Cross-Linked Alkaline Ionic Liquid-Based Polymer Electrolytes for Alkaline Fuel Cell Applications

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We report an effective and simplified procedure for the synthesis of cross-linked alkaline anion-exchange membranes (AEMs). AEMs based on alkaline imidazolium-type ionic liquids (ILs) were prepared via in situ cross-linking of 1-vinyl-3-methylimidazolium iodide ([VMIm][I]) with styrene and acrylonitrile, and followed by anion-exchange with hydroxide ions. The resulting cross-linked copolymer membranes exhibit high hydroxide ion conductivity (above 10^{-2} S/cm at room temperature) and good mechanical properties. The thermal stability of the produced AEMs is comparable to that of quaternary ammonia aromatic polymers. The membranes display an excellent chemical stability up to 400 h in high pH solution without an obvious loss of ion conductivity and mechanical properties. This synthetic procedure avoids the use of chloromethyl methyl ether and solution casting generally used for AEMs preparation. The results of the study suggest a feasible approach for the synthesis and practical applications of alkaline AEMs and are expected to promote the widespread use of alkaline fuel cells.

Introduction

Proton-exchange membrane fuel cells (PEMFCs) 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.[1,2] They are attracting a great deal of interest, because of their high power density, high energy-conversion efficiencies, low starting temperature, and easy handling.[3] Although PEMFCs are considered to be one of the most important technologies in the 21st century and great progress has been made in recent decades, there are still some scientific and technological difficulties that should be overcome before widespread commercialization. These issues mainly include the high costs of the platinum catalysts, carbon monoxide poisoning of noble-metal catalysts at low temperatures, and the limited working lifetime of proton-exchange membranes (PEMs).[3-6]

Among these obstacles, the dependence of platinum catalysts is the most important consideration in such power sources, because of the limited platinum resource in nature.[5,6] In addition, the most widely used Nafion membranes are expensive and not environmental friendly, with regard to recycling and the disposal of fluorinated polymers. Therefore, there is growing interest in developing anion-exchange membrane fuel cells (AEMFCs), rather than PEMFCs.

AEMFCs are a type of fuel cell that uses the alkaline anion-exchange membrane as the polymer electrolyte membrane, in which the charge carriers are hydroxide ions (or other anions) instead of protons. Compared to the traditional PEMFCs, both fuel oxidation and the oxygen reduction reaction kinetics have been greatly enhanced in AEMFCs. In addition, the catalysts are generally more stable in basic media and these improvements enable the use of nonprecious metal catalysts (such as nickel and silver),[5,6] thereby dramatically reducing the cost of fuel cells. Furthermore, AEMFCs also offer fuel flexibility, reduced fuel crossover, and high fuel cell efficiencies.[7-9] These advantages make the AEMFC technology financially and technically feasible.

The anion-exchange membrane (AEM), which acts as an electrolyte to transport anions from cathode to anode,

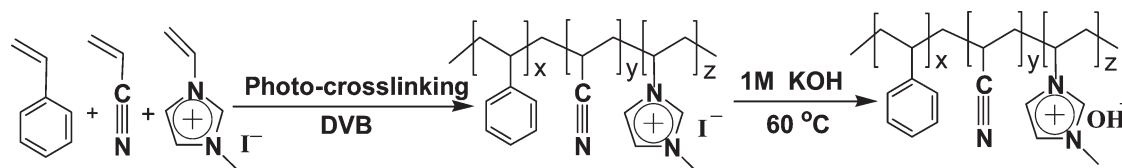*Author to whom correspondence should be addressed. E-mail: fyan@suda.edu.cn.

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Scheme 1. Reaction Scheme for the Preparation of Alkaline Ionic Liquid (IL)-Based Anion Exchange Membranes

is one of the key components of AEMFCs. AEMs have received much attention recently, and most of the studies are related to the development of materials based on quaternized polymers that contain quaternary ammonium groups. A variety of AEM-quaternized polymers, such as polysulfone,[5,10−12] 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(etherimide) (PEI),[16] and poly(vinyl alcohol) (PVA),[17,18] have been studied extensively. Most of these AEMs were prepared via a relatively complicated procedure: chloromethylation using chloromethyl ether and followed by quaternary of the polymers with tertiary amines. Since chloromethyl ether is carcinogenic and harmful to humans, it is desirable to prepare the AEMs via a relatively simple synthetic route, especially without the use of chloromethyl ether.[18]

In addition, most of the AEMs previously studied were prepared based on the solution casting method. However, one drawback of the solution-cast membranes is that the mechanical properties (such as swelling resistance) are generally poorer than these of cross-linked polymers, and, moreover, the treatment of hazardous chemical solvents is also a tedious problem. Chemical cross-linking is a feasible and effective method for the preparation of AEMs, which could not only suppress the water swelling but also improve the mechanical strength of membranes.[19]

Coates et al. recently reported the preparation of cross-linked membranes via ring-opening metathesis polymerization.[9] The chemical cross-linking supports the polymeric materials with both high conductivities and good mechanical properties.

Herein, we present a facile synthetic strategy for the synthesis of cross-linked AEMs based on alkaline ionic liquids (ILs), without the use of chloromethyl ether. ILs are mostly room-temperature organic salts with low volatility and high ion conductivity and have been used for the preparation of high-temperature PEMs[20] and AEMs.[21] The excellent ion-exchange capabilities of ILs make them very useful in many ion-exchange applications.[22] Polystyrene and polyacrylonitrile are well-known membrane-forming materials, because of their excellent chemical, thermal, and mechanical stability, and they have been applied in the preparation of polyelectrolytes.[20b,c,23] In this investigation, an IL monomer, 1-vinyl-3-methylimidazolium iodide ([VMIm][I]) was photocross-linked in situ with the proper monomer oils (styrene and acrylonitrile). The resulting membranes were converted to OH$^-$ form by changing the anions in the IL moiety of the copolymers with hydroxide anions, as shown in Scheme 1. It is expected that the hydrophilic region (alkaline ILs) of the membranes facilitates the transport of the hydroxide anion, while the hydrophobic region offers good mechanical strength. The hydroxide conductivity and mechanical properties of the membrane can be balanced by adjusting the content of alkaline ILs and cross-linking agents. The properties of the membranes, such as water uptake, swelling degree, ionic exchange capability (IEC), hydroxide ion conductivity, and chemical stability in high pH solution were investigated.

Experimental Section

Materials. Styrene, acrylonitrile, *N*-vinylimidazole, iodomethane, divinylbenzene (DVB), benzoin ethylether, ethylether, ethyl acetate, potassium hydroxide, sodium hydroxide, and hydrochloric acid were used as purchased. All of the vinyl monomers were made inhibitor-free by passing the liquid through a column filled with base Al_2O_3. Distilled deionized water was used for all experiments.

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Synthesis of 1-vinyl-3-methylimidazolium Iodide ([VMIm][I]). [VMIm][I] was synthesized by stirring the mixture of *N*-vinyl-imidazole with an equivalent molar amount of iodomethane at room temperature under nitrogen atmosphere. The resultant viscous oil was washed with ethyl ether three times and then dried in dynamic vacuum at room temperature for 24 h before use. ^{1}H NMR (400 MHz, D$_2$O): 8.98 (1H, s, N−CH−N), 7.76 (1H, s, N−CH=C), 7.52 (1H, s, C=CH−N), 7.12−7.17 (1H, q, N−CH=C), 5.81−5.78 (1H, q, C=*H*CH), 5.44−5.42 (1H, d, C=HC*H*), 3.94 (3H, s, N−CH$_3$). ^{13}C NMR (400 MHz, D$_2$O): δ 128.42, 124.27, 119.51, 109.59, 36.45. Calcd for C$_6$H$_9$N$_2$I: C, 30.53; H, 3.84; N, 11.87. Anal. Found: C, 28.68; H, 3.99; N, 11.06.

Preparation of Alkaline IL-Based Membranes. A mixture of styrene/acrylonitrile (1:3 weight ratio, 90−60 wt %), [VMIm][I] (10−40 wt %), divinylbenzene (2−10 wt %, relative to the formulation, based on the weight of monomer), and 1 wt % of benzoin isobutyl ether (as a photoinitiator) was stirred and ultrasonicated to obtain a homogeneous solution, which was then cast into a glass mold and photo-cross-linked via irradiation with ultraviolet (UV) light (wavelength of 250 nm) in a glass mold for 30 min at room temperature. The resultant IL-based membranes were immersed in a N$_2$-saturated 1 M KOH solution (KOH: [PVMIm][I] = 10:1, mole ratio) at 60 °C for 24 h to convert the membrane from I$^-$ to OH$^-$ form.[24] This process was repeated three times to ensure complete conversion displacement. The converted membranes then were immersed in N$_2$-saturated deionized water for 24 h and washed with deionized water until the pH of residual water was neutral.

Characterization. NMR spectra were recorded on a Varian 400 MHz spectrometer. Fourier transform infrared (FT-IR) spectra of the polymers were recorded on a Varian CP-3800 spectrometer in the range of 4000−400 cm^{-1}. Thermal analysis was carried out by Universal Analysis 2000 thermogravimetric analyzer (TGA). Samples were heated from 30 °C to 500 °C at a heating rate of 10 °C/min under a nitrogen flow. The tensile properties of membranes were measured using an Instron Model 3365 device at 25 °C at a crosshead speed of 5 mm/min. Scanning electron microscopy (SEM) images were taken with a Philips Model 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 Model S-4700 field-emission scanning electron miroscopy (FESEM) system.

Hydroxide Ion 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 (Zahner IM6 EX). The choice of the four-probe method instead of the two-probe method for the conductivity measurements is made because the effect of contact resistance on the four-probe ionic conductivity is much lower than that on two-probe method, especially in high humidity.[25] All the samples were fully hydrated in N$_2$-saturated deionized water for at least 24 h prior to the conductivity measurement. Conductivity measurements under fully hydrated conditions were conducted in a chamber filled with N$_2$-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 obtained at 10-min intervals, until no more change in conductivity was observed. The ionic conductivity of a given membrane (σ, expressed in units of S/cm) can be calculated from

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

where *l* is the distance between two stainless steel electrodes (given in centimeters), *A* the cross-sectional area of the membrane (given in units of cm^2), obtained from the membrane thickness multiplied by its width, and *R* the membrane resistance value from the AC impedance data (Ω).

Water Uptake and Swelling Ratio. The membrane samples were soaked in the N$_2$-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 (denoted by the variable W_w). The wet membrane then was dried under vacuum at a fixed temperature of 80 °C until a constant dry weight was obtained (W_d). The water uptake *W* was calculated with the following equation:

$$W\ (\%) = \frac{(W_w - W_d)}{W_d} \times 100$$

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

The swelling ratio was characterized by the linear expansion ratio (LER), which was determined using 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 following equation:

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

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

Ion Exchange Capacity (IEC). Ion exchange capacities (IECs) were determined via 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:

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

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 molar concentration of the 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 stability of the membranes in alkaline solution was examined by immersing the membrane samples in N$_2$-saturated 1 and 10 M KOH solution at 60 °C, respectively. The degradation of polymer membranes is evaluated by measuring the changes of hydroxide conductivity, mechanical properties, and IEC values.

Results and Discussion

To prepare the alkaline IL-based AEMs, a homogeneous solution containing [PVMIm][I] (10−40 wt %),

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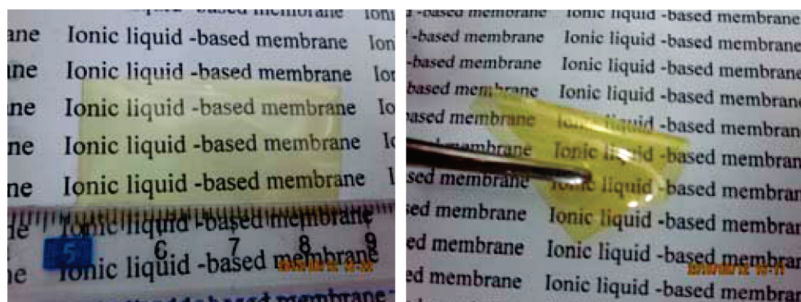
Figure 1. Photographs of the [PVMIm][OH]$_{40}$-DVB$_4$ membrane with a thickness of ~50 μm.
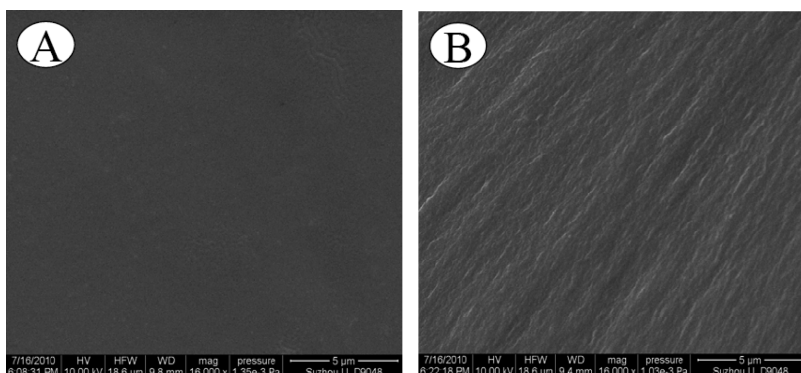

Figure 2. SEM images of the [PVMIm][OH]$_{40}$-DVB$_4$ membrane: (A) surface view and (B) cross-sectional view.

styrene/acrylonitrile (1:3 weight ratio, 90−60 wt %), and DVB (2−10 wt % to the formulation based on the weight of monomer) was photo-cross-linked by irradiation with UV light. The resultant copolymer membranes were immersed in N$_2$-saturated 1 M KOH solution at 60 °C for 24 h to convert the membrane from I$^-$ to OH$^-$ form. The produced membranes are denoted as [PVMIm][OH]$_x$-DVB$_y$, the subscript x and y indicate the weight ratio of [PVMIm][OH] and DVB in the membrane, respectively.

The cross-linked membranes with the [PVMIm][OH] content up to 40 wt % were obtained. All the membranes are transparent, flexible, and can be easily cut into any desired sizes and shapes or be bent with one pair of tweezers, even under dry conditions (see Figure 1). The morphology of the membranes in OH$^-$ form was characterized by scanning electron microscopy (SEM), which showed that the resultant membranes are uniform, compact, and without any visible pores on the surface and in the interior of the membranes (see Figure 2).

Figure 3 shows the Fourier transform infrared (FT-IR) spectra of the membranes in I$^-$ and OH$^-$ forms. Membranes in both two forms show the absorption bands of the cyano groups (C≡N) at 2242 cm^{-1}. The peaks at 3029−3150 and 1450−1600 cm^{-1} confirm the existence of polystyrene. Absorption peaks at ~1582 cm^{-1} and ~763 cm^{-1} arise from the vibrational mode of imidazolium cations. A strong absorption peak at 3439−3612 cm^{-1} in the OH$^-$ form membranes (Figure 3B) is attributed to the stretching vibration of O−H groups, indicating the successful anion change from I$^-$ form to OH$^-$ form. Moreover, the results of energy-dispersive X-ray (EDX) spectra show that no I$^-$ or K$^+$ ions could be detected in the OH$^-$ form
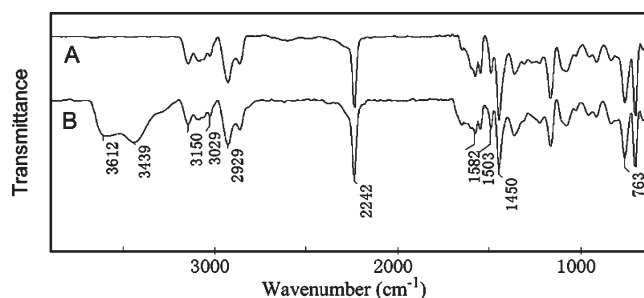

Figure 3. Fourier transform infrared (FT-IR) spectra of (A) [PVMIm][I]$_{40}$-DVB$_4$ and (B) [PVMIm][OH]$_{40}$-DVB$_4$ membranes.

membrane, which again confirms the anion exchange of membranes (see Figure 4).

Table 1 shows the mechanical properties of the produced AEMs, measured at room temperature. The tensile strength of all the membranes is in the range of 10−50 MPa, with a tensile modulus of 321−2779 MPa, and elongation-at-break values of 13%−136%. Chemical cross-linking is an effective method to improve the mechanical properties of polymer membranes. It is not surprising that the increase of DVB content could significantly increase the tensile strength and modulus of the membrane. When the content of DVB was increased from 2 wt % to 10 wt %, the tensile modulus of the membranes was increased from 321 MPa to 894 MPa, which significantly increased the membrane dimensional stability. Compared to Nafion-117, the produced membranes show a slightly lower tensile strength and a higher tensile modulus. However, the mechanical properties of produced AEMs are almost equivalent to those of quaternary ammonia poly(arylene ether sulfone).[11a] These results indicate that
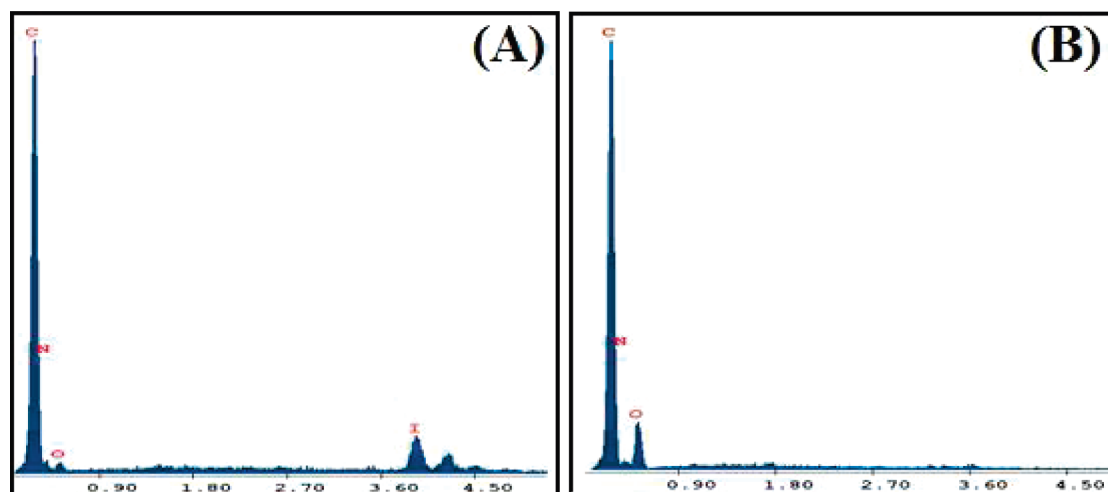
Figure 4. Energy-dispersive X-ray (EDX) spectra for (A) [PVMIm][I]$_{40}$-DVB$_4$ and (B) [PVMIm][OH]$_{40}$-DVB$_4$.

Table 1. Mechanical Properties of the [PVMIm][OH]$_x$-DVB$_y$ Membranes

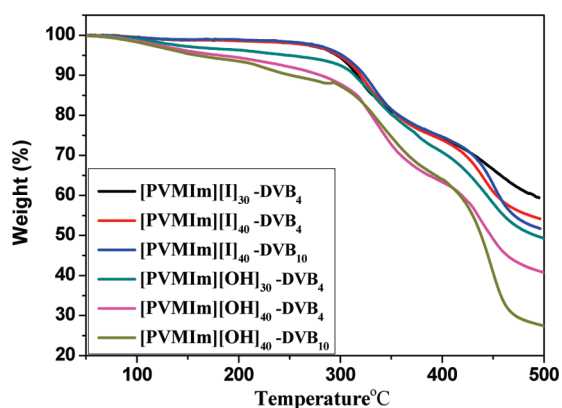| sample	tensile strength (MPa)	tensile modulus (MPa)	elongation at break (%)
[PVMIm][OH]$_{10}$-DVB$_4$	50.22 ± 8.73	2778.61 ± 121.08	13.38 ± 4.08
[PVMIm][OH]$_{20}$-DVB$_4$	15.44 ± 4.01	449.30 ± 38.23	102.66 ± 11.00
[PVMIm][OH]$_{30}$-DVB$_4$	14.32 ± 1.17	438.43 ± 40.16	67.67 ± 12.35
[PVMIm][OH]$_{40}$-DVB$_4$	13.57 ± 1.86	449.12 ± 42.33	51.75 ± 7.96
[PVMIm][OH]$_{40}$-DVB$_2$	10.86 ± 2.33	321.14 ± 24.05	136.46 ± 19.53
[PVMIm][OH]$_{40}$-DVB$_8$	16.33 ± 2.09	464.83 ± 31.62	51.91 ± 6.43
[PVMIm][OH]$_{40}$-DVB$_{10}$	18.51 ± 0.45	894.38 ± 24.53	29.48 ± 7.69
Nafion-117	21.11 ± 1.05	6.60 ± 1.35	370.62 ± 22.03
Poly(arylene ether sulfone)s[11a]	15.8−67.6	330−1700	10.4−71.4

Figure 5. Thermogravimetric analysis (TGA) curves of membranes under nitrogen flow. Heating rate: 10 °C/min.

the AEMs produced in this work should be tough enough for potential use as the AEM materials.

The thermal stability of the AEMs is always a concern for AEMFCs, because work at high temperature could enhance the reaction kinetics at both electrodes and reduce the thermodynamic voltage losses of AEMFCs. Figure 5 shows the typical thermogravimetric analyzer (TGA) curves of produced AEMs in both I$^-$ and OH$^-$ forms. All the membranes show a slight weight loss (∼4 wt %) below 120 °C, corresponding to the evaporation of absorbed water. The weight loss region at temperatures above 300 °C may due to the degradation of the backbone of copolymers. Polymers based on the aromatic backbones, such as poly(arylene ether sulfone)s and

poly(arylene ether ketone)s, are generally considered as the preferred candidates for high-temperature fuel-cell applications, because of their excellent thermal stability. It has already been demonstrated that imidazolium cations are thermally more stable than the tetraalkyl ammonium cations.[26] Here, we can see that the thermal stability of this type of alkaline IL-based cross-linked AEMs is comparable to that of quaternary ammonia polysulfone[10a] and quaternary guanidinium poly(arylene ether sulfone)s containing hydroxide groups.[11]

Table 2 shows the values of the ion-exchange capacity (IEC), water uptake, and swelling degree of the produced AEMs. The experimental IEC values were found to be 0.21−1.47 mequiv/g as the [PVMIm][OH] content increased from 10 wt % to 40 wt %, which may be due to the increased concentration of available ionic sites in the polymers. The water uptake increased with the increment of the [PVMIm][OH] content and the IEC values. We assume that the high content of OH$^-$ ions leads to the formation of the larger ion clusters within the membrane and, thus, led to the absorption of more water.[19a,27]

Swelling behavior of the membrane is an essential factor influencing the mechanical properties and the morphologic stability of membranes. As shown in Table 2, the swelling degree increases with the increment of [PVMIm]-[OH] content, because more water has been absorbed

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Table 2. Ion Exchange Capacity (IEC), Water Uptake, Swelling Degree, and Conductivity of [PVMIm][OH]$_x$-DVB$_y$ Membranes

sample	IEC (mequiv/g)		water uptake (%)[b]	swelling degree in water (%)[b]	swelling degree in methanol (%)[c]	Conductivity ($\times 10^{-2}$ S/cm)	
	theoretical[a]	experimental				at 30 °C	at 60 °C
[PVMIm][OH]$_{10}$-DVB$_4$	0.40	0.21 ± 0.02	2.58	0.87	0.78	0.16 ± 0.04	0.28 ± 0.11
[PVMIm][OH]$_{20}$-DVB$_4$	0.80	0.75 ± 0.06	86.56	29.37	12.44	2.47 ± 0.15	3.83 ± 0.33
[PVMIm][OH]$_{30}$-DVB$_4$	1.20	1.18 ± 0.04	116.42	36.42	16.62	3.08 ± 0.25	4.81 ± 0.29
[PVMIm][OH]$_{40}$-DVB$_4$	1.60	1.47 ± 0.08	156.88	42.39	20.05	3.27 ± 0.36	5.35 ± 0.42
[PVMIm][OH]$_{40}$-DVB$_2$			298.41	46.98	21.92	3.88 ± 0.26	5.58 ± 0.55
[PVMIm][OH]$_{40}$-DVB$_8$			73.86	19.03	10.84	1.44 ± 0.12	2.03 ± 0.25
[PVMIm][OH]$_{40}$-DVB$_{10}$			38.95	9.69	3.28	1.13 ± 0.14	1.69 ± 0.13
Nafion-117					34.50		

[a] Calculated from monomer ratio. [b] After immersing in water at room temperature (RT) for 24 h; average of two trials. [c] After immersing in methanol at room temperature (RT) for 24 h; average of two trials.
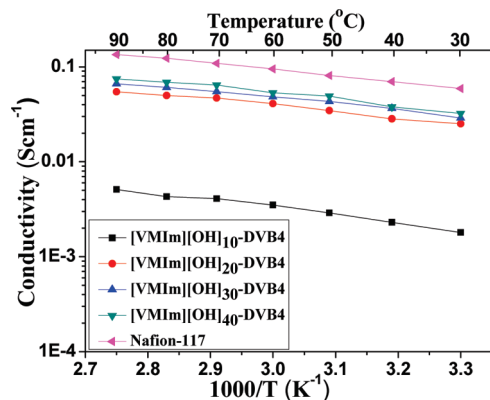

Figure 6. Conductivity Arrhenius plots of the Nafion-117 and [PVMIm]-[OH]$_x$-DVB$_4$ membranes, as a function of the weight content of [PVMIm][OH].

Table 3. Activation Energy for [PVMIm][OH]$_x$-DVB$_4$ and Nafion-117 Membranes

sample	activation energy, E_a (kJ/mol)
[PVMIm][OH]$_{10}$-DVB$_4$	15.46
[PVMIm][OH]$_{20}$-DVB$_4$	12.34
[PVMIm][OH]$_{30}$-DVB$_4$	12.31
[PVMIm][OH]$_{40}$-DVB$_4$	11.99
Nafion-117	12.75

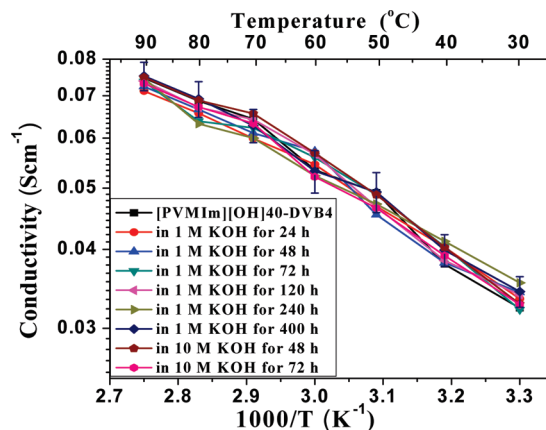**Figure 7.** Conductivity Arrhenius plots of the [PVMIm][OH]$_{40}$-DVB$_4$ membranes after immersion in 1 and 10 M KOH solution at 60 °C.

within the membrane. Furthermore, the swelling degree could be notably reduced, with the cross-linking agent content increasing because of the more compact network structures formed within the membranes, which reduce the free volume to retain water and eventually restrict the swelling degree of the membrane. The results of water uptake and swell behavior are in good agreement with the IEC. Note that the swelling degree of the membranes in pure methanol is much lower than that in water and also lower than that of Nafion-117 in methanol (34.5%) under the same experimental conditions. Such a good methanol tolerance of membrane is likely attributable to the presence of the aromatic cross-linker used in the membranes, which has less affinity to methanol than to water. Since the use of more-concentrated fuels leads to higher energy densities, these results suggest a feasible approach for practical applications in direct methanol fuel cells.

The hydroxide conductivity of the membranes is particularly important and plays an important role in fuel cell performance. The conductivity of polyelectrolyte membranes is significantly influenced by the IEC values and water uptake. Here, the conductivity of the AEMs was measured after the membranes were fully hydrated in deionized water at room temperature. Figure 6 shows the reproducible plot of hydroxide conductivity of the polymer membranes containing different content of [PVMIm]-[OH]. The changing trend in hydroxide conductivity was similar to the values of water uptake and swelling degree. The conductivity increases with increasing [PVMIm][OH]

and decreases with cross-linking agent content. One advantage of these cross-linked AEMs is that the hydroxide conductivity and mechanical properties of the membrane can be easily balanced by adjusting the content of alkaline ILs and DVB agent. For comparison, a poly(styrene-co-acrylonitrile) membrane (without [PVMIm][OH]) was immersed in a N$_2$-saturated 1 M KOH solution for 24 h. The resultant copolymer membrane shows a conductivity of 2.99×10^{-7} S/cm at 30 °C. Such a low conductivity value further confirms that the conductivity of AEMs is dependent on the [PVMIm][OH] content in the membrane. Most of the obtained AEMs prepared in this work show hydroxide ion conductivity above 10^{-2} S cm^{-1} at room temperature, which fulfills the basic conductivity requirement of fuel cells.[11b]

Note that there are dramatic property differences between [PVMIm][OH]$_{10}$-DVB$_4$ and [PVMIm][OH]$_{20}$-DVB$_4$ (see Tables 1 and 2). Although we are failed to distinguish the hydrophilic and hydrophobic regions from AFM images, we believe that there is a morphological

Table 4. Mechanical Properties and Ion-Exchange Capacity (IEC) Values of [PVMIm][OH]₄₀-DVB₄ Membranes after Immersion in 1 and 10 M KOH Solution at 60 °C

[KOH] (M)	time (h)	tensile strength (MPa)	tensile modulus (MPa)	elongation at break (%)	IEC (mequiv/g)[a]
0	0	13.57 ± 1.86	449.12 ± 42.33	51.75 ± 7.96	1.47 ± 0.08
1	48	12.18 ± 1.83	396.78 ± 45.60	44.67 ± 8.41	1.43 ± 0.05
1	72	7.05 ± 1.03	115.97 ± 19.90	49.86 ± 11.21	1.45 ± 0.11
1	96	6.92 ± 1.00	112.34 ± 2.38	48.28 ± 6.89	1.48 ± 0.06
1	120	6.32 ± 0.98	104.82 ± 12.10	53.21 ± 11.72	1.38 ± 0.07
1	240	5.88 ± 1.21	105.21 ± 14.38	54.88 ± 7.86	1.46 ± 0.07
1	400	6.21 ± 1.33	96.72 ± 8.96	53.69 ± 8.07	1.43 ± 0.04
10	24	10.69 ± 1.02	293.38 ± 15.68	37.70 ± 6.86	1.41 ± 0.08
10	48	6.74 ± 0.55	153.22 ± 26.81	24.33 ± 9.41	1.39 ± 0.05
10	72	6.65 ± 1.17	140.65 ± 21.06	30.67 ± 5.93	1.49 ± 0.06

[a] Theoretical IEC value: 1.60 mequiv/g.

transition of the hydrophilic domains from isolated to continuous with the increment of [PVMIm][OH] content. The continuous hydrophilic polymeric networks formed within the membranes significantly affect the properties of membranes, such as water uptake, swelling degree, and conductivity properties.

The hydroxide ion conductivity of the membranes gradually increases with increasing temperature because the free volume, in favor of ion transport and the mobility of anions, is increased as the temperature rises.[11a,c] The ionic conductivity of produced AEMs obtained at elevated temperatures can be used for the estimation of activation energy (E_a), using the following equation:[21]

$$E_a = -b \times R$$

where E_a is the activation energy (expressed in units of kJ/mol), R the universal gas constant ($R = 8.314$ J/(mol K)), and b the slope of the linear regression of ln σ (where σ is the ionic conductivity, given in units of S/cm) versus 1000/T plots. The calculated E_a values are presented in Table 3. The changing trend of E_a values is similar to that of ionic conductivity which is strongly related to the content of [PVMIm][OH]. For example, the [PVMIm][OH]₁₀-DVB₄ membrane shows the highest E_a value of ionic conductivity, indicating that ionic transfer needs more energy in the membranes. The highest E_a value of the [PVMIm][OH]₁₀-DVB₄ membrane is probably due to its lowest conductivity. The increment of the [PVMIm][OH] content increases the water uptake, which favors the formation of ionic-conductive networks in the membrane and leads to the lower E_a value.[11c] All the membranes show E_a values of ~11.99−15.46 kJ/mol (see Table 3), which is very similar to the values of Nafion-117 and quaternary ammonia polysulfone (13.3 kJ/mol).[10a]

To meet the requirements of the practical application in fuel cell applications, besides the excellent thermal stability and high ionic conductivity, the prepared AEMs must have good chemical stability, especially in the high-pH environments of the alkaline fuel cells. Since many quaternary ammonia polymers have a tendency to disintegrate in alkaline solution at high temperature,[9] the chemical stability of the AEMs is still a challenge, especially in the high-pH environment of alkaline fuel cells. Here, the long-term alkaline stability of produced membranes was investigated by immersing membrane samples

in 1 and 10 M KOH solution at 60 °C, respectively. The changes of hydroxide ion conductivity, the mechanical properties, and the IEC values of the tested membranes were measured.

Figure 7 shows the conductivity Arrhenius plots of the [PVMIm][OH]₄₀-DVB₄ membrane after certain testing times in 1 and 10 M KOH solution. All the membranes maintain the hydroxide conductivity, even after immersion in 1 M KOH solution at 60 °C for 400 h, indicating good chemical stability of the membranes in alkaline solution. Table 4 shows the mechanical properties and IEC values of the tested membranes. Note that the tensile strength and modulus of the membranes decreased after immersion in 1 M KOH solution for 72 h and then remained constant. Similar results were observed of the tested membranes in 10 M KOH solution for 48 h. Since the membranes prepared in this work are only partially cross-linked and they swelled during the alkaline stability test in KOH solution, we suppose that the decrement of tensile strength and modulus is mainly due to the disentanglement of some un-cross-linked polymer chains in the membranes, instead of the membrane degradation in alkaline solution. The IEC values of the membranes are almost unchanged before and after the test, which further confirms the excellent alkaline stability of the membranes. The alkyl quaternary ammonium polymers were unstable in alkaline solutions at high temperature because of the nucleophilic attack reaction of the cation sites by OH⁻ anions, which causes the loss of the quaternary ammonium groups.[6,9,28] The high stability of *N*-alkyl-substituted imidazolium cations in KOH solution is probably because of the internal conjugation of the π-electrons in the imidazole rings, which enhances the alkaline stability of the imidazolium cations.

Conclusions

In summary, we have demonstrated a facile and effective synthetic procedure for the preparation of novel AEMs based on alkaline imidazolium type ILs. The AEMs were prepared via in situ cross-linking and followed by anion-exchange with OH⁻ anions. The resultant membranes are flexible and tough enough for potential use as AEM

(28) Chempath, S.; Einsla, B. R.; Pratt, L. R.; Macomber, C. S.; Boncella, J. M.; Rau, J. A.; Pivovar, B. S. *J. Phys. Chem. C* **2008**, *112*, 3179–3182.

materials. The thermal stability of produced AEMs is comparable to that of quaternary ammonia aromatic polymers. The produced alkaline IL-based AEMs show the hydroxide ion conductivity above 10^{-2} S cm^{-1} at room temperature, and the excellent chemical stability in high pH solution at 60 °C, indicating that the membranes could overcome the alkaline instability of the alkyl quaternary ammonium functionalized polymers, and fulfill the basic conductivity requirement of alkaline fuel cells.

The main advantages of the synthetic strategy reported here are: i) the synthetic procedures of AEMs are simple and without the use of chloromethyl ether which is harmful to humans; ii) membranes can be produced with desired dimensions without the need for further processing steps, such as solvent casting or melt extrusion;

iii) the hydroxide conductivity and mechanical properties of the membrane can be easily balanced by adjusting the content of alkaline ILs and cross-linker agent.

The results of this study suggest a feasible approach for the synthesis and practical applications of alkaline AEMs, and should be expected to promote the widespread use of AEMFCs. The performance and stability of these materials in AEMFCs with methanol or hydrogen as fuels will be further explored in future work.