Article

A Soluble and Conductive Polyfluorene Ionomer with Pendant Imidazolium Groups for Alkaline Fuel Cell Applications

Bencai Lin, Lihua Qiu, Bo Qiu, Yu Peng, and Feng Yan*

Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China

Supporting Information

ABSTRACT: Solvent processable polyfluorene ionomers with pendant imidazolium groups were synthesized and characterized. The synthesized polymeric membranes are transparent, flexible, and mechanically strong and exhibit hydroxide ion conductivity above 10^{-2} S/cm at room temperature. The membranes are soluble in polar aprotic solvents such as



DMSO and DMF, while insoluble in water and aqueous methanol. The solubility properties of polyfluorene ionomers enable the use for not only alkaline anion-exchange membrane but also ionomer electrode material. ¹H NMR and hydroxide ion conductivity measurements demonstrated an excellent chemical stability of the synthesized polyfluorene ionomers in high-pH solution at elevated temperatures. The results of the study suggest a feasible approach for the synthesis and practical applications of alkaline anion-exchange membranes (AEMs).

INTRODUCTION

Fuel cells have been recognized as one of the most promising power generation technologies that could provide clean and efficient energy for stationary, transportation, and portable electronics.¹⁻⁶ Among the several types of fuel cells, protonexchange membrane fuel cells (PEMFCs), which operate under acidic conditions, are attracting a great deal of interest due to their high power density, high energy-conversion efficiencies, low starting temperature, and easy handling.³ Proton-exchange membranes (PEMs), which act as a barrier between the fuel and oxidant streams and simultaneously transport protons, have been considered as one of the key components of a PEMFC.^{1,2} The most commonly used PEMs, represented by Nafion perfluorosulfonic acid membranes, have high proton conductivities, good mechanical properties, and excellent chemical stability. However, application of PEMFCs is limited by their exclusively dependence of platinum catalysts because of the limited platinum resource in nature. Therefore, there is growing interest in developing anion-exchange membranes for alkaline anion-exchange membrane fuel cells (AEMFCs), in which the charge carriers are hydroxide ions (or other anions) instead of protons.

Compared with traditional PEMFCs, one main advantage of AEMFCs is their potential to use non-precious-metal-based electrocatalysts such as silver, cobalt, or nickel due to the low overpotentials associated with electrochemical reactions at high pH.^{5,6} Furthermore, AEMFCs also offer the fuel flexibility, reduced fuel (such as methanol) crossover, and enhanced reaction kinetics for both oxygen reduction and fuel oxidation.^{7–9} All these advantages make the AEMFC technology financially and technically doable. However, application of Nafion membranes in PEMFCs is limited to

acidic conditions, and it is desirable to develop new type of polymeric anion-exchange membranes (AEMs).

A variety of polymeric AEMs containing quaternary ammonium groups, such as polysulfone,^{10–12} radiation-grafted poly(tetrafluoroethene-*co*-hexafluoropropylene) (FEP), poly-(vinylidene fluoride) (PVDF), poly(ethylene-*co*-tetrafluoroethylene) (ETFE),^{13,14} poly(2,6-dimethyl-1,4-phenylene oxide) (PPO),¹⁵ poly(ether imide) (PEI),¹⁶ and poly(vinyl alcohol) (PVA),^{17,18a} have been synthesized and extensively studied. These membranes were typically prepared by attachment of chloromethyl groups to polymer backbones and followed by quaternization to form ammonium salts. However, chloromethyl ether is carcinogenic and harmful to human, and the precise control over the degree and location of functionalization is usually difficult. Therefore, it is desirable to prepare the AEMs in a relatively simple synthetic route, especially without the use of chloromethyl ether.¹⁸

Imidazolium-based ionic liquids (ILs) have been recently applied for the preparation of anhydrous PEMs because of their unique physicochemical properties, such as good thermal stabilities, low volatility, and high ion conductivity.^{19,20} The excellent ion-exchange capabilities of ILs makes them very useful in ion-exchange applications.²¹ Recently, AEMs based on the alkaline imidazolium-type ILs have been studied by several groups.^{22,23} Compared with membranes based on quaternary ammonium salts, imidazolium group functionalized AMEs show comparable ionic conductivity, however, better chemical stability in high-pH solution.²³ Yan et al. recently synthesized imidazolium-type IL-based AEMs via in situ cross-linking of 1-

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vinyl-3-methylimidazolium iodide and followed by anionexchange with hydroxide ions.^{22a} This approach provided facile synthetic access to membranes with high conductivity and mechanical properties and low swelling degree. However, the cross-linked AMEs are insoluble in all solvents and could not be used in the catalyst layer to build an efficient three-phase boundary to improve the utilization of the catalyst particles. Therefore, developing of solvent processable AEMs is in great demand.²⁴

Herein we present a facile synthetic strategy for the synthesis of solvent-soluble AEMs based on alkaline imidazolium-type IL-functionalized polyfluorene ionomers. The membranes are mechanically strong and soluble in polar aprotic solvents such as DMSO and DMF while insoluble in water and aqueous methanol. The solvent processable polyfluorene ionomers show high hydroxide conductivity and could be applied as both AEMs and electrode materials.

EXPERIMENTAL SECTION

Materials. 1,2-Dimethylimidazole, 1,6-dibromohexane, 2,7-dibromofluorene, 4-carboxybenzeneboronic acid, 4,4'-dichlorodiphenyl sulfone, [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (PdCl₂(dppf)), chloroform, dichloromethane,*N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO),*N*,*N*-dimethylacetamide (DMAc),*N*-methylpyrrolidone (NMP), tetrahydrofuran, toluene, acetonitrile, cesium carbonate, ethyl ether, ethyl acetate, potassium hydroxide, tetrabutylammonium bromide (TBAB), sodium hydroxide, and hydrochloric acid were used as purchased. Distilled deionized water was used for all experiments.

Synthesis of 2,7-Dibromo-9,9-bis(6'-bromohexyl)fluorene (Compound 1). 2,7-Dibromo-9,9-bis(6'-bromohexyl)fluorene was synthesized as documented in previous literature.²⁵ Briefly, a mixture of 2,7-dibromofluorene (5.0 g, 15 mmol), 1,6-dibromohexane (30 mL), TBAB (0.1 g), and sodium hydroxide (30 mL, 50 wt %) aqueous solution was stirred at 60 °C for 8 h under nitrogen. After diluting the reaction mixture with dichloromethane, the organic layer was washed with water and brine. The separated organic layer was dried over magnesium sulfate, and dichloromethane was evaporated. The unreacted 1,6-dibromohexane was distilled in vacuum, and 2,7-dibromo-9,9-bis(6'-bromohexyl)fluorene (7.6 g, 75.8%) was obtained as a white crystal by chromatography with petroleum ether as the eluent. ¹H NMR (CDCl₃) δ (ppm): 7.53–7.50 (d, 2H) 8.0 Hz), 7.46–7.44 (d, 2H), 7.42 (s, 2H), 3.30–3.27 (t, 4H), 1.93–1.89 (t, 4H), 1.68–1.55 (m, 4H), 1.20–1.17 (m, 4H), 1.09–1.06 (m, 4H), 0.57(m, 4H).

Synthesis of 2,7-Di(4'-phenol)-9,9-bis(6'-bromohexanyl)-fluorene (Compound 2). 2,7-Di(4'-phenol)-9,9-bis(6'bromohexanyl)fluorene was synthesized as follows:²⁶ A mixture containing 2,7-dibromo-9,9-bis(6'-bromohexyl)fluorene (5.0 g, 7.7 mmol), 4-carboxybenzeneboronic acid (1.2 g, 8.5 mmol) in THF (40 mL), and 2.0 M aqueous K₂CO₃ solution (30 mL) was charged with argon for 30 min. Then 160 mg of PdCl₂(dppf) was added under an argon atmosphere, and the mixture was then stirred at 70 °C for 24 h. The crude product was extracted with 50 mL of CHCl₃ three times. The combined organic phase was washed with brine and dried over anhydrous MgSO4, and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography using ethyl acetate/petroleum ether 1/4 (v/v) as eluent to obtain white solids (3.46 g, 66.2%). ¹H NMR (400 MHz, CDCl₃) δ : 7.74–7.73 (d, 2H), 7.58 (d, 2H), 7.56 (d, 2H), 7.54-7.52 (s, 2H), 7.49 (d, 2H), 6.96-6.94 (d, 4H), 4.88 (s, 4H), 3.26 (t, 4H), 3.28-3.24 (br, 4H), 2.04-2.00 (br, 4H), 1.68-1.61 (br, 6H), 1.21-1.16 (d, 4H), 1.10-1.07 (br, 4H), 0.70 (br, 4H).

Synthesis of 2,7-Di(4'-phenol)-9,9-bis(6'-(1,2dimethylimidazole))fluorene Bromine (Compound 3). A solution of 2,7-di(4'-phenol)-9,9-bis(6'-bromohexanyl)fluorene (2.0 g, 2.96 mmol) and 1,2-dimethylimidazole (1 mL, 12.5 mmol) in 20 mL of CH₃CN was stirred at 70 °C for 24 h. Upon cooling down to room temperature, the solvent and unreacted 1,2-dimethylimidazole were removed under vacuum. The residue was washed with ethyl acetate three times prior to being dried under vacuum at 80 °C for 24 h to produce the final yellow solid (2.45 g, 95.3%). ¹H NMR (400 MHz, DMSO) δ : 9.58 (d, 2H), 7.80–7.82 (d, 2H), 7.64 (d, 2H), 7.58–7.54 (br, 6H), 7.51(br, 2H), 7.48(br, 2H), 6.87–6.89 (d, 4H), 3.94–3.90 (t, 4H), 3.66 (s, 6H), 2.42 (s, 6H), 2.07 (br, 4H), 1.45 (br, 4H), 1.02 (br, 4H), 0.54 (br, 4H).

Synthesis of Polyfluorene Ionomer Containing Pendant Alkaline Imidazolium Ionic Liquids. A typical synthesis procedure was as follows: A mixture containing 4.34 g of 2,7-di(4'-phenol)-9,9bis(6'-(1,2-dimethylimidazole))fluorene bromine (5.0 mmol), 1.44 g of 4,4'-dichlorodiphenyl sulfone (5.0 mmol), and 3.58 g of Cs₂CO₃ (11.0 mmol) were added into a 100 mL three-neck flask equipped with a magnetic stirrer, a Deane-Stark trap, and a nitrogen inlet. Then, 25 mL of dried DMSO and 13 mL of toluene were added into the reaction flask under a nitrogen atmosphere. The reaction bath was heated to 130 °C to dehydrate the system for 4 h. After toluene and water was distilled off, the temperature of reaction was raised gradually to 140 °C and then stirred for 8 h. The reaction was cooled to room temperature, and 20 mL of DMSO was added to dilute the highly viscous solution, and the solution was then poured into deionized water. The precipitated polymers were washed with deionized water and ethanol several times prior to being dried under vacuum at 80 °C for 24 h to produce the final product.

Membrane Preparation and Evaluation. The membranes were prepared by casting a DMF solution of synthesized polyfluorene ionomers (2 wt %) onto a leveled Teflon sheet. To avoid air bubbles, the membranes were slowly dried at 80 °C for 12 h and then dried in vacuo at 100 °C for 24 h, forming thin films with the thickness of about 25 μ m. The resultant membranes were immersed in a N₂-saturated 1 M KOH (or Na₂CO₃) solution at 60 °C for 48 h to convert the membrane from Br⁻ to OH⁻ or CO₃^{2–} form.²² This process was repeated three times to ensure a complete conversion displacement. Then the converted membranes were immersed in a N₂-saturated deionized water for 24 h and washed with deionized water until the pH of residual water was neutral.

Characterization. ¹H NMR spectra were recorded on a Varian 400 MHz spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Varian CP-3800 spectrometer in the range 4000–400 cm⁻¹. Thermal analysis was carried out on Universal Analysis 2000 thermogravimetric analyzer (TGA). Samples were heated from 40 to 500 °C at a heating rate of 10 °C/min under a nitrogen flow. The tensile properties of membranes were measured by using an Instron 3365 at 25 °C at a crosshead speed of 5 mm/min. Scanning electron microscopy (SEM) images were taken with a Philips XL 30 FEG microscope with an accelerating voltage of 10 kV. Energy dispersive X-ray spectroscopy (EDX) measurements were performed with the spectrometer attached on the Hitachi S-4700 FESEM.

Hydroxide lon Conductivity. The resistance value of the membranes was measured over the frequency range from 1 Hz to 1 MHz by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an electrochemical workstation (CHI660C). All the samples were fully hydrated in N₂ saturated deionized water for at least 24 h prior to the conductivity measurement. Conductivity measurements under fully hydrated conditions were carried out in a chamber filled with a N₂-saturated deionized water to maintain the relative humidity at 100% during the experiments. All the samples were equilibrated for at least 30 min at a given temperature. Repeated measurements were taken with 10 min interval until no more change in conductivity was observed. The ionic conductivity σ (S/cm) of a given membrane can be calculated from

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

where l is the distance (cm) between two stainless steel electrodes, A is the cross-sectional area (cm²) of the membrane, obtained from the membrane thickness multiplied by its width,

Scheme 1. Synthetic Procedure and Photograph of Polyfluorene Ionomer Membrane^a



"Reagents and conditions: (a) 50 wt % KOH, TBAB, 60 °C, 8 h; (b) 4-carboxybenzeneboronic acid, PdCl₂(dppf), 1 mol %, 70 °C, 24 h, (c) 1,2dimethylimidazole, 70 °C, 24 h.



Figure 1. ¹H NMR spectra of synthesized polyfluorene ionomer with pendant ionic liquids.

and *R* is the membrane resistance value from the ac impedance data (Ω) .

Water Uptake and Swelling Ratio. The membrane samples were soaked in the N₂-saturated deionized water at room temperature for 24 h. The hydrated polymer membranes were taken out, and the excess water on the surface was removed by wiping with a tissue paper and weighed immediately (W_w). Then the wet membrane was dried under vacuum at 80 °C until a constant dry weight was obtained (W_d). The water uptake W was calculated with the equation

$$W(\%) = \frac{W_{\rm w} - W_{\rm d}}{W_{\rm d}} \times 100\%$$

where W_d and W_w are the mass of the dry and water-swollen samples, respectively.

The swelling ratio was characterized by linear expansion ratio (LER), which was determined by the difference between wet and dry dimensions of a membrane sample (3 cm in length and 1 cm in width). The calculation was based on the equation

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). Ion-exchange capacities (IEC) were determined by a back-titration. The AEMs were immersed in 100 mL

of 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

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

where $V_{0,\text{NaOH}}$ and $V_{x,\text{NaOH}}$ are the volume of the NaOH consumed in the titration without and with membranes, respectively, C_{NaOH} is the mole concentration of the NaOH, which are 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 polymer membranes was evaluated by measuring the changes of ¹H NMR, FT-IR, and hydroxide conductivity.

RESULTS AND DISCUSSION

Herein we present a facile synthetic strategy for the synthesis of solvent-soluble AEMs based on alkaline imidazolium-type ionic liquids (ILs)-functionalized polyfluorene ionomers. Scheme 1 shows the synthetic procedure for polyfluorene ionomers. We developed a novel fluorene derivative (compound 3) which contains saturated alkyl side chains and imidazolium groups.



Figure 2. FT-IR spectra of polyfluorene ionomers in (A) Br⁻ and (B) OH⁻ forms and (C) in OH⁻ form immersing in 1 M KOH for 400 h.



Figure 3. Energy dispersive X-ray (EDX) spectra for polyfluorene ionomer membranes in (A) Br⁻ and (B) OH⁻ forms with silicon as the substrate.



Figure 4. SEM images of polyfluorene ionomer membrane in OH⁻ form: surface (A) and cross-sectional view (B).

The purity and chemical structure of the synthesized compounds 1, 2, and 3 were confirmed by ¹H NMR measurements (see Supporting Information). The polyfluorene ionomer with pendant imidazolium groups was obtained from compound 3 and 4,4'-dichlorodiphenyl sulfone by nucleophilic substitution polycondensation (Scheme 1). By employing monomers with the ionic liquid moiety already present, AEM synthesis is greatly simplified because postpolymerization modifications could be avoided. The chemical structure of the resultant polyfluorene ionomers was characterized by ¹H NMR. Figure 1 exhibits the expected chemical shifts and intensities for a pure polyfluorene ionomer containing pendant alkaline

imidazolium ionic liquids (inserted chemical structure and chemical shift assignments). Chemical shifts of the fluorene units are observed at 7.69 and 7.80 ppm. The chemical shifts at 2.44, 3.67 ppm and the inserted spectrum which shows several minor chemical shifts at 7.51 ppm are attributed to the attached imidazolium groups.

The chemical structure of the resultant polyfluorene ionomers was further investigated by means of FT-IR spectrum. Figure 2 shows the FT-IR spectra of the polyfluorene ionomer membranes in Br⁻ and OH⁻ forms produced by solution casting. Membranes in both two forms show the absorption bands of methylene (CH₂) at 2856–2935 cm⁻¹. The peaks at

1465–1637 cm^{-1} confirm the existence of polyphenylene. Absorption peaks at around 1586 and 744 cm⁻¹ arise from vibrational mode of imidazolium cations. The peaks at 1317 and 1151 cm^{-1} confirm the existence of sulfone (SO₂), and the peak at 1245 cm^{-1} is the characteristic peak of aryl ethers. The results clearly confirm the successful copolymerization of compound 3 and 4,4'-dichlorodiphenyl sulfone. Compared with Figure 2A, a stronger absorption peak at around 3400 cm⁻¹ in Figure 2B,C is attributed to the stretching vibration of O-H groups, indicating the successful anion change of Br⁻ to OH⁻. Furthermore, no obvious changes between parts B and C of Figure 3 are observed, indicating that the copolymer is stable in alkaline solutions. Moreover, the results of energy dispersive X-ray (EDX) spectra (Figure 3) show that no bromine could be detected in OH- form, which again confirms the anionexchange of the polyfluorene ionomers.

Membranes were prepared by dissolving the polyfluorene polymers in DMF followed by casting on a leveled Teflon sheet. The membranes were dried under vacuum to remove residual solvent. The resultant membranes are transparent and flexible and can be easily cut into any desired sizes and shapes (Scheme 1). The morphology of the membranes in OH⁻ form was investigated by scanning electron microscopy (SEM). SEM images of the surface and cross section of the membranes showed that the produced membranes are uniform, compact, and without any visible pores (Figure 4). In addition, the synthesized alkaline polyfluorene ionomers exhibited outstanding solubility in polar aprotic solvents, such as DMF, DMAc, DMSO, and NMP, while insoluble in water and aqueous methanol. These solubility properties of polyfluorene ionomers enable the use for not only alkaline anion-exchange membrane but also ionomer electrode material.

The thermal stability of AEMs is always a concern for AEMFCs because some AEMs based on quaternary ammonium salts are usually unstable in KOH solution at elevated temperature.^{10a} Aromatic polymers are generally considered as the preferred candidates for high-temperature fuel cell applications due to their excellent thermal stability. Figure 5



Figure 5. TGA curves of polyfluorene ionomer membranes under nitrogen flow. Heating rate: 10 $^\circ C/min.$

shows the typical thermogravimetric analyzer (TGA) curves of produced copolymer membranes in Br^- and OH^- forms which were recorded under a nitrogen flow from 40 to 500 °C at a heating rate of 10 °C/min to assess their short-term thermal

stabilities. Both the membranes show a slight weight loss (less than 4 wt %) below 200 °C, probably corresponding to the evaporation of absorbed water or solvents (such as DMF). The weight loss region at temperatures above 300 °C may due to the degradation of the copolymer backbone. The thermal stability of the AEMs produced in this work is better than that of reported quaternary ammonium polysulfone^{10a} and quaternary guanidinium poly(arylene ether sulfone)s containing hydroxide groups.^{11a} These results confirm that this type of alkaline IL-based copolymer membranes indeed confers a high thermal stability, far beyond the range of interest for application in AEMFCs.

The tensile strength of the membrane in OH^- form is 50.41 MPa, with the Young's modulus of 1610.32 MPa, and values of elongation at break of 12.63% (Table 1). Compared with

Table 1. Mechanical Properties of Polyfluorene Ionomer, Nafion-117, and PSQNOH-50

membrane	tensile strength	tensile modulus	elongation at
	(MPa)	(MPa)	break (%)
polyfluorene ionomer	50.41	1610.32	12.63
Nafion-117	21.11	6.60	370.62
PSQNOH-50 ^{11d}	51.2	1520	28.4

Nafion-117, AEMs in this study showed a higher tensile strength and tensile modulus while a lower elongation at break because of the rigid ring-structured backbone. The mechanical properties of AEMs in the present work are equivalent to PSQNOH-50 which has similar polymeric backbone.^{11d} These results indicate that the AEMs produced in this work are tough and ductile enough for potential use as AEM materials.

Table 2 shows the values of ion-exchange capacity (IEC), water uptake, swelling degree, and conductivity of the produced polyfluorene ionomer membranes. The IEC values are generally considered responsible for ion transfer and thus are an indirect and reliable approximation of the ion conductivity. The IEC value of produced membrane is calculated to be 0.98 mmol/g, which is close to the theoretical value of polyfluorene (1.04 mmol/g). Swelling behavior of the membrane is an essential factor influencing the mechanical properties and the morphologic stability of membranes. Generally, the water uptake and swelling degree increase with the IEC values. However, the membranes have less water uptake and swelling degree compared to the cross-linked membrane with the same IEC value,^{22a} probably due to the presence of the aromatic backbone in the membrane. It should be noted that the water swelling degree of the membranes is even lower than that of Nafion-117 under the same experimental conditions. Such a good dimensional stability of membranes suggests a feasible approach for practical applications in fuel cells.

The hydroxide conductivity of the membranes is of particular important and plays a significant role in fuel cell performance. The conductivity of AEMs is significantly influenced by the IEC values because it links to the density of ionizable functional group in the membranes. As the IEC values increasing, which implying the improved hydrophilic properties of the membrane, the membrane becomes more hydrophilic and absorbs more water, which facilitates ion transport. Here, the conductivity of fully hydrated AEMs was measured by the four-probe method. The choice of the four-probe instead of two-probe method for the conductivity measurements is because the effect of contact

Table 2. Ion-Exchange Car	pacity (IEC), W	ter Uptake, Swelling	g Degree, and	Conductivity of AEMs
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	IEC (mequiv g ⁻¹)		water uptake (%) ^b		swelling degree $(\%)^b$		conductivity (×10 ⁻² S cm ⁻¹)	
membrane	theor ^a	expt	30 °C	60 °C	30 °C	60 °C	30 °C	60 °C
polyfluorene ionomer	1.04	0.98	17.26	24.76	5.56	10.81	2.35	4.28
Nafion-117	0.91		19.48	27.11	6.09	12.87	5.91	9.55
PSQNOH-50 ^{11d}	1.90	1.85		19		12		3.20
^{<i>a</i>} Calculated from monomer	ratio. ^{<i>b</i>} After im	mersing in wa	ter at 60 °C fo	r 24 h, average	of two trials.			

resistance on the four-probe ionic conductivity is much lower than that on two-probe method, especially in high humidity.²⁷ For comparison, the conductivity of AEMs was also measured by two-probe method, and the results are shown in Figure S4 (see Supporting Information). Figure 6 shows the reproducible



Figure 6. Conductivity Arrhenius plots of polyfluorene ionomer membranes in OH^- and CO_3^{2-} forms and Nafion-117 as a function of temperature.

plot of ionic conductivity of polyfluorene ionomer membranes in both OH^- and CO_3^{2-} forms as a function of temperature. For comparison, the conductivity of Nafion-117 was also measured under the same conditions. The ionic conductivity of the membranes gradually increases with the increase of temperature. For example, the ionic conductivity of polyfluorene ionomer membranes in OH^- form increased from 2.35 \times 10^{-2} to 4.28×10^{-2} S/cm, if the temperature rose from 30 to 60 °C (Figure 6). This is mainly due to faster migration of ions and higher diffusivity with the increasing of temperature. Simultaneously, the polymeric chain will be more flexible and more water will be adsorbed by the membrane at a higher temperature, leading to a more swollen membrane structure and wider ion transferring channel, resulting in more propitious ion transfer.^{11,22a,c} The conductivity of polyfluorene ionomer membranes in OH⁻ form was about 2-fold higher than that in CO_3^{2-} form probably because the infinite diffusion coefficient of OH^- anions is about 3.7 times higher than that of CO_3^{2-} anions.^{11b} The results suggest other factors such as cationanion interaction or insufficient equilibrium time may also impact the anion mobility.^{11b} The hydroxide conductivities of the synthesized polyfluorene ionomer membranes is comparable to the ionic conductivity of tetraalkylammonium-functionalized AEMs with the similar IEC values.^{11a}

Chemical stability of the AEMs is still a challenge for the practical application of fuel cells, especially in high-pH environment of alkaline fuel cells. Here, the alkaline stability of produced AEMs was investigated by immersing the membrane samples in 1 M KOH solution at 60 $^{\circ}$ C. The changes of ionic conductivity and the chemical structure of the tested membranes were characterized. Figure 7 shows ¹H NMR



Figure 7. $^1{\rm H}$ NMR spectra of polyfluorene ionomer membranes in Br $^-$ form and OH $^-$ form and after immersing in 1 M KOH solution at 60 $^{\circ}{\rm C}$ for 400 h.

spectra of the membranes after the alkaline stability test. It should be noted that no new chemical shifts of polymers were observed even after 400 h testing period in 1 M KOH at 60 $^{\circ}$ C, indicating an excellent alkaline stability of the membranes in high-pH alkaline solution. These results further support the FT-IR spectra results, as shown in Figure 2.

The alkaline stability of the polyfluorene ionomer membranes was further proved by measuring the hydroxide conductivity changes after certain testing time. The membranes maintain their conductivity even after immersion in 1 M KOH solution at 60 °C for 400 h, and the IEC value is 0.92 mequiv/ g, which is close to the initial value (0.98 mequiv/g). All these results indicate excellent long-term alkaline stability of AEMs in high-pH environment (Figure 8). AEMs functionalized with quaternary ammonium salts usually show high room temperature conductivity of hydroxide. However, hydroxide is an aggressive nucleophile and could degrade the quaternary ammonium cation sites on the polymeric AEMs because of nucleophilic substitution and (or) Hofmann elimination reaction, especially at high pH and elevated temperature.¹⁰ Although the Hofmann elimination reaction could be avoided by synthesizing β -hydrogen-absent quaternary ammoniums, quaternary ammonium-functionalized polymers are still suffering from the nucleophilic substitution reaction. The excellent alkaline stability of alkaline ionic liquid-functionalized polyfluorene ionomers is probably due to the resonance effect of the conjugated imidazole rings, which reduce the positive charge density of the cation and weaken the interaction with



Figure 8. Conductivity Arrhenius plots of the polyfluorene ionomer membranes after immersion in 1 M KOH at 60 $^\circ$ C.

the hydroxide ions and thus dramatically improve the imidazolium group-functionalized AEMs.^{22a,28}

CONCLUSIONS

In summary, alkaline imidazolium-type IL-functionalized polyfluorene ionomer AEMs were synthesized and applied for alkaline fuel cell applications. The AEMs prepared via polycondensation polymerization, casting from DMF solution, and followed by anion-exchange with OH⁻ anions are flexible and tough enough for potential use as the AEM materials. The hydroxide conductivity of the produced polyfluorene ionomer AEMs is above 10^{-2} S cm⁻¹ at room temperature, which fulfills the basic requirement of alkaline fuel cells. In addition, the synthesized alkaline ionic liquid-functionalized polyfluorene ionomer membranes show an excellent thermal stability, mechanically properties, and superior long-term stability in high-pH solution at elevated temperature, which indicated that the produced AEMs could overcome the drawbacks of alkyl quaternary ammonium-functionalized polymers. The solvent processability of these polyfluorene ionomers enables them to be used as both an AEM and ionomer electrode material. Compared with alkyl quaternary ammonium-functionalized polymers, the main advantage of the synthetic strategy reported here is that the synthetic procedures of AEMs are simple because postpolymerization modifications could be avoided. Furthermore, the use of chloromethyl ether which is harmful to humans could be avoided.

ASSOCIATED CONTENT

S Supporting Information

¹H NMR spectra of synthesized compounds and the conductivity measurements of AEMs. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: fyan@suda.edu.cn.

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