonium groups with excellent single cell performance should be a hot subject in the future.
Fig. 9. The polarization curves of H2/O2 cells using PES-MPRD, PES-MPY and PES-Im1 at 60 °C.

4. Conclusions

In summary, a series of side-chain-type AEMs bearing various cationic groups were obtained via demethylation and Williamson reaction. The well-developed conductive channels were observed for all the AEMs using SAXS and AFM. PES-MPRD demonstrates the maximum Br− conductivity of 60.4 ± 2.1 mS cm−1, and PES-Im1 shows the minimum Br− conductivity of 51.3 ± 1.7 mS cm−1 at 80 °C. The relative stability of AEMs is in the order of PES-MPY > PES-MPRD > PES-Im1 (65.1 mW cm−2). The ionic groups were obtained via demethylation and Williamson reaction. PES-Im1 and PES-MPRD achieve higher power density of 109.0 and 106.5 mW cm−2, respectively, than PES-Im1 (65.1 mW cm−2). This finding shows that heterocyclic quaternary ammonium groups like pyrrolidinyl and piperidinyl can be regarded as potential candidates for AEMs, so further work on them will be done in the future.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.memsci.2018.07.039.

References


