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Alkaline stable imidazolium-based ionomers containing poly(arylene ether sulfone) side chains for alkaline anion exchange membranes[†]

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Solvent processable anion exchange membranes (AEMs) containing imidazolium cation and poly(arylene ether sulfone) side chains were prepared *via* the ionization of poly(4-vinylbenzyl chloride)-*graft*-poly(arylene ether sulfone) copolymers, and followed by anion exchange with hydroxide ions. The ionized copolymers produced ductile, transparent membranes which possess a relatively high ionic conductivity (up to 1.6×10^{-2} S cm⁻¹ at room temperature). The yielded membranes are soluble in polar aprotic solvents, such as DMSO and DMF, while insoluble in water and methanol. The synthesized AEMs show good alkaline stability in 1 M KOH at 60 °C for 20 days, as well as high dimensional and thermal stability. These results should pave way to the practical application of this kind of AEM in alkaline fuel cells.

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Introduction

Proton exchange membrane fuel cells (PEMFCs) are one of the promising environmentally friendly power generation technologies, which possess high energy-conversion efficiency, quiet operation and high power density.¹⁻³ As one of the key components of PEMFCs, polymer electrolyte membranes could separate the fuel and oxidant streams and simultaneously transport protons.^{4,5} However, the widespread commercialization of PEMFCs is hindered by their exclusive dependence on precious metal-based electrocatalysts (such as platinum).^{6,7} Therefore, alkaline anion exchange membrane fuel cells (AEMFCs), in which the charge carriers are hydroxide ions, rather than protons, are attracting growing interest due to their enhanced oxygen reduction kinetics and the potential use of non-precious electrocatalysts, such as silver and nickel.^{8,9}

As one of the key components of AEMFCs, alkaline anion exchange membranes (AEMs) play an important role in influencing the performance of AEMFCs. Great efforts have been devoted to the development of AEMs with high-performance. Polymer membranes, based on various polymer backbones, such as polysulfone and its analogues,^{10,11} and poly(ether imide)¹² were prepared by a post-functionalized strategy, which is performed by chloromethylation of the polymers with chloromethyl ether and followed by quaternization to form quaternary ammonium cations.13 However, quaternary ammonium cations are generally unstable in high pH aqueous solution, because of the possible degradations via Hofmann elimination (E2),¹⁴ nucleophilic substitution(S_N2),^{15,16} or ylide formation.1 As potential alternative cations, tertiary sulfonium,17 guanidinium,18,19 phosphonium,20,21 imidazolium,22-24 benzimidazolium,25,26 phosphatranium,27 and metal-cations28 have been investigated for AEMs. Among the cations studied, imidazolium cation based AEMs have been recently studied by several groups, due to their relatively high chemical stability, which is largely attributed to the steric hindrance and the presence of the π conjugated structure.^{14,24,26,29-31} However, degradation of imidazolium cation based AEMs were also observed under vigorous conditions (high pH environment and elevated temperature) due to the nucleophilic attack of hydroxide ions to the imidazole rings.32,33 Our group previously has been engaging in the study of C2-substitutions on the alkaline stability of imidazolium cations.³⁴ A preliminary study suggested that C2-substituents are effective in stabilizing the imidazolium cations and the resulting AEMs.35 These observations inspired the preparation of imidazolium cation-based highly stable AEMs for practical applications.

On the other hand, cross-linked AEMs, such as polystyrene and poly(aryl ether sulfone)-based membranes have been recently synthesized, which possess enhanced dimensional stability and intensified fuel resistance.^{1,36} However, crosslinked polymers are generally insoluble in solvents and thus can not be used in the catalyst layer to build an efficient three-phase boundary to improve the utilization of the catalyst particles.^{21,37} Therefore, the development of soluble AEMs with high conductivity and good physicochemical properties is

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In the present study, we report the preparation of polymeric membranes via a graft-onto reaction between poly(4-vinylbenzyl chloride) with pendent benzyl chloride groups and poly(arylene ether sulfone) with terminal phenol groups, and followed by ionization with 1-butyl-2-methyl imidazole. Anion exchange of the membranes with hydroxide ions produced imidazoliumbased AEMs. For the first time, the highly stable C2 (methyl) and N3-(butyl) substituted imidazolium cation was selected for the preparation of AEMs. Due to the graft-onto of poly(arylene ether sulfone), the resultant polymeric membranes are robust, flexible, and transparent and soluble in polar aprotic solvents such as N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), while insoluble in water and methanol. The soluble imidazolium functionalized ionomers show relatively high hydroxide ion conductivity, good alkaline stability and mechanical properties, demonstrating their potential practical applications in fuel cells.

Experimental

Materials

2-Methylimidazole, bromobutane, potassium hydroxide (KOH), acetonitrile, dichloromethane (CH₂Cl₂), anhydrous magnesium sulfate (MgSO₄), 4-vinylbenzyl chloride, trimethylamine aqueous solution (30%), 2,2'-azobisisobutyronitrile (AIBN), 4, 4'-dichlorodiphenylsulfone, bisphenol A, potassium carbonate, toluene, *N*-methylpyrrolidone (NMP), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), ethanol, and *N*,*N*-dimethylforma-mide (DMF) were used as purchased. All of the vinyl monomers were made inhibitor-free by passing the liquid through a column filled with basic alumina to remove the inhibitor and then stored at -5 °C before use. Distilled deionized water was used throughout the experiments.

Synthesis of 1-butyl-2-methylimidazole

1-Butyl-2-methylimidazole was synthesized as follows: a mixture containing 2-methylimidazole (2.00 g, 0.024 mol), bromobutane (3.34 g, 0.024 mol), and KOH (2.69 g, 0.048 mol) in acetonitrile (30 mL) was stirred at room temperature, for 4 h, under an argon atmosphere. The solvent was removed under dynamic vacuum, and the crude product was extracted with CH_2Cl_2 three times. The combined organic phase was washed with distilled water and dried over anhydrous MgSO₄, and the solvent was removed under vacuum. The resultant yellow oil was dried in a dynamic vacuum at room temperature (yield: 3.05 g, 92%). ¹H NMR (400 MHz, CDCl₃) δ : 7.04 (s, 1H), 6.95 (s, 1H), 3.96 (t, 2H), 2.51(s, 3H), 1.84 (m, 2H), 1.48 (m, 2H), 1.09 (t, 3H).

Synthesis of 1-benzyl-2-methy-3-butylimidazolium chloride

1-Benzyl-2-methy-3-butylimidazolium chloride ([BMBIm][Cl]) was synthesized by stirring a mixture containing 1-butyl-2methylimidazole and an equivalent molar amount of benzyl chloride at room temperature under a nitrogen atmosphere. The resultant white solid was washed with ethyl ether three times and then dried in a dynamic vacuum at room temperature for 24 h (yield: 4.42 g, 90%). ¹H NMR (400 MHz, D₂O): 7.36–7.42 (m, 5H), 7.34 (ds, 2H), 5.37 (s, 2H), 4.14 (t, 2H), 2.60 (s, 3H), 1.81 (m, 2H), 1.34 (m, 2H), 0.93 (t, 3H).

Synthesis of poly(4-vinylbenzyl chloride)

Poly(4-vinylbenzyl chloride) was synthesized by the free radical polymerization of 4-vinylbenzyl chloride (initiated by 1 wt% of AIBN) in DMF at 65 °C for 8 h under a nitrogen atmosphere. The resultant polymer was precipitated and purified with ethanol, and then dried at 60 °C in a vacuum overnight. ¹H NMR (400 MHz, DMSO-d₆) δ : 7.14 (m, 2H), 6.52 (m, 2H), 4.66 (s, 2H), 2.75 (m, 2H), 1.45 (m, 2H), 1.25 (m, 2H), 1.26 (t, 3H), 0.86 (t, 3H).

Synthesis of poly(arylene ether sulfone)

A typical synthesis procedure is as follows: a mixture containing bisphenol A (5.0 g, 21.9 mmol), 4,4'-dichlorodiphenylsulfone (6.29 g, 21.9 mmol), and potassium carbonate (4.53 g, 32.8 mmol) were added to a three-neck round bottom flask. Then, a solvent mixture containing NMP (65 mL) and toluene (30 mL) was added to the reaction mixture under a nitrogen atmosphere. The reaction bath was heated to 150 °C for 5 h to dehydrate the system. After the removal of toluene and water, the reaction temperature was gradually increased to 180 °C and stirred for 24 h. After cooling to room temperature, an additional 30 mL of NMP was added, so as to dilute the highly viscous solution, after which the solution was dropped into stirred deionized water. The precipitate was filtered off and washed with deionized water and ethanol several times, prior to being dried under a vacuum to produce the final product.

Graft-onto reaction between poly(arylene ether sulfone) and poly(4-vinylbenzyl chloride)

The graft-onto reaction was carried out as follows:⁴¹ 0.9 g poly(arylene ether sulfone) and 0.05 g potassium carbonate were dissolved in 100 mL DMF in a three neck round bottom flask at 150 °C. Then, an excess amount of the synthesized poly(4-vinylbenzyl chloride) (1 g) was added to the flask and the mixture was refluxed for 24 h. The cooled mixture was poured into deionized water, and the precipitate was Soxhlet extracted with THF, to remove the ungrafted poly(arylene ether sulfone). The synthesized polymer powder was washed with deionized water and methanol and dried at 60 °C under a vacuum.

Preparation of the imidazolium-based anion exchange membrane ([PUVBIm][OH])

1-Butyl-2-methylimidazole, in a slight excess amount, was added to a solution of the graft copolymer in DMF (5 wt%). The mixture was stirred at 80 $^{\circ}$ C for 24 h. The resulting solution was

then cast onto a level Teflon® sheet and heated at 80 °C for 24 h, to remove the solvent and the unreacted 1-butyl-2-methylimidazole. The resultant membranes were converted from the Cl⁻ to OH⁻ by anion exchange with hydroxide ions in a 1 M KOH solution at 60 °C for 48 h, to produce the imidazolium-based AEM ([PUVBIm][OH]). Then, the converted AEMs were washed with deionized water until the pH of the residual water was neutral.

Characterization

The ¹H NMR spectra were recorded on a Varian 400 MHz spectrometer. The Fourier transform infrared (FT-IR) spectra were recorded on a Varian CP-3800 spectrometer in the range 4000-400 cm⁻¹. The thermal transition temperatures of the polymer membranes were measured on a Perkin-Elmer DSC 4000, at a scanning rate of 10 $^{\circ}$ C min⁻¹, under a N₂ atmosphere. The thermal analysis was performed on Universal Analysis 4000 thermogravimetric analyzer (TGA) system. The samples were heated from 30 to 600 °C, at a heating rate of 10 °C min⁻¹, under a nitrogen flow. The isothermal TGA analysis was carried out by heating the membranes to 150 °C, for 12 h, under a nitrogen flow. The scanning electron microscopy (SEM) images were taken with a Philips XL 30 FEG microscope, with an accelerating voltage of 10 kV. The energy-dispersive X-ray spectroscopy (EDX) measurements were performed with the spectrometer attached on the Hitachi Model S-4700 field-emission scanning electron microscopy (SEM) system. The atomic force microscopy (AFM) images were measured with a NT-MDT Solver P47 AFM in a tapping mode. The oscillation frequency was set to approximately 255 kHz with a Si cantilever, which had a spring constant of about 11.5 N m⁻¹. All the AFM images were taken at room temperature. The tensile properties of the membranes were measured using an Instron 3365, at 25 °C, at a crosshead speed of 5 mm min⁻¹. The measurements of the membranes were conducted on membrane samples of 3 mm width and 9 mm length. Each sample was tested at least three times to reach an average value. The number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers were determined using a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive index detector (Waters 2414), DMF was used as the eluent at a flow rate of 1.0 ml min⁻¹ at 30 °C. The samples were injected using a Waters 717 plus autosampler and the column was calibrated with polystyrene standards, purchased from Waters.

Hydroxide conductivity

The resistance of the prepared membranes was measured by four-point probe alternating current (ac) impedance spectroscopy over the frequency range from 1 Hz to 1 MHz, using an electrochemical workstation (Zahner IM6 EX). All the samples were fully hydrated in N_2 saturated deionized water for at least 24 h prior to the conductivity measurements. Conductivity measurements under fully hydrated conditions were carried out in a chamber filled with a N_2 saturated deionized water to maintain the relative humidity at 100% during the experiments. Before the measurements at each temperature set point, the samples were held at a constant temperature for at least 30 min. Repeated measurements were obtained at 10 min intervals, until no more change in the conductivity was observed. The ionic conductivity (S cm⁻¹) of a given membrane can be obtained using the following formula:

$$\sigma = \frac{d}{RA}$$

where *d* is the distance (cm) between two gold electrodes, A is the cross-sectional area (cm²) of the membrane, obtained from the membrane thickness multiplied by its width, and *R* is the membrane resistance value from the AC impedance data (Ω).

Water uptake and swelling ratio

A membrane sample was immersed in N₂ saturated deionized water at room temperature for 24 h. The hydrated membrane was taken out of water, and the excess surface water was removed by wiping with a tissue paper and the mass was quickly measured (W_w). Then, the wet membrane was dried under a vacuum at 80 °C, until a constant dry weight (W_d). The water uptake W was calculated as follows:

$$W(\%) = rac{(W_{
m W} - W_{
m d})}{W_{
m d}} imes 100\%$$

The swelling ratio was characterized by a linear expansion ratio, which was determined by the difference between the wet and dry dimensions of a membrane sample (4 cm in length and 1 cm in width). The calculation was based on the following equation:

$$\text{Swelling}(\%) = \frac{X_{\text{wet}} - X_{\text{dry}}}{X_{\text{dry}}} \times 100\%$$

where X_{wet} and X_{dry} are the lengths of wet and dry membranes, respectively.

Ion exchange capacity (IEC)

The IEC was measured using a back-titration method. The AEMs were dried at 80 °C under a vacuum for 24 h before the mass was recorded (m_{dry}) and immersed in 100 mL of a 0.01 M HCl standard solution for 24 h. The solutions were then titrated with a standardized NaOH solution using phenolphthalein as an indicator. The IEC value was calculated using the expression:

$$IEC = \frac{V_{0,\text{NaOH}}C_{\text{NaOH}} - V_{\text{x,NaOH}}C_{\text{NaOH}}}{m_{\text{dry}}}$$

where $V_{0,\text{NaOH}}$ and $V_{x,\text{NaOH}}$ are the volumes of NaOH consumed in the titration without and with membranes, respectively. C_{NaOH} is the molar concentration of NaOH, which is titrated by the standard oxalic acid solution, and m_{dry} is the mass of the dry membranes. Three replicates were conducted for each sample.

Membrane stability in alkaline solution

The alkaline stability of the membranes was examined by immersing the membrane samples in N_2 -saturated 1 M KOH solution at 60 °C. The degradation of the polymer membranes

was evaluated by measuring the changes of FT-IR, IEC, and hydroxide conductivity.

Results and discussion

Base stability of imidazolium and quaternary ammonium cations

Quaternary ammonium cation-based polymers have been extensively studied and applied in formulating AEMs.⁴³ However, quaternary ammonium cations are generally sensitive towards β -hydrogen elimination and direct nucleophilic substitution under alkaline conditions.¹⁴ It has already been demonstrated that both cation chemistry and polymer backbone play important roles in influencing the alkaline stability of AEMs. Once a chemical stable cationic-group is identified, an appropriate polymer backbone can then be rationally designed.⁴²

Here, an imidazolium cation, 1-benzyl-2-methy-3- butylimidazolium ([BMBIm]⁺), was synthesized and the alkaline stability was further studied. For comparison, a typical quaternary ammonium cation, benzyltrimethylammonium ($[BnNMe_3]^+$), was also studied under the same experimental conditions. Scheme 1 shows the chemical structures of [BMBIm]⁺ and [BnNMe₃]⁺ studied in this work. The alkaline stability of two model compounds was studied by ¹H NMR spectra. Fig. 1A shows the ¹H NMR spectra of [BMBIm][Cl] before and after exposure to 1 M KOH CD₃OD/D₂O solution at 80 °C. The presence of methanol could accelerate the cation degradation and dissolve polyatomic cations better than a pure aqueous solution.²⁰ It can be found that the [BMBIm]⁺ reacts rapidly with D_2O_2 , with hydrogen/deuterium (H/D) exchange of the ring protons belonging to C-4, C-5, α-protons in the C-2 substituents and position 13, where the ¹H signals gradually disappeared. In addition, the chemical shift of the protons belonging to D_2O changed along with the degradation of the cations (1,4-dioxane as an internal standard). It should be noted that a new peak at around 2.4 ppm and 7.5 ppm appeared in the ¹H NMR spectra after a testing period of 120 h, indicating the degradation of $[BMBIm]^+$ and $[BnNMe_3]^+$, respectively. Scheme 2 shows the possible degradation mechanism of two cations in alkaline solution.14,20,44 The degradation degrees of the cations were investigated by a detailed analysis of ¹H NMR spectra (Fig. 1). The new peak at about 2.4 ppm is associated with the protons belonging to the -NH- of the degradation products (Fig. 1A). Meanwhile, a new peak at about 7.5 ppm is ascribed to the protons belonging to the degradation products of benyl alcohol (Fig. 1B). The degradation degree (in 1 M KOH, at 80 °C for 120 h) estimated by the relative integrations of the indicated ¹H resonances was determined to be 5.02% and 16.05% for [BMBIm]⁺ and [BnNMe₃]⁺, respectively, suggesting that imidazolium cations should be another promising class of functional group choice for AEMs.

Membrane preparation and characterizations

Based on the alkaline stability of the model compounds studied above, imidazolium cation based polymer membranes were



Scheme 1 Chemical structures of the model compounds studied in this work.

further synthesized and studied. The synthetic procedure and a photograph of the prepared membranes are illustrated in Scheme 3. It can be clearly seen that the resultant membranes are transparent, flexible and can be easily cut into any desired size and shape, or bent with a pair of tweezers. Fig. 2 exhibits the expected chemical shifts and intensities for the produced ionomer containing pendant imidazolium groups and poly(arylene ether sulfone) chains (inserted chemical structure and chemical shift assignments). The chemical shift at around 5.12



Fig. 1 ¹H NMR spectra for (A) [BMBIm][Cl], and (B) [BnNMe₃][Cl] in a mixture of CD₃OD, 1,4-dioxane (internal standard), KOH/D₂O solution (1 M KOH, V_{CD3OD} : $V_{D2O} = 3$: 1) at 80 °C for 120 h. The red squares indicate the degradation peaks.



Scheme 2 The possible degradation mechanisms of [BnNMe₃]⁺ (up) and [BMBIm]⁺ (bottom) in alkaline solution.

ppm, corresponding to the protons in $Ph-CH_2O$ was observed, suggesting the success of the graft-onto reaction. The chemical shifts at around 7.21, 4.45, 2.91, 1.57, 1.31, and 0.92 ppm are attributed to the attached imidazolium groups.

The successful synthesis of the imidazolium-based AEMs was further confirmed by means of the FT-IR spectra. Fig. 3 shows the FT-IR spectra of the graft copolymer AEMs in Cl⁻ and OH⁻ forms. The peaks appear at 1148 and 1377 cm⁻¹ are associated with a sulfone (-SO₂), and the peak at 1244 cm⁻¹ is a characteristic peak of aryl ethers. The peaks at 1485-1696 cm⁻¹ confirm the existence of phenylene. The absorption peak at around 1586 cm⁻¹ is attributed to the vibration of imidazolium cations. The bands at around 2848-2965 cm⁻¹ arise from aliphatic C-H stretching vibrations. The peak at around 3400 cm⁻¹ is ascribed to the stretching vibration of O-H groups, indicating the successful anion change of Cl⁻ to OH⁻. Fig. 4 shows the EDX spectra of the membranes, where only a trace amount of Cl (~0.33 wt%) was left in the membrane, indicating the successful anion exchange of the polymeric membranes. The number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(arylene ether sulfone)-g-poly(4-vinylbenzyl chloride) are determined to be 14 300 g mol⁻¹ and 1.81, respectively (Fig. S1, see ESI⁺). Based on the analysis of the ¹HNMR and EDX, the average value of y, z, n, was determined to be 26.4, 1.1 and 12.4, respectively (Fig. 2).

The morphology of the prepared membranes in the OH⁻ form was characterized by scanning electron microscopy (SEM)



Fig. 2 ¹H NMR spectrum of [PUVBIm][Cl] membrane.

and atomic force microscopy (AFM). As shown in Fig. S2 (see the ESI†) both the surface and cross-section of the membranes are uniform, compact, smooth and without any visible pores. Fig. 5 shows the surface micrographs of the produced [PUVBIm][OH] membrane. The hydrophilic/hydrophobic microphase separation could be observed. The dark regions are generally attributed to the hydrophilic domains containing 1-benzyl-2-methy-3-butylimidazolium cation groups, whereas the brighter regions are ascribed to the hydrophobic regions.^{44,45} In addition, the membranes are soluble in polar aprotic solvents, such as DMF and DMSO, while insoluble in water. These properties facilitate



Scheme 3 Synthetic procedure and photograph of the produced [PUVBIm][OH] membrane: (a) K_2CO_3 , NMP, toluene; (b) poly(4-vinylbenzyl chloride), K_2CO_3 , DMF.



Fig. 3 FT-IR spectra of the produced membrane in (A) Cl⁻ and (B) OH⁻ forms and (C) in OH⁻ form after immersion in 1 M KOH at 60 °C for 20 days.



Fig. 4 Energy-dispersive X-ray (EDX) spectra for the produced membrane in (A) Cl^- and (B) OH^- forms.



Fig. 5 AFM tapping (A) phase image and (B) height image of the produced [PUVBIm][OH] membrane. Each image frame is 2 μm \times 2 $\mu m.$

the preparation of polymer impregnated electrodes and the membrane electrode assembly.

Thermal stability

The thermal properties of the produced membranes were investigated by DSC and TGA. Fig. S3 (see the ESI[†]) shows the DSC curves of the membranes synthesized. The glass transition (T_g) temperature of poly(arylene ether sulfone), poly(4-vinyl-benzyl chloride), and the corresponding poly(arylene ether



Fig. 6 (A) TGA curves of the produced [PUVBIm][OH] membrane under the nitrogen flow. Heating rate: 10 °C min⁻¹, (B) isothermal TGA thermograms of anion exchange membranes at 150 °C under the nitrogen flow.

sulfone)-g-poly(4-vinylbenzyl chloride) membrane was determined to be 186 $^{\circ}$ C, 118 $^{\circ}$ C, and 162 $^{\circ}$ C, respectively, suggesting the successful graft-onto reaction of the poly(arylene ether sulfone).

Thermogravimetric analysis (TGA) is a key property for AEM applications. Fig. 6A shows the typical TGA curves of the membranes in the OH^- form, which were recorded from 30 to 600 °C, under a nitrogen flow, at a heating rate of 10 °C min⁻¹ to assess their short-term thermal stabilities. The membranes show a less than 5% weight loss below 200 °C, probably due to the evaporation of absorbed water or solvent (DMF). The mainchain degradation of polymers may take place at around 400 °C, which is comparable to that of the phenyltrimethylammonium



Fig. 7 Temperature dependence of the hydroxide conductivity for [PUVBIm][OH] membrane before and after immersion in N₂ saturated 1 M KOH solution at 60 °C for 20 days.

functionalized polysulfone,⁴⁶ suggesting that the membranes indeed confer a high thermal stability, far beyond the range of interest for application in AEMFCs. The long-term thermal stability of the membranes was assessed by isothermal TGA analysis at 150 °C, under the nitrogen flow. It can be seen from Fig. 6B that less than a 2% weight loss for 12 h at 150 °C was observed, indicating that the membranes have good thermal stability.

Hydroxide conductivity

The hydroxide conductivity is particularly important for AEMs used in fuel cells. Fig. 7 shows the temperature dependence of the hydroxide conductivity of the membranes in OH^- form. It can be seen that there is a positive correlation between the conductivity and temperature, probably due to the increase of free volume in favour of ion transport and the mobility of anions with rising temperature. It can be clearly seen that the conductivity of the produced membranes in the temperature range from 30 °C to 80 °C are all above 10^{-2} S cm⁻¹, which fulfils the basic conductivity requirement of AEMFCs.

Ion exchange capacity (IEC), water uptake and swelling ratio

The ion-exchange capacity (IEC), water uptake and swelling degree are all important properties for AEMs. The IEC value of the membranes reflects the exchangeable groups in the polymer, which plays a key role in determining the conductivity of AEMs. Water uptake and physical swelling are generally considered to be essential factors which influence the morphologic and mechanical stability of the membranes. Table 1 shows the values of IEC, water uptake, and swelling degree of the produced AEMs. The experimental IEC value of the AEM produced in this work is 1.65 mequiv g^{-1} . It is noteworthy that under the same experimental conditions, the produced membranes possess lower water uptake and swelling degree along with comparable IEC than the cross-linked AEMs reported, which is likely attributed to the presence of aromatic structures in the membranes.

Mechanical properties

Table 2 shows the mechanical properties of the produced dry membranes in the OH⁻ form. The tensile strength at break of the membrane is 24.14 M Pa, with a tensile modulus of 1106.24 M Pa, and elongation-at-break values of 14.08%. It should be noted that the produced membranes in this study possess higher tensile modulus and tensile strength, while a lower elongation at break, when compared with these of the Nafion-117 membranes, suggesting the membranes produced in this work are tough enough for potential use as the AEM materials.

Long-term alkaline stability

The alkaline stability of the produced membranes was investigated by immersing the membranes in a 1 M KOH solution at 60 °C, for 20 days and characterized by measuring the changes of the conductivity, IEC, ¹H NMR and FT-IR spectra of the membranes. During the testing period, none of the membranes was broken into small pieces, and all of the samples remained in a good membrane form. There was no significant conductivity loss observed for the [PUVBIm][OH] membrane before and after the immersion in a N2 saturated 1 M KOH solution at 60 °C for 20 days (Fig. 7). The IEC value is calculated to be 1.6 mequiv g^{-1} , which is close to the initial value (1.65 mequiv g^{-1}). While the IEC value of IM-PFEKS was reduced to 83% of its original IEC at 60 °C.48 It should also be noted that no new chemical shifts and peaks of the tested membrane were observed in both ¹HNMR (Fig. 8) and FT-IR spectra (Fig. 3), respectively. All of the results confirmed the highly stability of the AEMs synthesized in this work.

Conclusions

In summary, soluble imidazolium functionalized AEMs were successfully synthesized *via* the ionization of poly(4-vinylbenzyl chloride)-*graft*-poly(arylene ether sulfone) graft copolymers, and followed by anion-exchange with hydroxide. The conductivities

Table 1 Ion-exchange capacity, water uptake, and swelling degree of [PUVBIm][OH] membrane

Sample	Water uptake (%)		IEC/mequiv g ⁻¹		
		Swelling degree (%)	Experimental	Theoretical ^a	
[PUVBIm][OH]	37.25 ± 2.54	12.28 ± 1.23	1.65 ± 0.16	1.80	
PMVBIm OH]47	86.39	20.83	1.58	1.70	
PSQNOH-50 (ref. 39)	15.00	11.00	1.85	1.90	

^a Calculated from ¹H NMR and EDX spectra.

Table 2	Mechanical	properties	of the	[PUVBIm][OH]	membrane	(dry	state)
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Sample	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
[PUVBIm][OH] Nafion-117 (ref. 6)	$\begin{array}{c} 24.14 \pm 2.26 \\ 21.11 \pm 1.22 \end{array}$	$\begin{array}{c} 1106.24 \pm 64.34 \\ 6.60 \pm 1.01 \end{array}$	$\begin{array}{c} 14.08 \pm 1.29 \\ 370.62 \pm 20.82 \end{array}$



Fig. 8 $\,^{1}\text{HNMR}$ spectra of the ionomer membranes before and after immersion in 1 M KOH solution at 60 $^{\circ}\text{C}$ for 20 days.

of produced membranes at the temperature range from 30 °C to 80 °C are all above 10^{-2} S cm⁻¹, which fulfils the basic conductivity requirement of AEMFCs. The yielded membranes showed a relatively good alkaline stability in a 1 M KOH aqueous solution at 60 °C, as well as high dimensional and thermal stability, demonstrating the potential practical application in alkaline anion exchange membranes fuel cells. The results of this work suggested that it is possible to optimize the membrane performance by adopting a varied backbone and cation group structures, which should pave the way for high performance AEM design and fabrication.

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