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PAPER

Novel anion exchange membranes based on polymerizable imidazolium salt for alkaline fuel cell applications

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A new polymerizable imidazolium salt monomer, 1-(4-vinylbenzyl)-3-methyl-imidazolium chloride ([VBMI]Cl), has been readily synthesized by reaction of 4-vinylbenzyl chloride with 1-methylimidazole. Novel anion exchange membranes (AEMs) based on the copolymers of [VBMI]Cl and styrene have been prepared and characterized. Excellent thermostability of the membranes is observed through the thermo-gravimetric analysis (TGA) curves. Water uptake and ion exchange capacity (IEC) of the OH^- form AEMs range from 26.1% to 61.9% and from 0.95 to 1.45 mmol g^{-1}, respectively. This type of AEM displays significant ionic conductivities over the order of 10^{-2} S cm^{-1} in deionized water at room temperature, and the membranes are stable in 10 mol L^{-1} NaOH solution at 60 °C for 120 h. For the H_2/air single fuel cell at 30 °C with this novel AEM, the peak power density of 33 mW cm^{-2} is obtained at a current density of 59 mA cm^{-2}.

Introduction

With the over-exploitation and massive consumption of energy resources, developing new economically viable alternative energy systems is necessary and exigent to relieve the energy crisis. Fuel cells are regarded as one of the most promising clean and efficient energy conversion devices.[1,2] Polymer electrolyte membrane fuel cells have attracted considerable interest during the past few decades, especially the proton exchange membrane fuel cells (PEMFCs).[3,4] This is mainly due to the vigorous development of proton exchange membranes (PEMs), in particular, the Nafion membrane (DuPont), which presents excellent chemical, mechanical and thermal stability as well as high ionic conductivity. Unfortunately, inherent properties in acidic conditions bring various limitations to PEMFCs, such as high-priced platinum catalysts, sluggish reaction kinetics, high fuel permeability and complex water management.[1,5,6]

Alkaline anion exchange membranes fuel cells (AEMFCs), combining the advantages of conventional alkaline fuel cells (using lye as electrolyte) and solid polymer electrolyte membranes, have become a new hot area recently.[7–14] Due to employment of solid polymer electrolyte membranes, carbonate precipitates and electrolyte leakage would be circumvented.[15,16] In comparison to acidic fuel cells, alkaline fuel cells have more facile kinetics of the oxygen reduction reactions and fuel oxidation, which provide the attractive opportunity for the use of non-noble metal catalysts such as silver, nickel, and palladium.[7] In addition, the metal materials used in alkaline environments suffer less corrosion, and thus greatly reduce the cost of the fuel cell. In contrast to the PEMs, the anion exchange membranes (AEMs) are designed to conduct hydroxide ions. As such, the direction of the electro-osmotic drag is from the cathode to the anode, which can potentially simplify water management (water is produced at the anode and consumed at the cathode) and reduce fuel permeability (OH^- and fuel move in opposite directions).[7,17]

As a key component in AEMFCs, AEMs play a crucial role in separating fuel and oxygen (or air), and achieving anion transfer simultaneously. Accordingly, the availability of suitable AEMs is one of the main challenges in the development of AEMFCs. The basic requirements in developing an AEM for an AEMFC are that it should have sufficient mechanical strength, good thermal and chemical stability and suitable ionic conductivity. Recently, some impressive research results of AEMs have been reported. The research team of Varcoe and Slade developed the quaternary ammonium radiation grafted mixed fluorocarbon/hydrocarbon membranes.[7,12,15] Yang prepared an alkaline cross-linked PVA/TiO_2 composite polymer membrane using glutaraldehyde as the cross-linker.[13] Matsuoka *et al.* synthesized a 4-vinylpyridine-based AEM by plasma polymerization.[18] Coates *et al.* recently reported novel AEMs that use tetraalkyl ammonium-functionalized norbornenes to copolymerize with cross-linkers.[19] Additionally, AEMs based on chloromethylation quaternary amination polymers containing phenyl on the backbone chains have been reported by some groups, and include polysulfone,[20] polyethersulfone cardo,[21] poly (phthalazinone ether sulfone ketone),[14] poly (2,6-dimethyl-1,4-phenylene oxide),[22] poly (phthalazinone ether sulfone)[23] and cardo polyetherketone (PEK-C).[24] Meanwhile, there are still some outstanding problems in the process of developing AEMs for AEMFC

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application, for example, the lower conductivity of AEMs compared with PEMs and the chemical stability of the cationic groups attached to AEMs, and cost-effective AEMs are scarce as yet. Therefore, developing new AEMs with cost-effectiveness, ease of preparation and high performance is urgently needed.

The polymerizable imidazolium salt is known as a functional monomer that can provide ionic conduction.[25] To date, preparing AEMs based on imidazolium salts have been rarely reported in the literature. In this study, we have been exploring novel AEMs based on a polymerizable imidazolium salt that could yield some advantages over conventional quaternary alkyl ammonium type AEMs. The imidazolium cation is thermally more stable than the conventional quaternary alkyl ammonium cations, and it has good resistance to oxidation at high temperature.[25,26] The polymer for preparing AEM was synthesized by free radical copolymerization. This method is an effective way to control the properties of the copolymer by adjusting the monomer ratio in the reactants. After the polyreaction, the cationic group of the imidazolium salt can be fixed directly to the polymer chain, and thus the copolymer can transfer anion straightforwardly. The synthetic route also avoids the process of chloromethylation or quaternization. Besides, through the introduction of other co-monomers on demand, the macromolecular structure, mechanical property and thermodynamic property could be modified easily. In this paper, we originally report novel AEMs which are based on 1-(4-vinylbenzyl)-3-methyl-imidazolium chloride ([VBMI]Cl). The properties of the AEMs, such as thermal stability, water uptake, ion exchange capacity, ionic conductivity and chemical stability, have also been investigated in detail. In addition, a membrane electrode assembly (MEA) based on the novel AEM was used for preliminary H_2/air fuel cell testing.

Experimental section

Materials

4-Vinylbenzyl chloride (98%) was purchased from Changzhou Wujin Linchuan Chemical Co., Ltd. Styrene, 2,6-di-*tert*-butyl-4-methyl phenol (DBMP) and 2,2′-azobisisobutyronitrile (AIBN) were purchased from China National Medicines Co., Ltd. 1-Methylimidazole (99%) was obtained from Shanghai DEMO Chemical Co., Ltd. 4-Vinylbenzyl chloride, styrene and 1-methylimidazole were distilled under reduced pressure before use. AIBN was dissolved in boiled methanol, then recrystallized in an ice bath and dried at room temperature under vacuum. All other reagents were of analytical grade and used as received. Deionized water was used throughout.

Synthesis of imidazolium salt monomer

The imidazolium salt monomer was synthesized through chemical modified method and the details are as follows. A solution of DBMP (0.10 g, the inhibitor) in methanol (20 ml), 4-vinylbenzyl chloride (14.2 ml, 0.10 mol) and 1-methylimidazole (8 ml, 0.10 mol) were added to a dried 100 ml three-neck round-bottomed flask, then the mixture was magnetically stirred at 45 °C under a nitrogen atmosphere for 6 h.

The resulting viscous liquid was extracted with cyclopentane to remove the unreacted 4-vinylbenzyl chloride, then dried in a vacuum oven at 40 °C for 6 h. After that, the product, [VBMI]Cl, was washed with an excess of ethyl ether to remove the unreacted 1-methylimidazole and dried in a vacuum oven at 40 °C for 10 h.

Synthesis of the copolymers

The polymer based on the imidazolium salt monomer was prepared through a free radical copolymerization using AIBN as an initiator and ethanol as a solvent. The copolymerization of [VBMI]Cl with styrene was carried out in a three-neck round-bottomed flask with a magnetic stirrer. Under a nitrogen atmosphere, the mixture was stirred at 65 °C for 24 h. The resulting yellowish viscous solution was then dried in a vacuum oven at 60 °C for 6 h. After that, the obtained spongy solid was washed with tetrahydrofuran several times, and dried overnight under a vacuum at 60 °C to produce the final polymer.

Preparation of the membranes

The membranes were prepared by the solution-casting and evaporation method. The polymers were dissolved in dimethyl sulfoxide (DMSO) to form a 5–10 wt% solution. These polymer solutions were cast onto glass plates, and dried in a vacuum oven at 80 °C for 12 h. Then, the membranes were peeled off from the glass plates and soaked in 1 mol L^{-1} NaOH solution at room temperature for 48 h to exchange the chloride ions to hydroxide ions. Finally, the membranes were thoroughly washed with deionized water for further use.

Characterization

The FT-IR spectra of [VBMI]Cl and copolymer were scanned using a Nicolet FT-IR740SX spectrophotometer (Thermo Electron Corporation, USA) with a resolution of 4 cm^{-1}. Elemental analyses were performed on an Vario EL III Elemental analyzer (Elementar Analysen Syetem GmbH, Germany). The inherent viscosities were determined on 0.5 g dL^{-1} concentration of copolymers in DMSO with an Ubbelohde capillary viscometer at 20 ± 0.1 °C. Thermo-gravimetric analysis (TGA) was performed under a nitrogen atmosphere with a TG209F1 system (NETZSCH, Germany) at a heating rate of 10 °C min^{-1} from 30 to 600 °C.

Water uptake

Water uptake was determined for all the membranes in their OH^- forms. The membranes were dried at 60 °C under vacuum until constant dried weights were obtained. Then the dry membranes were immersed in deionized water at room temperature and periodically weighed until constant water uptake weights were recorded. The water uptake was calculated from eqn (1):

$$\text{water uptake (WU)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \qquad (1)$$

where W_{dry} and W_{wet} are the weights of dry and corresponding water-swollen membranes, respectively.

Ion exchange capacity (IEC)

The IEC of these membranes was measured using standard back titration methods. The dry OH^- form membranes were soaked in 0.1 mol L^{-1} HCl solution (25 ml, V_{HCl}, the volume for membranes soaking) at room temperature and equilibrated for 48 h. The solutions were then titrated with standardized 0.1 mol L^{-1} NaOH solution (V_{NaOH}, the volume for back titration). After that, the Cl^- form membranes were dried at 60 °C under vacuum until constant weights were obtained. The IEC values were calculated using eqn (2):

$$\mathrm{IEC} = \frac{(V_{HCl} - V_{NaOH}) \times C}{W_{dry}} \tag{2}$$

where C is the concentration of HCl and NaOH solutions, and W_{dry} is the weight of the dry Cl^- form membrane.

Ionic conductivity

The in-plane ionic conductivity of each OH^- form membrane was estimated from four-probe electrochemical impedance spectroscopy using Parstat 263 electrochemical equipment (Princeton Advanced Technology, USA). All the membranes were equilibrated in deionized water for fully hydrated conditions. Membrane samples were clamped between two stainless steel electrodes, and soaked in a thermostatic chamber filled with deionized water. The impedance measurements were carried out over the frequency range from 0.1 Hz to 100 kHz. The ionic conductivity was calculated by eqn (3):

$$\sigma = \frac{L}{R \times A} \tag{3}$$

where L (cm) is the distance between two stainless steel electrodes, R (Ω) is the resistance of the membrane, and A is the cross-sectional area (cm^2) of the membrane sample.

Chemical stability

The chemical stability of the OH^- form membrane was tracked by estimating the effects of alkaline concentration at elevated temperature on the ionic conductivity. Five membrane samples were separately immersed into different concentrations of NaOH solution (2, 4, 6, 8 and 10 mol L^{-1}) at 60 °C for 120 h. For comparison purpose, one sample was immersed in 1 mol L^{-1} NaOH solution at room temperature for 48 h. After the free NaOH inside the membranes was completely removed, the ionic conductivities of the samples were measured in deionized water at room temperature (23 °C).

Membrane electrode assembly and fuel cell test

The membrane electrode assembly (MEA) consisted of an AEM, anode/cathode catalyst layers (Pt/C, 40 wt% Pt, Johnson Matthey) and diffusion layers. Membrane A was used as the AEM for testing. Teflon-treated carbon paper (Toray-250) was used as diffusion layer, which combined with catalyst layer to make an electrode. Ionomer solution (5 wt%) was prepared using the ClO_4^- form membrane A which was obtained by immersion of a piece of copolymer A in 0.1 mol L^{-1} $HClO_4$ solution at room temperature. The catalyst ink for the electrode was prepared by mixing the ionomer solution, the catalyst powder and propanetriol. Prior to being sprayed on the carbon paper, the ink was stirred for 24 h to reach mixture uniformity. The content of ionomer in the catalyst layer was 30 wt%. The resulting electrode with an active area of 4 cm^2 had a catalyst loading of 2 mg cm^{-2}. The AEM and the electrodes were sandwiched together and then hot-pressed at 2 MPa for 5 min at 50 °C. Then the MEA was soaked in 1 mol L^{-1} NaOH solution to exchange the ClO_4^- in the ionomer for OH^-. After full exchange of ions, the MEA was thoroughly washed with deionized water to remove the remaining NaOH.

The MEA was assembled into a single fuel cell with serpentine flow channels. H_2 at the anode and air at the cathode were fed with the flow rate of 50 mL min^{-1} and 100 mL min^{-1}, respectively. Single cell test was performed at 30 °C with relative humidity of 100% using an electronic load (ZY8714, ZHONGYING Electronic Co., Ltd.).

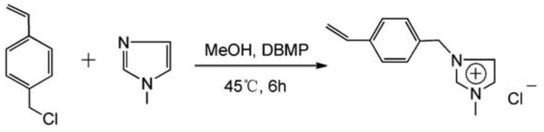
Results and discussion

Synthesis of imidazolium salt monomers[27]

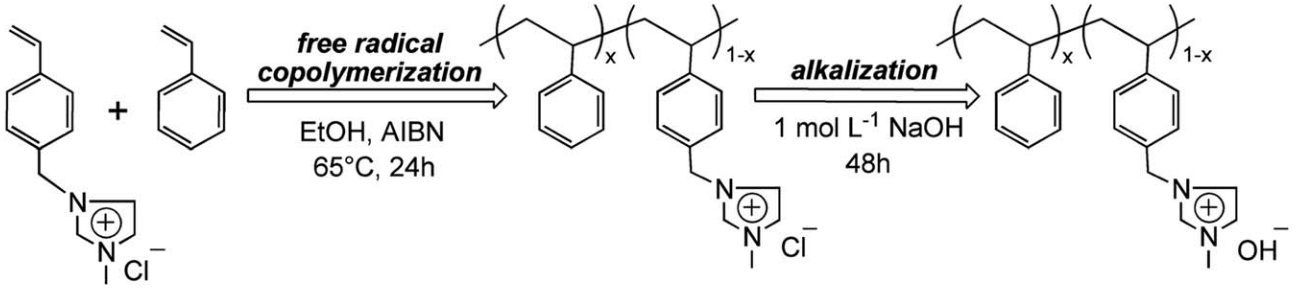
Scheme 1 shows the synthesis route of [VBMI]Cl monomer from 4-vinylbenzyl chloride and 1-methylimidazole. Due to the strong nucleophilicity and steric accessibility of N3 nitrogen (the number three nitrogen atom) in 1-methylimidazole,[28] and the relatively high reactivity of 4-vinylbenzyl chloride, the reaction could be readily carried out, and the product yield was up to 87.7%.The use of DBMP and the low-temperature reaction were to inhibit the self-polymerization of the reactants. The resulting imidazolium salt monomer was a pale yellow sticky-solid, and soluble in water, alcohols and DMSO, but insoluble in ethyl ether, chloroform and tetrahydrofuran. To confirm the existence of chloride ion, we dissolved the product in silver nitrate solution, and soon white precipitate came out of solution. The imidazolium cation, chloride ion and ion-pair all can form hydrogen bonds with water molecules,[29] which is leads to good water solubility of the salt. Based on the polymerizable and ion conductivity, [VBMI]Cl was used in the following copolymerization.

Preparation of the polymers and OH^- form membranes

For preparing anion exchange membranes, the copolymers of [VBMI]Cl and styrene were synthesized by free radical copolymerization adopting AIBN (0.3 wt%) as initiator, as presented in Scheme 2. The copolymerization was carried out in ethanol under reflux. With a strong hydrophilic imidazolium cation group, [VBMI]Cl was soluble in water. To prevent the excessive water uptake of membranes, styrene was incorporated into the polymer system due to its fine hydrophobic property. Additionally, styrene is cheap and easily available. The feed ratio of



Scheme 1 Synthetic route to [VBMI]Cl.



Scheme 2 Preparation of OH^- form membrane based on [VBMI]Cl and styrene.

[VBMI]Cl/styrene, nitrogen content of copolymers and the composition of copolymers calculated from nitrogen content are summarized in Table 1. Three kinds of copolymers named A, B and C were obtained. It can be seen in Table 1 that [VBMI]Cl/styrene feed ratios were set to increase in a proportional and continuous manner, the nitrogen content of copolymer increased in line. Nitrogen only existed in the imidazole ring of the unit in a polymer chain, therefore, the amount of imidazolium cation groups in the copolymer could be exhibited by the nitrogen content inside the copolymer. It was demonstrated that by changing [VBMI]Cl/styrene feed ratios, the amount of imidazolium cation groups in the copolymer could be easily controlled. Thus it was confirmed that the synthesis method in this paper is feasible and can be controlled well. The copolymers were soluble in DMSO and alcohols, but not in tetrahydrofuran, chloroform, ethyl ether or dimethyl formamide. Inherent viscosity values of three copolymers are shown in Table 1. They were higher than 1.14 dL g^{-1} in DMSO at 20 °C, which provided a qualitative inference of the high molecular weight of the copolymers and indicated successful polymerization. Because the copolymers were soluble in certain organic solvents, the membranes could be easily prepared by solution casting method. After casting from copolymer solutions, the transparent flexible membranes were formed and showed more flexibility in the presence of water. These membranes showed affinity to water, which is essential for anion mobility. With an increase of the nitrogen content of the copolymer, the amount of imidazolium cation groups contained in the obtained membrane increased gradually. However, an excess amount of imidazolium cation groups would make the obtained copolymer too hydrophilic to form a film. Additionally, an excess amount of phenyl group would make the resulting membrane too brittle to use. The membrane in Cl^-, HSO_4^- or ClO_4^- form could be dissolved in methanol, ethanol or DMSO, but not in ethyl ether, chloroform or tetrahydrofuran. Peculiarly, the OH^- form membrane was insoluble in these solvents described above.

Fig. 1 shows the FT-IR spectra of [VBMI]Cl and copolymer A. The broad and strong absorption band around 3425 cm^{-1} is assigned to the stretch vibration of O–H. The synthesis of [VBMI]Cl can be confirmed by the corresponding absorption peaks. The sharp peaks at 1572 and 1161 cm^{-1} are associated with the stretching vibration of C=N and the flexural vibration of C–H in the imidazole ring, respectively. The peaks at 2852 and 2929 cm^{-1} correspond to the symmetrical and asymmetric stretching vibration of the methylene between the two aromatic rings. The peaks appearing at the fingerprint region of 760–850 cm^{-1} confirm the presence of *p*-substituted benzene ring. The peak at 1627 cm^{-1} is assigned to the stretching vibration of C=C in vinyl, and it disappears in the spectrum of the copolymer A. After copolymerization, the intensities of the two peaks at 2850–2930 cm^{-1} are found to be substantially enhanced, which is likely attributed to the vibration of the methylene in polymer main chains. A new sharp peak appearing at 700 cm^{-1} in the spectrum of copolymer A is related to the styrene unit in the copolymer.

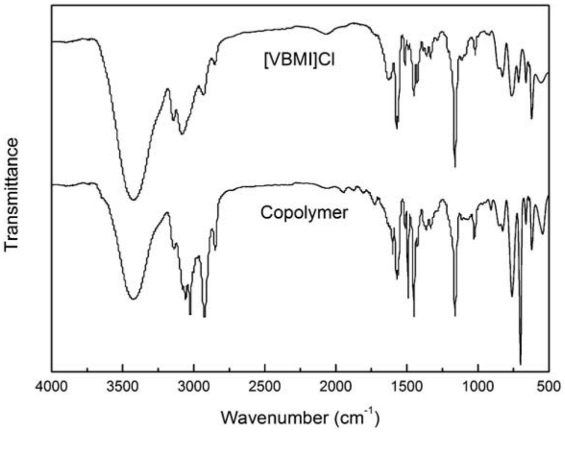


Fig. 1 FT-IR spectra of [VBMI]Cl and copolymer A.

Table 1 Characterization of copolymers

Copolymer	Feed ratio of [VBMI]Cl/styrene (mole)	η_{inh} [a] (dL g^{-1})	N Content (wt%)	Molar ratio of [VBMI]Cl/Styrene in copolymer
A	1 : 3	1.25	4.230	1 : 4.24
B	1 : 4	1.14	3.442	1 : 5.70
C	1 : 5	1.19	2.873	1 : 7.25

[a] Inherent viscosity measured at a concentration of 0.5 g dL^{-1} in DMSO at 20 °C.

Thus, the results of FT-IR spectroscopy clearly confirm the successful copolymerization of [VBMI]Cl with styrene.

Thermal stability

Thermo-gravimetric measurements were carried out on [VBMI]Cl, polystyrene (Ps) and OH^- form membranes. Fig. 2 shows the TGA curves of the three kinds of membranes. The initial slight weight loss (<2.5%) was ascribed to the evaporation of hydrated water or solvents (such as DMSO). As shown in the TGA curves, the weight loss between 200–300 °C increases with increasing imidazole group content of the membrane. Table 2 lists the weight loss percentage and onset decomposition temperatures in this region. This weight loss stage was associated with the degradation of the imidazole group. This can be confirmed by Fig. 3, which shows the TGA curves of [VBMI]Cl and Ps. The Ps curve shows a sharp single step decomposition temperature occurred at 418.6 °C and it conforms to that found in the literature,[30] which is due to the main chain decomposition. Thus it was seen that the phenyl group was stable below 400 °C, and the initial decomposition of [VBMI]Cl at 296.2 °C was ascribed to the degradation of the imidazole group, corresponding to about 30% weight loss of the [VBMI]Cl sample. The further weight loss of the three membranes occurring from 400 °C was related to the degradation of the main chain. The results indicate that these OH^- form membranes showed good thermal stability.

Water uptake and ionic exchange capacity

The water uptake of ion exchange membranes is known to have a profound effect on ion migration. On condition that the dimensional stability is ensured, sufficient water uptake can facilitate a high migration rate of ions. Table 2 lists the water uptake of the three membranes in OH^- form. These data were determined by measuring the mass variation of the membranes, respectively, before and after immersion in water. It can be observed that an increase in the imidazole group content in the membrane leads to an increase in the water uptake of the membrane. This can be attributed to the strong hydrophilicity of the imidazolium salt. The membrane contains more imidazolium cation groups, leading to stronger hydrophilicity, and thus a higher water uptake. Membrane A shows the highest content of imidazolium cation groups with a water uptake of 61.9%. Additionally, the introduction of hydrophobic monomer (styrene) into the copolymer system can prevent excessive water uptake, and ensure dimensional stability of the membrane. In conclusion, the water uptake is regulated and controlled by the combination of the content of imidazolium cation groups and the hydrophobic performance of the co-monomer.

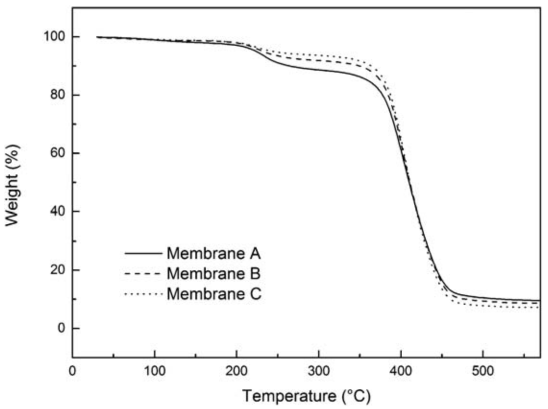


Fig. 2 TGA traces of the three kinds of OH^- form membranes.

Ionic exchange capacity (IEC) provides an indication of the ion exchangeable groups present in membranes. The theoretical IEC values of the OH^- form membranes A, B and C were 1.51, 1.23 and 1.03 mmol g^{-1}, respectively, which were calculated based on the nitrogen content of each copolymer. As listed in Table 2, the experimental values of IEC from titration test corresponded to the theoretical values. The IEC increased with an increasing feed ratio of [VBMI]Cl to the copolymer and was strongly dependent upon the amount of imidazolium cation groups of the membrane. It can thus be concluded that IEC of membrane would be governed by the dosage of [VBMI]Cl. As the anion transport is water-assisted, the IEC of membrane has a significant effect on the amount of water uptake. Table 2 shows a clear trend of increasing water uptake with the enhancement of IEC. Additionally, the increase in water uptake is also likely propitious to sufficient anion exchange inside the membrane. Membrane A exhibited the highest IEC of 1.45 mmol g^{-1} with water uptake of 61.9%.

Ionic conductivity

The ionic conductivity of the OH^- form membrane as a function of the temperature is shown in Fig. 4. At a given temperature, the conductivities of the membranes increase with the content of imidazole group, that is due to the increasing charge carrier concentration. Table 2 lists conductivities of the three membranes at 30 °C. It is found that the initial dosage of [VBMI]Cl has a significant effect on the formed membrane conductance. An increase in the conductivities of all three membranes is observed when the temperature continues to increase. The ionic conductivity of membrane A increases from 1.24×10^{-2} S cm^{-1} at 30 °C to 4.07×10^{-2} S cm^{-1} at 90 °C. 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 at a higher temperature and more water will be adsorbed by the membrane above a critical temperature,[31,32] leading to a more swollen membrane structure and wider ion transferring channel, resulting in more propitious ion transfer.[33] This may explain why the ionic conductivity increases dramatically from about 60 °C in contrast to the tardy rise at initial heating-up. Combined with the results in Fig. 4, it can be concluded that the ionic conductivities of membranes are mainly governed by the concentration of charge carriers and the water uptake of membranes. Among the three membranes, Membrane A shows the best conductivity at a given temperature, which is the result of the highest content of imidazolium cation groups and a significantly higher water uptake.

Chemical stability

The chemical stability of AEMs is crucial to the development of AEMFCs. Under the high pH operating conditions of AEMFCs, the cationic groups of AEMs will be suffering constant chemical

Table 2 Characterization of membranes

			IEC(mmol g^{-1})			σ(10^{-2} S cm^{-1})	
Membrane	T_{dt} ^{a} (°C)	TGA Weight loss between 200–300 °C (wt%)	theor	expt	Water Uptake (wt%)	30 °C	90 °C
A	233.9	9.96	1.51	1.45	61.9	1.24	4.07
B	220.9	6.81	1.23	1.11	36.5	0.63	2.56
C	227.4	5.31	1.03	0.95	26.1	0.47	1.74

^{a} The TGA onset decomposition temperatures of the three kinds of OH$^-$ form membranes.

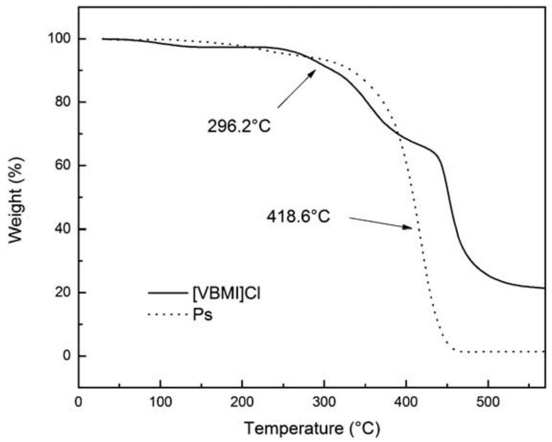


Fig. 3 TGA traces of [VBMI]Cl and polystyrene (Ps) with the onset decomposition temperature.

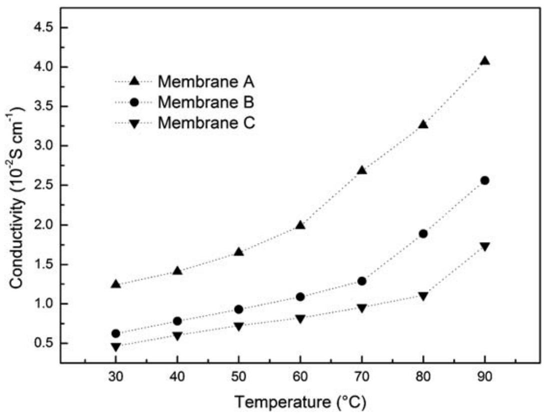


Fig. 4 Variations in ionic conductivities of the three OH$^-$ form membranes as a function of temperature.

attack. In addition, in order to optimize fuel cell performance, raising temperature is favorable. Therefore, AEMs with stability in the high pH range at elevated temperature are highly required. This study has taken membrane A as a representative. Fig. 5 shows the conductivities of the five samples after treatment with different concentrations of NaOH solution at 60 °C for 120 h. The conductivity ranged from 1.01 to 1.10 × 10^{-2} S cm^{-1}. There was no significant change through comparison with the conductivity of the contrast sample (1.03 × 10^{-2} S cm^{-1}). The result indicates that the membranes based on imidazolium cation groups display fairly good stability to high pH conditions at temperature up to 60 °C.

For many quaternary alkyl ammonium cation groups, Hofmann degradation or nucleophilic substitution reaction will occur on them under high pH and elevated temperature.[34] Specifically, there is no β hydrogen around the imidazolium cation group and the positive charge is located in the imidazole ring with a big π bond conjugated system, thus the two reactions can be avoided.[7,35] Consequently, the AEMs based on the imidazolium salt exhibit excellent chemical stability.

Fabrication of MEA and fuel cell test

The OH$^-$ form Membrane A was used for an initial MEA fabrication. In the process of preparing ionomer solution, there should be no presence of Cl$^-$ which could result in the deactivation of Pt catalyst. Therefore, Cl$^-$ in the copolymer must be fully exchanged for ClO_4^- until no Cl$^-$ can be detected. The fuel cell test was performed in the absence of any liquid electrolyte, such as KOH and NaOH. Fig. 6 shows the voltage–current density relationship and the polarization curves of the cell using Membrane A under 100% humidity at 30 °C and ambient pressure. It was observed that the open circuit voltage (OCV) of the H_2/air fuel cell was 1.028V. The high OCV was likely due to the lower permeation of reactant gases through the membrane and more favorable electrochemical reaction kinetics in an alkaline environment.[36] A peak power density of 33 mW cm^{-2} was obtained at a current density of 59 mA cm^{-2}. With the increasing of the current density, the voltage of the cell decreased gradually. The voltage losses are mainly attributed to the electrode overpotentials at high current densities.[37] This cell behavior was

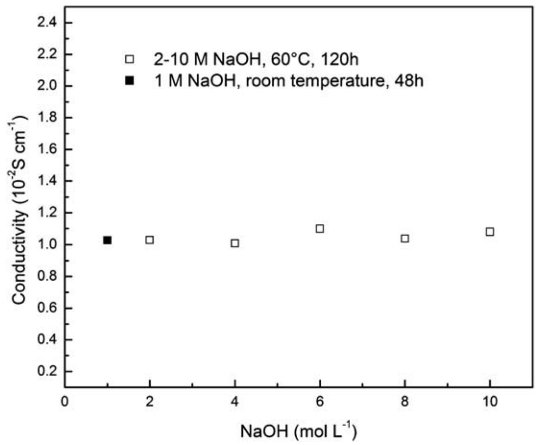


Fig. 5 The conductivities of the OH$^-$ form membrane A samples after treatment with different concentrations of NaOH.

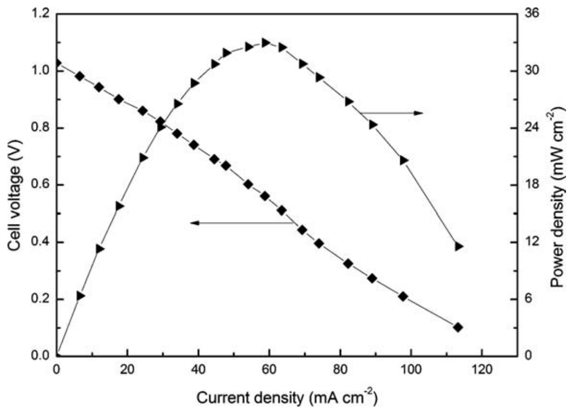


Fig. 6 Result of the H_2/air fuel cell with Membrane A as the anion membrane under 100% humidity at 30 °C and ambient pressure.

affected by the surface activity of the electrode. In addition, the interfacial property between the electrode and the membrane played a significant role in the performance of the fuel cell.[38] Study on the performance of the H_2/air fuel cell of Membrane A based MEA was preliminary. Future work will be devoted to the optimization of the electrode structure and testing conditions. There is great potential to improve the performance of AEMFCs. During the fuel cell test, no metal hydroxides were added. Without free metal cation in the electrolyte, there would be no carbonate precipitates. Therefore, the electrode and electrolyte would not be affected by CO_2 in the air.

Conclusions

A new imidazolium salt [VBMI]Cl has been synthesized from 4-vinylbenzyl chloride and 1-methylimidazole. Novel AEMs based on [VBMI]Cl were successfully prepared *via* free radical copolymerization and solution-casting method. The raw materials used in this study are relatively cheap and the synthetic routes are simple. Characterization by TGA measurements showed adequate thermal stability of the membranes. Onset decomposition temperature of the membranes is *ca.* 230 °C. Apparently, when the dosage of [VBMI]Cl was increased, a high level of water uptake, IEC and ionic conductivity were achieved. The water uptake of the OH^- form membrane is in the range of 26.1–61.9% and the IEC is in the range of 0.95–1.45 mmol g^{-1}. The ionic conductivity of membrane A is as high as 1.24×10^{-2} S cm^{-1} in deionized water at room temperature. Furthermore, the ionic conductivity could be further improved by the use of co-monomer with not only stronger hydrophobicity but also lower steric effects. These imidazolium salt based AEMs have superior chemical stability compared with the conventional quaternary alkyl ammonium functionalized AEMs. After treatment with 10 mol L^{-1} NaOH solution at 60 °C for 120 h, the membrane still retains good ionic conductivity. The power densities of the H_2/air fuel cell attain a peak value of 33 mW cm^{-2} at a current density of 59 mA cm^{-2}. The testing result exhibited a promising performance of the AEMFC with the novel AEM developed in this study. The results demonstrate the great prospect of these membranes for AEMFCs application. Further work to optimize the MEA fabrication and testing conditions is in progress.

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