Journal of
Materials Chemistry A

PAPER

View Article Online
View Journal | View Issue

Cite this: *J. Mater. Chem. A*, 2015, **3**, 8559

Received 23rd January 2015
Accepted 17th March 2015

DOI: 10.1039/c5ta00562k

www.rsc.org/MaterialsA

Highly alkaline stable N1-alkyl substituted 2-methylimidazolium functionalized alkaline anion exchange membranes†

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Steric hindrance and hyperconjugative effects, introduced at the N1 position of 2-methylimidazolium, greatly enhance the alkaline stability of the 2-methylimidazolium functional group. 2-Methylimidazolium small molecule compounds with N1-substituents (butyl, hexyl or octyl) are stable in 1 M KOH at 80 °C for more than 3000 h. Accordingly, the membranes based on N1-butyl, hexyl or octyl-substituted 2-methylimidzolium exhibited much more alkaline stability than membranes based on other substituted 2-methylimidazolium compounds, reflected by the almost unchanged IEC, conductivity and dimensions of the membranes after being exposed to 1 M KOH at 60 °C for hundreds of hours. This work reports the preparation of highly alkaline stable 2-methylimidazolium-based membranes by modifying the N1 position of 2-methylimidazolium.

Introduction

Alkaline anion exchange membrane fuel cells (AAEMFCs) are attracting more and more significant interest due to their lower cost than proton exchange membrane fuel cells (PEMFCs).[1–4] However, alkaline anion exchange membranes (AAEMs), a critical component of AAEMFCs, face the issue of inadequate alkaline stability in a high pH environment at elevated temperature. Although the chemical stability of both polymer backbone and functional groups of AAEMs would be challenged under alkaline conditions,[5–8] the degradation of positively charged groups is more severe under alkaline conditions involving hydroxide ions, a potent nucleophile.[9–13] Therefore, it is necessary to discover and explore positively charged groups with high alkaline stability. Imidazolium cations, possessing a π-conjugated imidazole ring (which could reduce the S_N2 substitution, Hofmann elimination reactions and (or) ylide formation), have been the topic of extensive research as the functional groups of AAEMs.[14–22] However, experimental evidence and DFT calculation study have indicated that C2-unsubstituted imidazolium cations might degrade *via* the nucleophilic addition–elimination pathway.[15,23–25] In this pathway, OH^- first attacks the C2 position of C2-unsubstituted imidazolium cations, and then one of the C–N bonds is broken and the ring is opened. It has been suggested that steric interference, introduced by substitution at the C-2, C-4, and C-5 positions, has a significant and positive impact on the alkaline stability of imidazolium according to the DFT results.[25] The experimental data have proven that C2- and (or) N3-substituents, especially C2-methyl or N3-isopropyl, indeed enhance the stability of imidazolium cations under alkaline conditions.[19,21,26] However, Varcoe *et al.* recently proposed that 1,2-dimethylimidazolium-based AAEMs are unstable in 1 M KOH at 60 °C.[27] They found that the conductivity and IEC of these membranes would degrade greatly after the exposure to alkaline solution for one day. In our previous experiments, we also found that 1,2-dimethylimidazolium functionalized styrene polymeric membranes are not stable enough. The conductivity, IEC and dimensions of these membranes would diminish after the exposure to 1 M KOH at 60 °C for about 100 h (as shown in Table S1†). Thus, to meet the requirements of AAEMs, designing a new and highly stable 2-methylimidazolium cation is still a major challenge.

From a theoretical aspect, steric hindrance and (or) hyperconjugative effects are effective methods to alleviate the attack of OH^- on the C2 position of imidazolium. However, the straight introduction of steric hindrance at the C2 position of imidazolium was not a good option to stabilize the imidazolium, confirmed by the Price group.[26] What if both steric hindrance and hyperconjugative effects were simultaneously

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† Electronic supplementary information (ESI) available: The change of conductivity, IEC and dimensions of the 1,2-dimethylimidazolium-based membrane after the exposure to 1 M KOH at 60 °C, detailed synthetic courses and NMR characterization of 2-methylimidazolium salts, calculation of the OH^- concentration in the cathode under the typical fuel cell conditions, ^{13}C NMR of $[DMBEIm]^+$, $[BMBEIm]^+$, $[HMBEIm]^+$, $[OMBEIm]^+$ and $[DoMBEIm]^+$ cations before and after the exposure to 1 M KOH solution at 80 °C, the degradation mechanism of 2-methylimidazolium cations, ^1H NMR polystyrene chloride, conductivities of the membranes used for the fuel cell test, and the resistance of ADMFCs using different membranes. See DOI: 10.1039/c5ta00562k

brought at the N1 position of 2-methylimidazolium? So in this work, the influence of N1-alkyl substituents on the alkaline stability of 2-methylimidazolium small molecule compounds was systematically investigated *via* changing the length of the N1-alkyl substituent. The corresponding membranes with enhanced alkaline stability were designed, prepared and characterized.

Experimental section

Synthesis of N1-alkyl substituted 2-methylimidazolium salts

The synthesis of 2-methylimidaolium salts with different N1-alkyl substituents contains two steps.

Firstly, N1-alkyl substituted 2-methylimidazole was synthesized.[28,29] 2-Methylimidazole (4 g, 48.8 mmol) was dissolved in dry DMF (10 mL). Potassium *tert*-butoxide or sodium hydride (1.2 times the molar amount of 2-methylimidazole) was slowly added to the above solution at 0–5 °C, followed by the slow addition of alkyl bromide (1.5 times the molar amount of 2-methylimidazole). After the mixture reacted at room temperature overnight, the solution mixture was poured into water. The solution was extracted with ethyl acetate 3–4 times. Then the extract was dried over anhydrous magnesium sulfate. Finally, the crude products were purified *via* column chromatography using ethyl acetate to obtain the desired N1-alkyl substituted 2-methylimidazole.

Secondly, the synthesis of N1-alkyl substituted 2-methylimidzolium salts was carried out as follows. The above synthesized N1-alkyl substituted 2-methylimidazole and an equivalent molar amount of benzyl chloride were stirred at 60 °C for 24 h. The products obtained were white or light yellow and should be stored in a glove box.

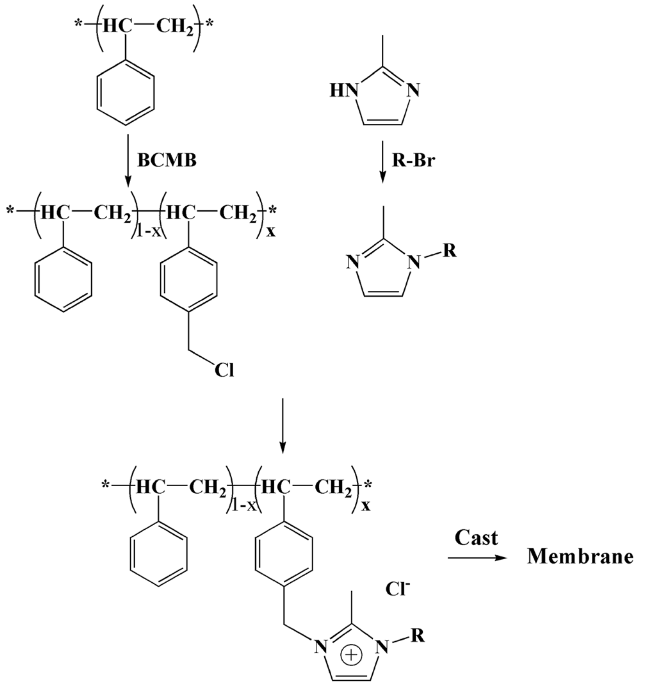
Alkaline stability of N1-alkyl substituted 2-methylimidazolium salts

The alkaline stability of different N1-alkyl substituted 2-methylimidazolium salts was investigated in 1 M KOH at 80 °C. The salts in Cl^- form were directly treated in NMR tubes.

Preparation of N1-alkyl substituted 2-methylimidazolium functionalized membranes

N1-alkyl substituted 2-methylimidazolium functionalized polymers were synthesized by the nucleophilic substitution reaction of polystyrene chloride and the synthesized N1-substituted 2-methylimidazole. The synthetic routes are shown in Scheme 1.

Firstly, the synthesis of polystyrene chloride was carried out. Polystyrene ([η] is 0.95 in DMSO solvent at 35 °C) (2 g) was dissolved in CCl_4 (50 mL) at 40 °C. Anhydrous tin chloride (1 mL) was added into the solution at 5 °C, followed by the dropwise addition of 1,4-bis(chloromethoxyl)butane (BCMB, 10 mL). The mixture was stirred below 15 °C and poured into ethanol. After being washed with ethanol and water several times, the white solid was dried under vacuum conditions below 50 °C. The chloromethylation degree of polystyrene was calculated by the relative integrated intensities of ^1H resonances (as shown in Fig. S16†).



Scheme 1 Synthetic routes to N1-alkyl substituted 2-methylimidazolium functionalized polymeric membranes.

Secondly, the synthesis of N1-alkyl substituted 2-methylimidazolium functionalized polymers was carried out. Polystyrene chloride and different N1-alkyl substituted 2-methylimidazoles were stirred in DMAc at 60 °C. The solution was filtered and poured onto a glass plate to cast the membrane. The membranes in OH^- form were obtained *via* treating the membranes in Cl^- form in 1 M KOH solution at room temperature for two days. In this work, the functional degree of the polymeric membranes based on different N1-alkyl substituted 2-methylimidazolium is the same.

NMR spectra

^1H and ^{13}C NMR spectra were recorded on a Bruker ACIII 400 spectrometer. The change of N1-alkyl substituted 2-methylimidazolium cations before and after being treated in KOH solution was investigated using the NMR spectra (D_2O as solvent). The chloromethylation degree of polystyrene was determined by using the ^1H NMR spectrum ($CDCl_3$ as solvent). The chloromethylation degree of polystyrene used to determine the alkaline stability of the functional groups is 22% and the chloromethylation degree of polystyrene used for the fuel cell test is 27.8%.

IEC, WU, SD, λ and WU_S of the membranes

The IEC of the membranes was determined by the back-titration method at room temperature. The titration end-point was determined by using a pH meter.

The IEC of the membranes is calculated using the following expression:

$$\mathrm{IEC}\left(\mathrm{mmol\ g^{-1}}\right) = \frac{n_{0\mathrm{HCl}} - n_{\mathrm{iHCl}}}{m} \times 1000$$

where $n_{0\mathrm{HCl}}$ and n_{iHCl} are the moles of HCl before and after the neutralization of the membrane, and m is the mass of the dried membrane in $\mathrm{OH^-}$ form.

The water uptake and the swelling degree of the membranes in $\mathrm{Cl^-}$ form are calculated from the weight and dimension differences of membranes after soaking in deionized water for 48 h at room temperature and after drying in a vacuum oven.

The water uptake is calculated by using the following equation:

$$\mathrm{WU}(\%) = \frac{W_{\mathrm{wet}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}} \times 100$$

where W_{wet} and W_{dry} are the weights of wet and dry membranes in $\mathrm{Cl^-}$ forms in grams, respectively.

The swelling degree was calculated by using the following equation:

$$\mathrm{SD}(\%) = \frac{L_{\mathrm{wet}} - L_{\mathrm{dry}}}{L_{\mathrm{dry}}} \times 100$$

where L_{wet} and L_{dry} are the geometric widths of the wet and dry membranes in $\mathrm{Cl^-}$ forms, respectively.

The number of absorbed water molecules per functional group, λ, was calculated using the following equation:

$$\lambda = \frac{\mathrm{WU}}{M_{\mathrm{H_2O}} \times \mathrm{IEC}} \times 10$$

The ratio of water uptake to swelling degree (noted as $\mathrm{WU_S}$) is also given in this work. The value is calculated using the following equation:

$$\mathrm{WU_S} = \mathrm{WU/SD}$$

Ionic conductivity of the membranes

The in-plane conductivity was calculated as follows:

$$\sigma = \frac{L}{WTR}$$

where σ is the conductivity of the membrane in S $\mathrm{cm^{-1}}$, L is the length of the membrane between sensor II and reference electrodes in cm, W and T are the width and thickness of the membrane in cm, respectively. R is the resistance of the membrane in ohm. The resistance of the membrane was measured with a Solartron AC impedance spectrometer.

Alkaline stability of the membranes

The alkaline stability of the membranes was monitored by measuring the changes of the ionic conductivity, dimensions and IEC values of the membrane before and after being kept in 1 M KOH solution at 60 °C. Before testing the conductivity, dimensions and IEC, the membranes were thoroughly washed with deionized water until the conductivity of the water used for washing the membranes is close to that of pure deionized water (1.86 μS $\mathrm{cm^{-1}}$).

Single cell tests

The single cell was fabricated by using 60 wt% PtRu/C (Johnson Matthey) with a metal loading of 2.6 mg $\mathrm{cm^{-2}}$ as the anode and 60 wt% Pt/C (Johnson Matthey) with a metal loading of 1 mg $\mathrm{cm^{-2}}$ as the cathode. The 1-hexyl-2-methylimidazolium-based polymer was used as the ionomer, with 2% and 20% loading at the anode and cathode, respectively. 1 M $\mathrm{CH_3OH}$ containing 1 M KOH at a flow rate of 1 mL $\mathrm{min^{-1}}$ was fed to the anode and simultaneously 80 sccm of $\mathrm{O_2}$ was fed to the cathode.

Results and discussion

Alkaline stability of N1-alkyl substituted 2-methylimidazolium cations

To estimate the steric hindrance and hyperconjugative effects on the alkaline stability of the 2-methylimidazolium functional group, different N1-alkyl substituted 2-methylimidazolium small molecular compounds were first synthesized. The chemical structures of imidazolium cations are shown in Fig. 1 and the chemical structures and purity of these imidazolium cations were confirmed by ^{1}H and ^{13}C NMR spectra (as shown in ESI Fig. S1–S6†). The cations were termed $[\mathrm{DMBEIm}]^+$, $[\mathrm{BMBEIm}]^+$, $[\mathrm{HMBEIm}]^+$, $[\mathrm{OMBEIm}]^+$, $[\mathrm{DeMBEIm}]^+$ and $[\mathrm{DoMBEIm}]^+$. To judge the alkaline stability of N1-alkyl substituted 2-methylimidazolium, the compounds were treated in 1 M KOH, the typical concentration of $\mathrm{OH^-}$ generated in the cathode of AAEMFCs (validated in the ESI†). Then, the samples were characterized by ^{1}H and ^{13}C NMR spectroscopy.

There were two new peaks (2.2 and 1.9 ppm) emerging in the ^{1}H NMR spectra of $[\mathrm{DMBEIm}]^+$ after the exposure to 1 M KOH at 80 °C for 168 h (Fig. 2A), indicating that $[\mathrm{DMBEIm}]^+$ is unstable in 1 M KOH at 80 °C. However, the introduction of butyl, hexyl or octyl at the N1 position of 2-methylimidazolium cations has greatly enhanced the alkaline stability of imidazolium. No new peaks were observed in the ^{1}H NMR spectra (Fig. 2B–D) of $[\mathrm{BMBEIm}]^+$, $[\mathrm{HMBEIm}]^+$ and $[\mathrm{OMBEIm}]^+$ cations after the exposure to 1 M KOH solution at 80 °C for more than 3000 h. Furthermore, no new peaks emerged in the ^{13}C NMR spectra (as shown in Fig. S9–S11†) of $[\mathrm{BMBEIm}]^+$, $[\mathrm{HMBEIm}]^+$ and $[\mathrm{OMBEIm}]^+$ cations after being treated in the same KOH solution.

Strangely, N1-decyl or dodecyl substituted 2-methylimidazolium cations are unexpectedly unstable under these conditions (Fig. 2E and F). In addition, $[\mathrm{DeMBEIm}]^+$ (16.0%)

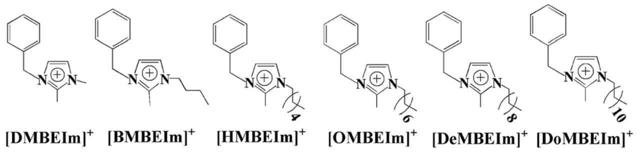


Fig. 1 Chemical structures of N1-substituted 2-methylimidazolium cations.

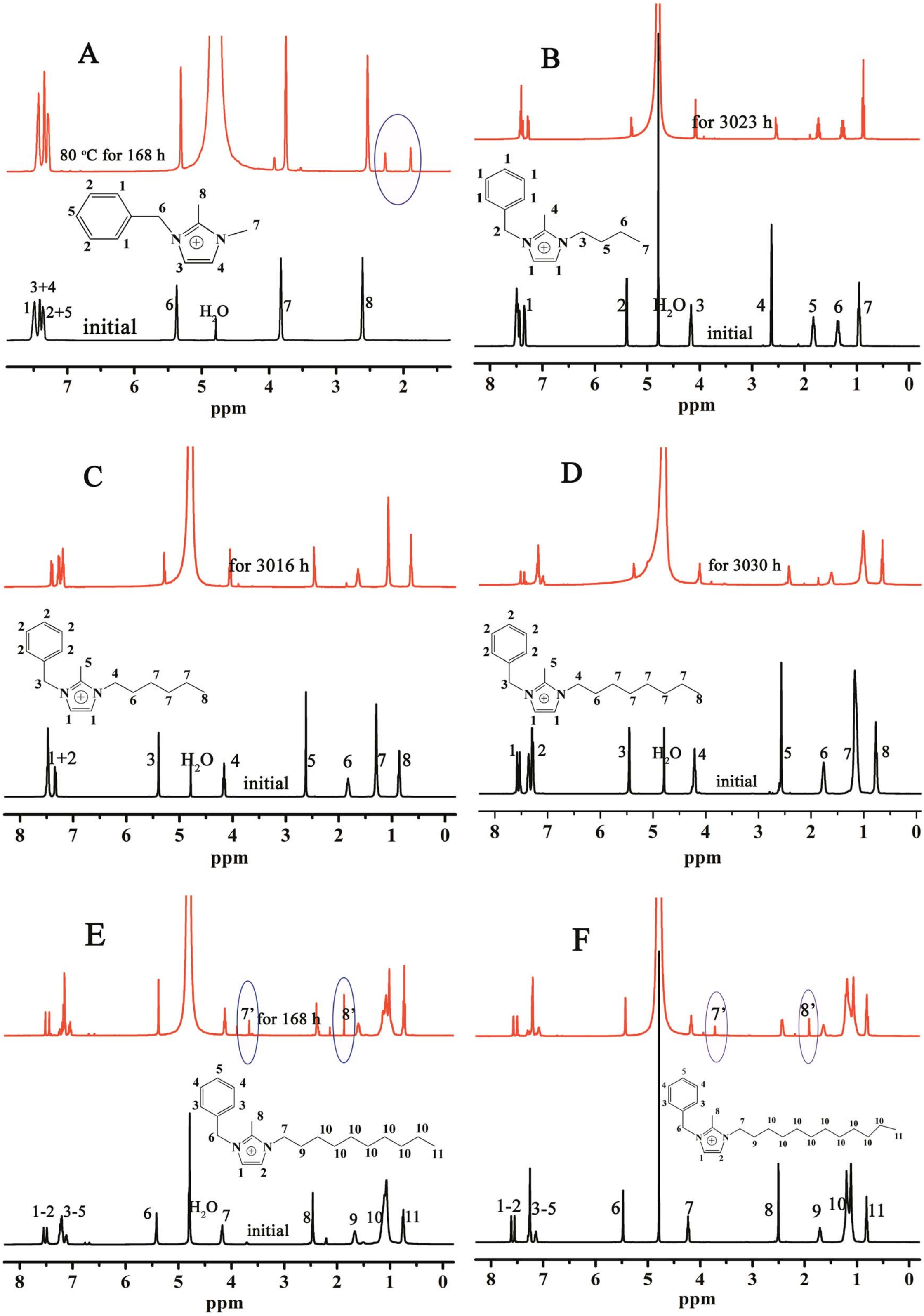


Fig. 2 ^{1}H NMR spectra of 2-methylimidazolium cations before and after the exposure to 1 M KOH solution at 80 °C: (A) $[DMBEIm]^+$; (B) $[BMBEIm]^+$; (C) $[HMBEIm]^+$; (D) $[OMBEIm]^+$; (E) $[DeMBEIm]^+$; (F) $[DoMBEIm]^+$.

and $[DoMBEIm]^+$ (14.6%) degraded much more severely than $[DMBEIm]^+$ (5.3%), confirmed by the relative integrated intensities of the ^{1}H resonances of ^{1}H NMR (as shown in the ESI†).

From the alkaline stability of 2-methylimidazolium cations, it can be concluded that the alkaline stability would not be always enhanced with the increase of the length of the N1-alkyl chain. N1-butyl, hexyl and octyl groups could greatly improve the alkaline stability of 2-methylimidazolium cations, which is due to the steric hindrance effect arising from the N1-substituted imidazolium. Though the hyperconjugative effect between the substituents (for example, C–H (σ bond) of the methyl group) and the π-conjugated imidazole ring[19,21] exists in $[DMBEIm]^+$, $[BMBEIm]^+$, $[HMBEIm]^+$ and $[OMBEIm]^+$ cations, the steric hindrance effect with the increase in the N1-alkyl length could effectively protect the C2 position of imidazolium from the attack of OH^- and enhance the alkaline stability. The unstability of $[DeMBEIm]^+$ and $[DoMBEIm]^+$ could be explained by the fact that when the chain length reaches a limit, decyl, dodecyl or longer group, an aggregate or a micelle would form, obstructing the formation of hyperconjugative effects between the decyl or dodecyl group and the π-conjugated imidazole ring or increasing the space between the imidazolium ions, which would result in the C2 position of 2-methylimidazolium cations easily attacked by OH^- and the degradation of 2-methylimidazolium functional groups.[21,30,31]

This result indicates that when the C2 (such as methyl) and N3 (benzyl) substituents are fixed, the alkaline stability of 2-methylimidazolium cations could be enhanced by appropriately modifying the N1-alkyl substitution.

Preparation and characterization of N1-alkyl substituted 2-methylimidazolium-based membranes

According to the alkaline stability of N1-alkyl substituted 2-methylimidazolium cations, the membranes based on N1-alkyl (including methyl, butyl, hexyl or octyl) substituted 2-methylimidazolium were prepared and characterized to evaluate the alkaline stability of the modified 2-methylimidazolium functional groups used in AAEMs. The membrane samples were named [PVDMIm][X], [PVBMIm][X], [PVHMIm][X] and [PVOMIm][X], respectively. X is OH for the IEC test and Cl for the test of other parameters.

The ion-exchange capacity (IEC), water uptake (WU), swelling degree (SD), hydration number (λ) and ratio of water uptake to swelling degree (WU_S) of the membranes are shown in Table 1.

From Table 1, it can be found that the WU, SD and λ of the membranes decrease with increasing the length of the N1-alkyl substituents of 2-methylimidazolium, as the substituents are methyl, butyl and hexyl groups. However, these values of the [PVOMIm][X] membrane with lower IEC are unexpectedly higher than those of [PVBMIm][X] and [PVHMIm][X], even higher than those of [PVDMIm][X]. Because the WU value might be lowered due to the excess SD of the membranes, so in order to eliminate the influence of SD on WU, we have introduced a parameter, WU_S, the ratio of WU to SD. As shown in Table 1, though the WU of the [PVOMIm][X] membrane is higher than those of [PVBMIm][X] and [PVHMIm][X] membranes, the WU_S of [PVOMIm][X] is much lower. This could be accounted for by the fact that the [PVOMIm][X] membrane has better hydration ability, but the larger SD results in a lower WU value as a function of the dimension change of the membrane.

Table 1 IEC, WU, SD, λ and WU_S of the N1-substituted 2-methylimidazolium-based membranes

Samples	IEC[a]/mmol g^{-1}	SD[a]/%	WU[a]/%	λ	WU_S
[PVDMIm][X]	0.45 ± 0.01	8.4 ± 4.1	12.5 ± 3.3	15	1.49
[PVBMIm][X]	0.42 ± 0.07	5.8 ± 1.1	7.9 ± 1.4	10	1.36
[PVHMIm][X]	0.53 ± 0.04	5.3 ± 2.4	6.4 ± 0.6	7	1.21
[PVOMIm][X]	0.33 ± 0.11	10.3 ± 0.8	8.5 ± 1.9	14	0.80

[a] Tested at room temperature.

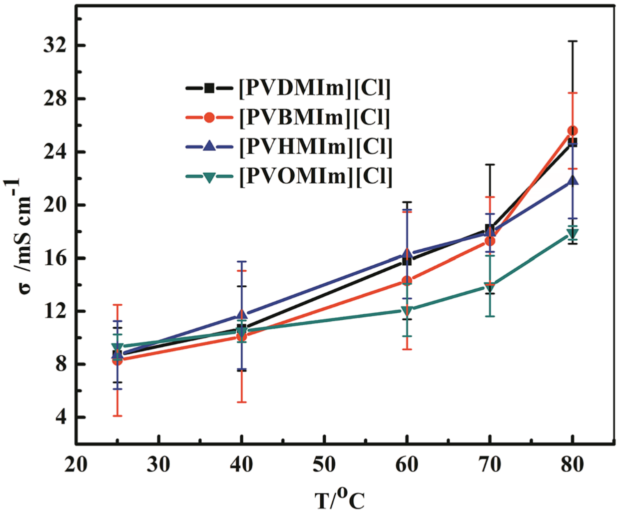


Fig. 3 Conductivity of the N1-alkyl substituted 2-methylimidazolium-based membranes as a function of temperature.

It can be seen that the IEC and WU_S values of 2-methylimidazolium-based membranes would decrease with the increase of the length of N1-alkyl substituents. Furthermore, the conductivity of the membranes would simultaneously increase as the length of the N1-alkyl chain increases when the test temperature was at 80 °C (Fig. 3). This result is due to the fact that the higher molecular weight (longer N1-alkyl substituents) leads to the reduction of functional groups in the unit mass of the membranes.

By comparing the changes of the IEC, conductivity and dimensions of the membranes after the exposure to 1 M KOH at 60 °C, it can be seen that the alkaline stability of the [PVBMIm][OH], [PVHMIm][OH] and [PVOMIm][OH] membranes was much better than that of the [PVDMIm][OH] membrane. The conductivity, IEC and dimension values of [PVBMIm][OH], [PVHMIm][OH] and [PVOMIm][OH] membranes basically remain the same, especially the conductivity and IEC values (as shown in Fig. 4). From the results shown in Table S1† and Fig. 4, it can be concluded that [PVBMIm][OH], [PVHMIm][OH] and [PVOMIm][OH] membranes are more stable than the [PVDMIm][OH] membrane. The alkaline stability of these membranes is consistent with that of the 2-methylimidazolium small molecule compounds with the same N1-alkyl substituents, indicating that the steric hindrance or hyperconjugative effects of N1-alkyl substitution could greatly enhance not only the

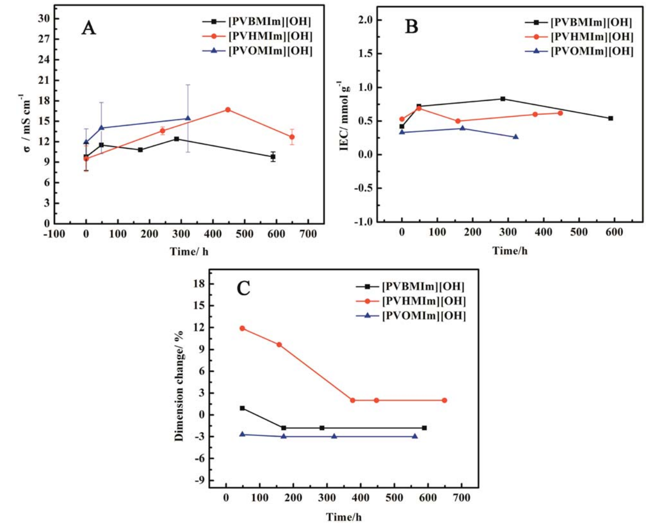


Fig. 4 Conductivity, IEC and dimension changes of [PVBMIm][OH], [PVHMIm][OH] and [PVOMIm][OH] membranes as a function of time after immersion in 1 M KOH solution at 60 °C: (A) conductivity; (B) IEC; (C) dimension.

alkaline stability of single small molecular compounds but also the stability of the functional group attached to the polymeric chain.

Performance of fuel cells using N1-alkyl substituted 2-methylimidazolium membranes

The alkaline direct methanol fuel cells (ADMFCs) using the membranes were also tested to evaluate these membranes in the fuel cell environment. In order to meet the requirement of ADMFCs for the conductivity of the membranes, membranes with a higher functionalization degree were prepared in this work. The conductivity of the fabricated membranes in the Cl^- form is shown in Fig. S17.† It can be seen that the conductivities are all above 10^{-2} mS cm^{-1} at room temperature, which could fulfil the basic conductivity requirement for fuel cell applications (Table 2).[32]

Herein, the more stable [PVBMIm][Cl], [PVHMIm][Cl] and [PVOMIm][Cl] membranes were used as AAEMs to fabricate the membrane electrode assembly (MEA). The fuel cell performance is shown in Fig. 5. All the fuel cells using different membranes possessed a high open voltage (>0.9 V), indicating the low methanol cross-over and the high activity of the catalysts. Considering the influence of ohmic polarization (as shown in Table 2), the performances of the fuel cells using different membranes decrease in the following order: [PVBMIm][Cl] > [PVHMIm][Cl] > [PVOMIm][Cl]. The peak power densities of the fuel cells using [PVBMIm][Cl], [PVHMIm][Cl] and [PVOMIm][Cl] membranes are 33.4, 29.6 and 24.3 mW cm^{-2}, respectively. Although such fuel cell performance is not as good as those in previous reports,[33–35] we believe that it could be improved by optimizing the electrode structure which will be further studied in future work.

Table 2 The parameters of the membranes used to fabricate MEAs

Samples	Thickness/ μm	Conductivity[a]/ mS cm^{-1}	Relative resistance
[PVBMIm][X]	45	24.6	1.83
[PVHMIm][X]	60	30.9	1.94
[PVOMIm][X]	54	17.4	3.1

[a] Tested at 60 °C in deionized water.

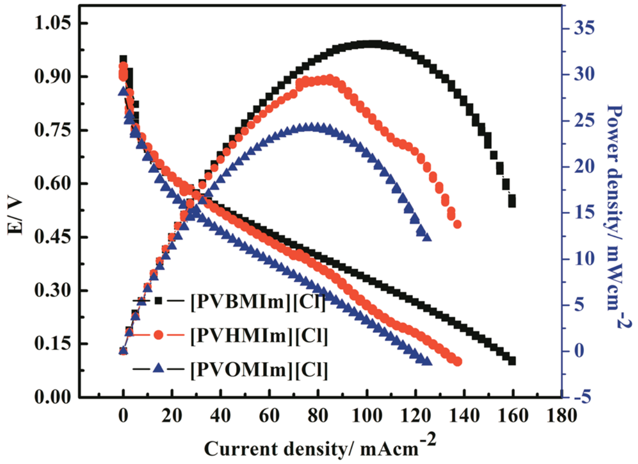


Fig. 5 Polarization and power density curves of the alkaline direct methanol fuel cell assembled with [PVBMIm][OH], [PVHMIm][OH] and [PVOMIm][OH] membranes. The test temperature was 60 °C.

Conclusions

In this study, highly alkaline stable 2-methylimidazolium cations with different N1 substituents were designed, synthesized and investigated to evaluate their potential application as the functional groups of AAEMs. The introduction of steric hindrance and hyperconjugative effects at N1 substituents of 2-methylimidazolium could greatly enhance the stability of imidazolium. Compared with 1,2-dimethylimidazolium, N1-butyl, hexyl or octyl substituted 2-methylimidazolium exhibited much more alkaline stability in 1 M KOH at 80 °C (for more than 3000 h). Accordingly, the *N*-butyl, hexyl or octyl substituted 2-methylimidazolium-based AAEMs show a stable conductivity, IEC and dimension after the exposure to 1 M KOH at 60 °C. Furthermore, the peak power densities of the ADMFCs using [PVBMIm][Cl], [PVHMIm][Cl] and [PVOMIm][Cl] membranes are 33.4, 29.6 and 24.3 mW cm^{-2} without any optimization of the electrodes, which indicates that these membranes have potential application in ADMFCs. The new approach proposed in this work to stabilize 2-methylimidazolium in alkaline solution at elevated temperature gives rise to potential application of such types of membranes in AAEMFCs.

Acknowledgements

This work is financially supported by the National Basic Research Program of China (2012CB215500).

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