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PAPER

Highly Alkaline Stable N1-Alkyl Substituted 2-Methylimidazolium Functionalized Alkaline Anion Exchange Membranes

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

15 ## Introduction

Alkaline anion exchange membrane fuel cells (AAEMFCs) are attracting more and more significant interest due to its lower cost than that of proton exchange membrane fuel cells (PEMFCs).[1-4] However, alkaline anion exchange membranes (AAEMs), a
20 critical component of AAEMFCs, are facing the issue of inadequate alkaline stability in high pH environment at elevated temperature. Although the chemical stability of both polymer backbone and functional groups of AAEMs would be challenged in alkaline condition[5-8], the degradation of the positively charged
25 groups is more severe in alkaline conditions involving hydroxide ions, a potent nucleophile.[9-13] Therefore, it is necessary to discover and explore the positively charged group with high alkaline stability. Imidazolium, possessing a π-conjugated imidazole ring (which could reduce the S_N2 substitution,
30 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-
35 elimination pathway.[15, 23-25] In this pathway, OH$^-$ first attacks at 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 interferences, introduced by substitutions at the C-2, C-4, and C-5 positions, have a significant
40 and positive impact on the alkaline stability of imidazolium according to the DFT result.[25] The experimental data have proved that C2- and (or) N3-substituents, especially C2-methyl or N3-isopropyl, indeed enhance the stability of imidazolium cations in alkaline condition.[19, 21, 26] However, Varcoe et al. recently

45 proposed that 1,2-dimethylimidazolium-based AAEMs were unstable in 1 M KOH at 60 $^{\circ}$C.[27] They found that the conductivity and IEC of this membrane would degrade greatly after the exposure to alkaline solution for one day. In our previous experiments, we also found that the 1,2-dimethylimidazolium
50 functionalized styrene polymeric membranes is not stable enough. The conductivity, IEC and dimension of this membrane would diminish after the exposure to 1 M KOH at 60 $^{\circ}$C for about 100 h (as shown in Table S1). Thus, to meet the requirement of AAEMs, designing a new and highly stable 2-methylimidazolium
55 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 to the C2-position of
60 imidazolium was not a good option to stabilize the imidazolium, confirmed by Price'group.[26] What if both steric hindrance and hyperconjugative effects were simultaneously brought into the N1-positionof 2-methylimidazolium? So in this work, the influence of the N1-alkyl substitutions on the alkaline stability of
65 2-methylimidazolium small molecules compounds was systemically investigated via changing the length of the N1-alkyl substitution. The corresponding membranes with enhanced alkaline stability were designed, prepared and characterized.

Experimental section

70 **Synthesis of N1-alkyl substituted 2-methylimidazolium salts**

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

Firstly, it is for the synthesis of N1-alkyl substituted 2-

methylimidazole.[28, 29] The 2-methylimidazole (4 g, 48.8 mmol) was dissolved in dry DMF (10 mL). Potassium tert-butoxide or sodium hydride (1.2 times molar amount of 2-methylimidazole) was slowly added to the above solution at 0-5 ^{o}C, followed by the slow addition of alkyl bromide (1.5 times molar amount of 2-methylimidazole). After the mixture reacted at room temperature overnight, the mixture solution was poured into water. The solution was extracted with ethyl acetate for 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 is as follows. The above synthesized N1-alkyl substituted 2-methylimidazole and an equivalent molar amount of benzyl chloride were stirred at 60 ^{o}C for 24 h. The products were white or light yellow and should be stored in glove box.

Alkaline stability of N1-alkyl substituted 2-methylimidazolium salts

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

Preparation of the N1-alkyl substituted 2-methylimidazolium functionalized membranes
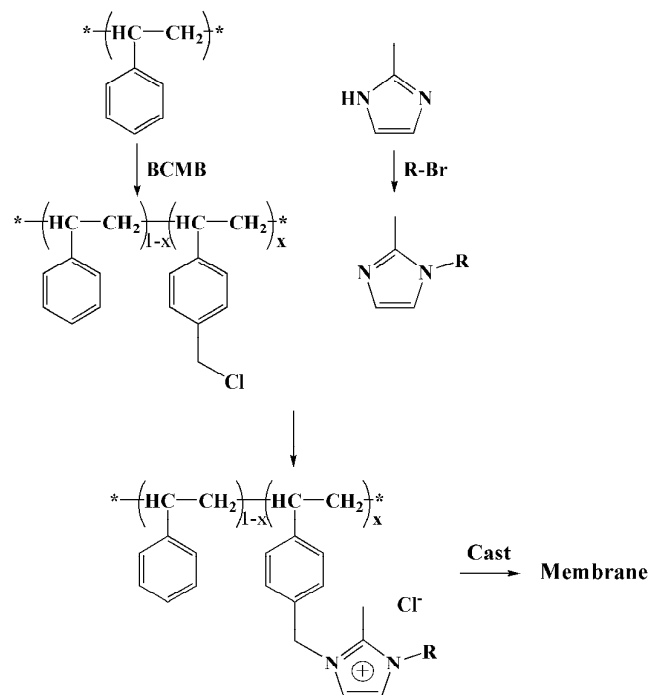
Scheme 1. Synthetic routes of N1-alkyl substituted 2-methylimidazolium functionalized polymeric membranes.

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

Firstly, it is the synthesis of polystyrene chloride. Polystyrene ([η] is 0.95 in DMSO solvent at 35 ^{o}C) (2g) was dissolved in CCl$_4$ (50 mL) at 40 ^{o}C. Anhydrous tin chloride (1 mL) was added into the solution at 5 ^{o}C, followed by the drop addition of 1,4-bis(chloromethoxy) butane (BCMB, 10 mL). The mixture was stirred below 15 ^{o}C and poured into ethanol. After being washed with ethanol and water for several times, the white solid was dried under vacuum condition below 50 ^{o}C. The chloromethyl degree of polystyrene was calculated by the relative integrated intensities of the ^{1}H resonances (as shown in Figure S16).

Secondly, it is for the synthesis of the N1-alkyl substituted 2-methylimidazolium functionalized polymers. Polystyrene chloride and different N1-alkyl substituted 2-methylimidazoles were stirred in DMAc at 60 ^{o}C. The solution was filtrated and poured onto a glass plate to cast membrane. The membranes in OH$^-$ form were received 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 substitutions 2-methylimidazolium is the same.

NMR spectra

^{1}H and ^{13}C NMR spectra were carried out on Bruker ACIII 400 spectrometer. The change of the N1-alkyl substituted 2-methylimidazolium cations before and after being treated in KOH solution was investigated by the NMR spectra (D$_2$O as solvent). The chloromethylation degree of polystyrene was determined by the ^{1}H 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 WUs of the membranes

IEC of the membranes was determined by the back-titration method at room temperature. The titration-end point was determined by pH meter.
IEC of the membranes is calculated using the following expression:

$$IEC(mmo\lg^{-1}) = \frac{n_{0HCl} - n_{iHCl}}{m} \times 1000$$

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

The water uptake and the swelling degree of the membranes in 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 the equation as follows:

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

where W_{wet} and W_{dry} are the weight of wet and dry membranes in Cl$^-$ forms in grams, respectively.
The swelling degree was calculated by the equation as follows:

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

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

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

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

10 The ratio of water uptake to swelling degree (noted as WU_S) is also given in this work. The value is calculated as the following equation:

$$WU_S = WU / SD$$

Ionic conductivity of the membranes

15 The in-plane conductivity was calculated as follows:

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

where σ is the conductivity of the membrane in S cm^{-1}, L is the length of the membrane between sensor II and reference
20 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

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

Single cell tests

The single cell was fabricated by using 60 wt% PtRu/C (Johnson
35 Matthey) with metal loading of 2.6 mg cm^{-2} as the anode and 60 wt% Pt/C (Johnson Matthey) with metal loading of 1 mg cm^{-2} as the cathode, respectively. 1-Hexyl-2-methylimidazolium-based polymer was used as the ionomer, with 2% and 20% loading at anode and cathode, respectively. 1 M CH$_3$OH containing 1 M
40 KOH with the flow rate of 1 mL min^{-1} was fed to the anode and simultaneously 80 sccm of O$_2$ was fed to the cathode.

Results and discussion

Alkaline stability of N1-alkyl substituted 2-methylimidazolium cations

45 To estimate the steric hindrance and hyperconjugative effects on the alkaline stability of 2-methylimidazolium functional group, different N1-alkyl substituted 2-methylimidazolium small molecular compounds were firstly synthesized. The chemical structures of imidazolium cations were shown in Fig. 1 and the

50 chemical structures and purity of these imidazolium cations were confirmed by ^{1}H and ^{13}C NMR spectra (as shown in Supporting Information Figure S1-S6). The cations were termed as [DMBEIm]$^+$, [BMBEIm]$^+$, [HMBEIm]$^+$, [OMBEIm]$^+$, [DeMBEIm]$^+$ and [DoMBEIm]$^+$. To judge the alkaline stability of
55 N1-alkyl substituted 2-methylimidazolium, the compounds were treated in 1 M KOH, the typical concentration of OH$^-$ generated in the cathode of AAEMFCs (validated as Supporting Information). Afterwards, the samples were characterized by ^{1}H and ^{13}C NMR spectroscopy.

[DMBEIm]$^+$ [BMBEIm]$^+$ [HMBEIm]$^+$ [OMBEIm]$^+$ [DeMBEIm]$^+$ [DoMBEIm]$^+$

60 **Fig. 1.** Chemical structures of N1-substituted 2-methylimidazolium cations.
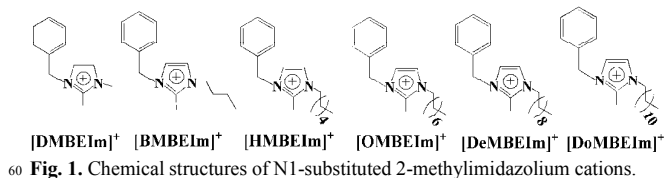
There were two new peaks (2.2 and 1.9 ppm) emerging in the ^{1}H NMR spectra of [DMBEIm]$^+$ after the exposure to 1 M KOH at 80 °C for 168 h (Figure 2A), indicating that [DMBEIm]$^+$ is unstable in 1 M KOH at 80 °C. However, the introduction of
65 butyl, hexyl or octyl to the N1-position of 2-methylimidazolium cations has greatly enhanced the alkaline stability of imidazolium. It can be seen that no new peaks were observed in the ^{1}H NMR spectra (Fig.2B, 2C, 2D) of [BMBEIm]$^+$, [HMBEIm]$^+$ and [OMBEIm]$^+$cations after the exposure to 1 M KOH solution at 80
70 °C for more than 3000 h. Furthermore, no new peaks emerged in the ^{13}C NMR spectra （as shown in Figure S9-S11） of [BMBEIm]$^+$, [HMBEIm]$^+$ and [OMBEIm]$^+$cations after being treated in the same KOH solution.

Strangely, N1-decyl or dodecyl substituted 2-
75 methylimidazolium cations are unexpectedly unstable in this condition (Fig. 2E and 2F). Even more, [DeMBEIm]$^+$ (16.0%) 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
80 Supporting Information).

From the alkaline stability of 2-methylimidazolium cations, it can be concluded that the alkaline stability would be not always enhanced as the increase of the length of N1-alkyl. N1-butyl, hexyl and octyl groups could greatly improve the alkaline
85 stability of 2-methylimidazolium cations, which is due to the steric hindrance effect arose from the N1-substituents imidazolium. Though the hyperconjugative effect between the substitutions (for example, C−H (σ bond) of methyl group) and the π-conjugated imidazole ring[19, 21] exists in [DMBEIm]$^+$,
90 [BMBEIm]$^+$, [HMBEIm]$^+$ and [OMBEIm]$^+$cations, the steric hindrance effect with the increase in the N1-alkyl length could effectively protect C2-position of imidazolium from the attack of OH$^-$ and enhance the alkaline stability. The unstability of [DeMBEIm]$^+$ and [DoMBEIm]$^+$ could be explained that when the
95 chain length reaches a limit, decyl, dodecyl or longer group, the aggregation or the 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-
100 position of 2-methylimidazolium cations easily attacked by OH-and the degradation of 2-methylimidazolium functional groups.[21, 30, 31]
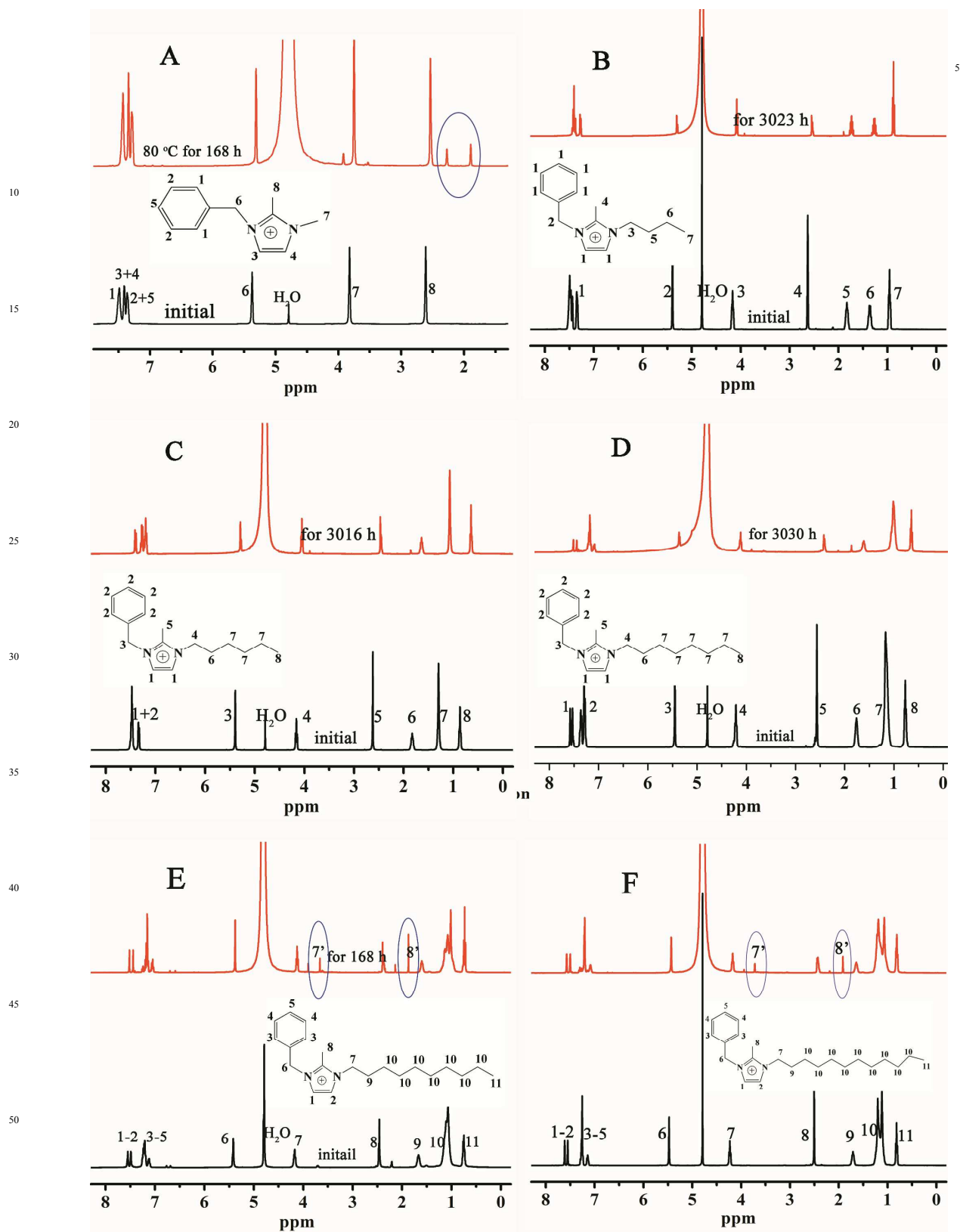
Fig.2. ^{1}H NMR spectra of 2-methylimidazolium cations before and after the exposure to 1 M KOH solution at 80 °C: (A) [DMBEIm]$^+$; (B) [BMBEIm]$^+$; (C) [HMBEIm]$^+$; (D) [OMBEIm]$^+$; (E) [DeMBEIm]$^+$; (F)[DoMBEIm]$^+$.

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

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

According to the alkaline stability of the N1-alkyl substituted 2-methylimidazolium cations, the membranes based on the 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 as [PVDMIm][X], [PVBMIm][X], [PVHMIm][X] and [PVOMIm][X], respectively. X is OH for the IEC test and Cl for the other parameter test.

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.

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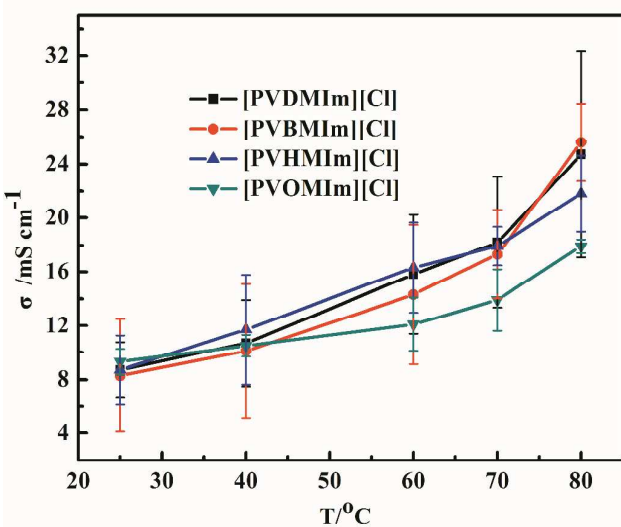

Fig. 3 Conductivity of the N1-alkyl substituted 2-methylimidazolium-based membranes as a function of temperature.

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 substitutions of 2-methylimidazolium as the substitutions are methyl, butyl and hexyl groups. However, these values of the [PVOMIm][X] membrane with lower IEC are unexpectedly

higher than that of [PVBMIm][X] and [PVHMIm][X], even higher than that 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 the SD on the WU, we brought in a parameter, WU$_s$, the ratio of WU to SD. As shown in Table 1, though the WU of [PVOMIm][X] membrane is higher than that of [PVBMIm][X] and [PVHMIm][X] membranes, the WU$_S$ of [PVOMIm][X] is much lower. This could be accounted for that [PVOMIm][X] membrane has the better hydration ability, but the larger SD results in a lower WU value as a function of the dimension change of the membrane.

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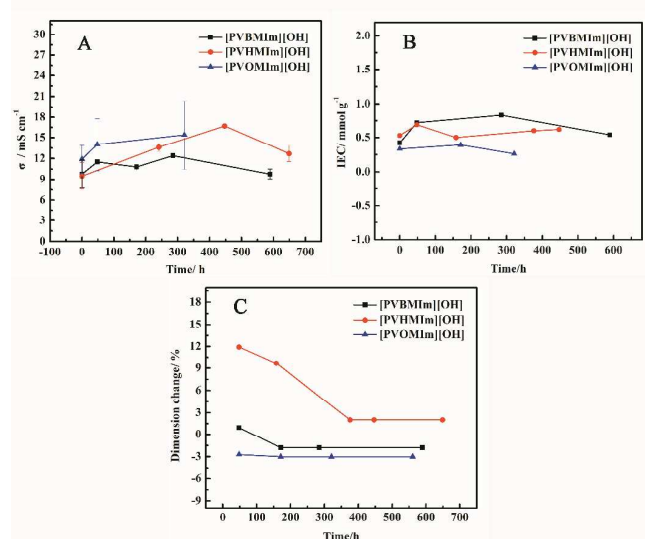

Fig. 4 Conductivity, IEC and dimension changes of [PVBMIm][OH], [PVHMIm][OH] and [PVOMIm][OH] membranes as a function of time after immersion in 1 M KOH solution at 60 °C: (A) conductivity; (B) IEC; (C) dimension.

By comparing the changes of the IEC, conductivity and dimension 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 [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, Fig.4, it can be concluded that [PVBMIm][OH], [PVHMIm][OH] and [PVOMIm][OH] membranes are more stable than [PVDMIm][OH] membrane. The alkaline stability of these membranes is consistent with that of the 2-methylimidazolium small molecules compounds with the same N1-alkyl substitutions, indicating that the steric hindrance or hyperconjugative effects of N1-alkyl substitution could greatly

enhance not only the alkaline stability of the single small molecular compounds but also the stability of the functional group attached to the polymeric chain.

5 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 10 ADMFCs for the conductivity of the membranes, membranes with higher functionalized degree were prepared in this work. The conductivity of the fabricated membranes in the Cl⁻ form is shown in Figure S17. It can be seen that the conductivities are all above 10^{-2} mScm⁻¹ at room temperature, which could fulfil the 15 basic conductivity requirement for fuel cell application.[32]

Table 2. The parameters of the membranes used to fabricate MEAs.

Samples	Thickness /μm	Conductivitya /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

ᵃtested at 60 ºC in deionized water.

Herein, the more stable [PVBMIm][Cl], [PVHMIm][Cl] and [PVOMIm][Cl] membranes were used as AAEMs to fabricate 20 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 (>0.9V), indicating the low methanol cross-over and the high activity of the catalysts. Considering the influence of ohmic polarization (as shown in 25 Supporting Information in Table 2), the performances of the fuel cells suing 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 30 and 24.3 mW cm⁻², respectively. Although such fuel cell performance is not as good as the previous reports[33-35], we believe it could be improved by optimizing the electrode structure which will be further studied in the future work.
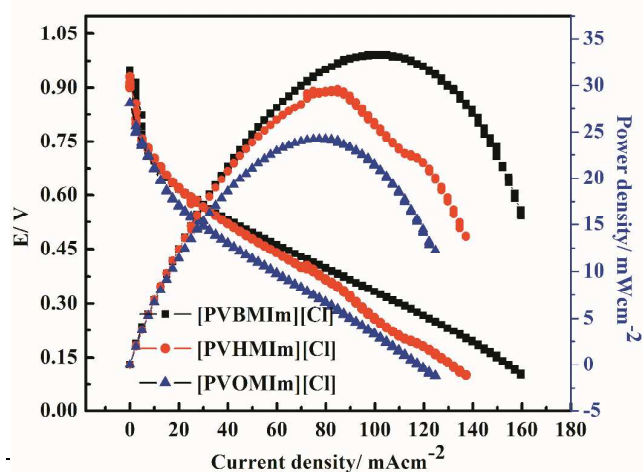

Fig. 5. Polarization and power density curves of alkaline direct methanol fuel 35 cell assembled with [PVBMIm][OH], [PVHMIm][OH] and [PVOMIm][OH] membranes. The test temperature was 60 ºC.

4. Conclusions

The highly alkaline stable 2-methylimidazolium cations with different N1-substituents were designed, synthesized and 40 investigated to evaluate the potential application as the functional groups of AAEMs. The introduction of steric hindrance and hyperconjugative effects into N1-substitutions of 2-methylimidazolium could greatly enhance the stability of imidazolium. Comparing with 1,2-dimethylimidazolium, N1-45 butyl, hexyl or octyl substituted 2-methylimidazolium exhibited much more alkaline stability in 1 M KOH at 80 ºC (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 ºC. 50 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 the potential application in ADMFCs. The new approach proposed in 55 this work to stabilize the 2-methylimidazolium in alkaline solution at elevated temperature give a potential application of such type of membranes in AAEMFCs.

Notes and references

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† Electronic Supplementary Information (ESI) available: The change of conductivity, IEC and dimension of 1,2-dimethylimidazolium-based 70 membrane after the exposure to 1 M KOH at 60 ºC, detailed synthetic courses and NMR characterization of 2-methylimidazolium salts,calculation of the OH⁻ concentration in cathode for the typical fuel cell condition, ¹³C NMR of [DMBEIm]⁺,[BMBEIm]⁺, [HMBEIm]⁺,[OMBEIm]⁺and[DoMBEIm]⁺cations before and after the 75 exposure to 1 M KOH solution at 80 ºC, degradation mechanism of 2-methylimidazolium cations, ¹H NMR polystyrene chloride,conductivities of the membranes used for the fuel cell test, and resistance of ADMFCs using different membranes. See DOI: 10.1039/b000000x/

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Alkaline stability
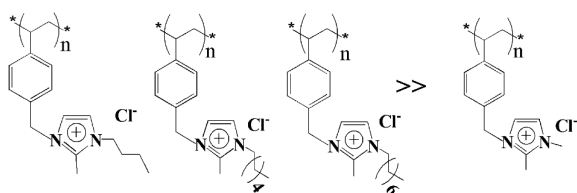
The N1-butyl, hexyl or octyl-substituted 2-methylimidazolium functional groups are much more stable than 1,2-dimethylimidazolium functional group.