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# Comparison of alkaline stability of quaternary ammonium- and 1,2-methylimidazolium-based alkaline anion exchange membranes

Congrong Yang<sup>a,b</sup>, Suli Wang<sup>a</sup>, Wenjia Ma<sup>a</sup>, Luhua Jiang<sup>a</sup>, Gongquan Sun<sup>a,\*</sup>

<sup>a</sup> Division of Fuel Cell & Battery, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China

<sup>b</sup> University of the Chinese Academy of Sciences, Beijing 100039, PR China

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## ABSTRACT

The alkaline stability of 1,2-dimethylimidazolium with various N3-substituents (including butyl, benzyl and vinylbenzyl) and corresponding quaternary ammonium small molecular compounds, and the 1,2-dimethylimidazolium- and quaternary ammonium-based membranes are systematically studied in the same condition. The spectroscopy (such as NMR, FT-IR, XPS and mass spectrum) results of the two kinds of small molecular compounds indicate that the quaternary ammonium cations are more stable than 1,2-dimethylimidazolium cations in 3 M KOH at elevated temperature, especially at 80 °C. Moreover, the alkaline stability of the 1,2-dimethylimidazolium cations would be influenced by the N3-substitutions of the imidazolium, and N3-butyl substituted cation shows a better alkaline stability. The quaternary ammonium-based membrane are also more stable than the 1,2-dimethylimidazolium-based membrane in 1 M KOH at 60 °C. In addition, the performance of the alkaline direct methanol fuel cell using quaternary ammonium-based membrane (22 mW cm<sup>-2</sup>) is much better than that of the fuel cell using 1,2-dimethylimidazolium-based membrane (0.04 mW cm<sup>-2</sup>).

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## 1. Introduction

Recently, alkaline anion exchange membrane fuel cells (AAEMFCs) have been evoked great interests due to the much faster kinetics of fuel electro-oxidation in alkaline environment than that in an acidic media [1–3]. Consequently, non-noble metals or inexpensive metals/metal oxides can be used as catalysts under alkaline conditions, which can greatly reduce the cost of the AAEMFCs. Moreover, the utilization of alkaline anion exchange membranes (AAEMs) replacing the aqueous KOH electrolyte may fundamentally solve the problem in conventional alkaline fuel cells, including the electrolyte leakage and carbonation problem [2].

However, one of the major challenges associated with the development of AAEMFCs is the availability of suitable alkaline anion exchange membranes (AAEMs) that provide suitable hydroxide conductivity and chemical stability under basic conditions. In the past several years, the conductivity of the AAEMs has been improved by an order of magnitude (from 10<sup>-2</sup> S cm<sup>-1</sup> to 10<sup>-1</sup> S cm<sup>-1</sup>) with the

efforts of the researchers [4,5]. However, the poor chemical stability, especially the poor stability of the functional groups, limits the application of AAEMs in alkaline conditions involving hydroxide ions, a potent nucleophile. Therefore, it is crucial to search for a stable functional group for AAEMs. Quaternary ammonium, commonly used as functional group for AAEMs, has been extensively studied [6–11]. Recently, some other functional groups, such as guanidinium [12], phosphonium [13], imidazolium [14–24], benzimidazolium [25] and metal-cation [26], are also being proposed. Among them, the imidazolium functional groups are thought to be environment friendly and to some extent alkaline stable due to the presence of the  $\pi$ -conjugated imidazole ring. However, is 1,2-dimethylimidazolium more stable than quaternary ammonium in the same condition? And are 1,2-dimethylimidazolium-based AAEMs indeed more suitable than quaternary ammonium-based membranes for the environment of AAEMFCs?

The objective of this work is to: (1) systematically compare the alkaline stability of quaternary ammonium and 1,2-dimethylimidazolium small molecular compounds; (2) compare the alkaline stability of 2-methylimidazolium- and quaternary ammonium-based membranes; and (3) test the performances of the 1,2-dimethylimidazolium- and quaternary ammonium-based membranes in the alkaline direct methanol fuel cells (ADMFCs).

\* Corresponding author. Tel.: +86 411 84379063; fax: +86 411 84379063.

E-mail address: [gqsun@dicp.ac.cn](mailto:gqsun@dicp.ac.cn) (G. Sun).

## 2. Experimental section

### 2.1. Materials

4-Vinylbenzyl chloride (VBC, 90%) was purchased from TCI (Shanghai) Development Co., Ltd. n-Butylbromide, trimethylamine alcoholic solution 33% and benzyl chloride were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,2-Dimethylimidazole was purchased from Aladdin Industrial Corporation.  $\alpha,\alpha'$ -Dichloro-p-xylene was purchased from Energy Chemical. Polystyrene was from national polymer corporation and its  $[\eta]$  is 0.95 (DMSO as solvent at 35 °C). The reagents were used as purchased without being further purified. Deionized water was used in the experiments.

### 2.2. Synthesis of quaternary ammonium and 1,2-methylimidazolium salts

The 1,2-methylimidazolium cations with various N3-substituents (butyl, benzyl and vinylbenzyl) and the corresponding trimethylammonium salts, including 1,2-dimethyl-3-butylimidazolium bromide [DMBUI][Br], 1,2-dimethyl-3-benzylimidazolium chloride ([DMBEIM][Cl]), 1,2-dimethyl-3-vinylbenzylimidazolium chloride ([DMVBIM][Cl]), butyltrimethylammonium bromide ([BUTMA][Br]), benzyltrimethylammonium chloride ([BETMA][Cl]) and vinylbenzyltrimethylammonium chloride ([VBTMA][Cl]) were synthesized via the nucleophilic substitution reaction. All the reactions were conducted in oven-dried, sealable, Schlenk reaction tubes under magnetically stirring.

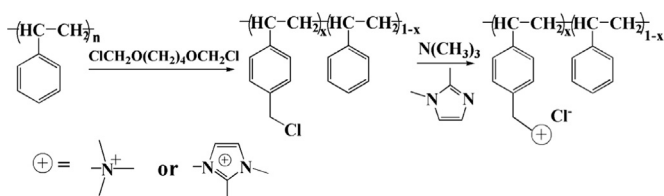
[BUTMA][Br] was synthesized by stirring a solution containing trimethylamine (TMA) and a twice molar amount of n-butyl bromide at 40 °C for 2 h. Then the white solid was obtained by pouring the solution into ethyl acetate and washed with ethyl acetate for three times. Finally the solid was dried in vacuum oven at 50 °C overnight.

Other quaternary ammonium salts and the 1,2-dimethylimidazolium salts were synthesized in the similar way.

The alkaline stability of the 1,2-dimethylimidazolium and quaternary ammonium cations was tested by directly treating the salts in  $X^-$  ( $X=Cl$  and Br) form in KOH solution at different temperatures.

### 2.3. Preparation of 1,2-dimethylimidazolium- and quaternary ammonium-based membranes

The membranes were prepared using the 1,2-dimethylimidazolium- and quaternary ammonium-based polymers. The polymers were synthesized by two steps, including chloromethylation and functionalization. Scheme 1 shows the synthetic routes of the polymers. Firstly, it was the synthesis of polystyrene chloride. Polystyrene reacted with 1,4-bis(chloromethoxyl) butane catalyzed by Lewis acid below 15 °C for 4 h. Then the 1,2-dimethylimidazolium and quaternary ammonium functionalized polymers were obtained by stirring the mixture solution of polystyrene chloride and equivalent molar amount of 1,2-dimethylimidazole or trimethylamine/alcohol solution in DMAc at 60 °C. In this work, to alleviate the swelling degree (SD) of the membranes, the  $\alpha,\alpha'$ -



**Scheme 1.** Synthetic route of 1,2-dimethylimidazolium- and quaternary ammonium-based polymers.

dichloro-p-xylene (10 mol% to the unchloromethylated CMPS) used as cross-link reagent was added into the membrane-forming solution to prepare the cross-linked membranes. The thickness of the cast membranes was controlled between 30  $\mu\text{m}$  and 40  $\mu\text{m}$ . Finally, the membranes in  $\text{Cl}^-$  form were exchanged into  $\text{OH}^-$  form by treating the membranes in 1 M KOH solution at room temperature for two days.

### 2.4. Nuclear Magnetic Resonance (NMR) spectra

NMR was measured on Bruker ACIII 400 spectrometer. The change of the quaternary ammonium and the 1,2-dimethylimidazolium cations was investigated by the NMR spectra ( $\text{D}_2\text{O}$  was used as solvent). The chloromethylation degree of polystyrene was also determined by NMR spectrum ( $\text{CDCl}_3$  as the solvent).

### 2.5. Morphological characterization of the membranes

The morphologies of the membranes were characterized by scanning electron microscopy (SEM) with JEOL 6390LV. For observation, the membrane samples were sputtered with gold.

### 2.6. Water uptake (WU), SD and ion-exchange capacity (IEC) of the membranes

IEC of the membranes was determined by the back-titration method.

The calculation of IEC was as follows:

$$\text{IEC}(\text{mmol g}^{-1}) = \frac{N_{\text{OHCl}} - N_{\text{HCl}}}{m}$$

where  $N_{\text{OHCl}}$  and  $N_{\text{HCl}}$  are the moles of HCl before and after the membrane neutralization, and  $m$  is the mass of the dried membrane in  $\text{OH}^-$  form.

The WU and SD of the membranes in  $\text{Cl}^-$  form were calculated from the weight and dimension differences of the membranes after soaking in deionized water for 48 h at room temperature and after drying in a vacuum oven.

The WU was calculated by the equation as follows:

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

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

The SD was calculated by the equation as follows:

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

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

### 2.7. Ionic conductivity of the membranes

The ionic conductivity was calculated as follows:

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

where  $\sigma$  is the conductivity of the membrane in  $\text{S cm}^{-1}$ ,  $L$  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 ohms. The resistance of the membranes in  $\text{Cl}^-$  form was measured in-plane with a Solartron AC impedance spectrometer.

## 2.8. Alkaline stability of the membranes

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.

## 2.9. Thermal and mechanical stability of the membranes

The thermal stability of the membranes was investigated by a thermo gravimetric analysis (TGA) in a temperature range from room temperature to 800 °C at a heating rate of 10 °C min<sup>-1</sup> under argon atmosphere.

The mechanical stability of the membranes was investigated using a Q800 DMA from TA Instruments in the stretching mode. It was conducted with a constant increasing strain (10% rate) until membrane fraction occurred. The average membrane mechanical stability was tested by measuring at least three times.

## 2.10. Single cell tests

The AAEMFC single cell was fabricated by using 60 wt% PtRu/C (Johnson Matthey) with metal loading of 2.6 mg cm<sup>-2</sup> as the anode and 60 wt% Pt/C (Johnson Matthey) with metal loading of 2 mg cm<sup>-2</sup> as a cathode, respectively. Nafion used as the ionomer in both the anode and the cathode was calculated to be 20 wt%.

The polarization curves of AAEMFCs were evaluated by a fuel cell test system (FCTS, Arbin Co.). 1 M CH<sub>3</sub>OH containing 1 M KOH with the flow rate of 1 mL min<sup>-1</sup> was fed to the anode and simultaneously 80 sccm of O<sub>2</sub> was fed to the cathode.

## 3. Results and discussion

### 3.1. Chemical stability of quaternary ammonium and 2-methylimidazolium cations in 3 M KOH

Fig. 1 shows the chemical structures of the different 2-methylimidazolium and the corresponding trimethylammonium cations, including ([DMBUIM]<sup>+</sup>), ([DMBEIM]<sup>+</sup>), ([DMVBIM]<sup>+</sup>), ([BUTMA]<sup>+</sup>), ([BETMA]<sup>+</sup>) and ([VBTMA]<sup>+</sup>).

The chemical structure and purity of these 2-methylimidazolium and quaternary ammonium cations were confirmed by the <sup>1</sup>H and <sup>13</sup>C NMR spectra (as shown in Supporting information Figs. S1–S6).

To judge the chemical stability of quaternary ammonium and 1,2-dimethylimidazolium cations in alkaline quickly, the compounds were directly treated in 3 M KOH, a more severe alkaline environment than the fuel cell working condition (the alkaline concentration of 1 M confirmed in Supporting Information), for a certain time. Afterwards, the samples were characterized by NMR and FT-IR spectroscopy. The effects of substitutions and treated-temperature on the alkaline stability of the quaternary ammonium and 1,2-dimethylimidazolium cations are also investigated.

Fig. 2 and Figs. S8 and S9 are the <sup>1</sup>H NMR spectra of quaternary ammonium salts before and after being treated in 3 M KOH solution at different temperatures. It can be seen that though the

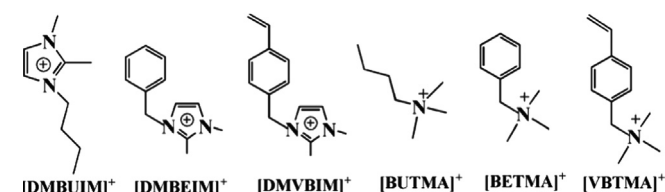


Fig. 1. The chemical structures of 2-methylimidazolium and the corresponding quaternary ammonium cations.

peak integrals of <sup>1</sup>H NMR shifted slightly due to the influence of KOH, there is no any new matter formed in quaternary ammonium/3 M KOH solution either at 25 °C or higher temperatures (60 and 80 °C). Moreover, the precipitates formed in quaternary ammonium/3 M KOH at 80 °C is only KOH, K<sub>2</sub>CO<sub>3</sub> or K<sub>2</sub>SiO<sub>3</sub> rather than the degraded-composition, confirmed by the FT-IR spectra (Fig. S14). From the NMR and FT-IR results, it can be concluded that the quaternary ammonium salts studied in this work would be stable in 3 M KOH solution.

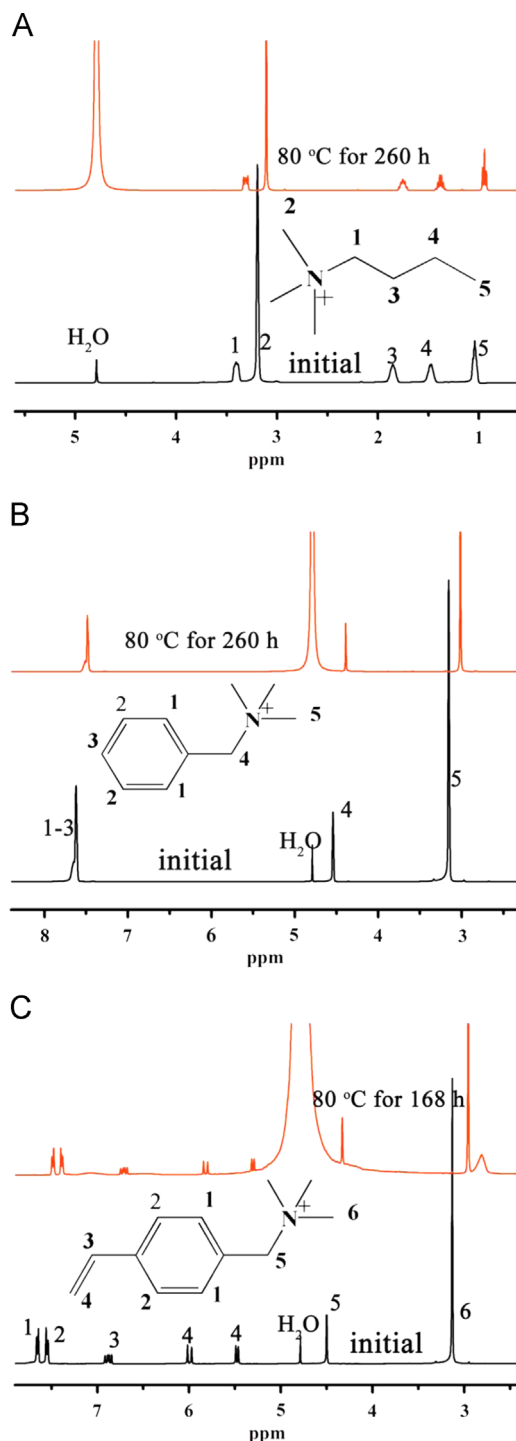
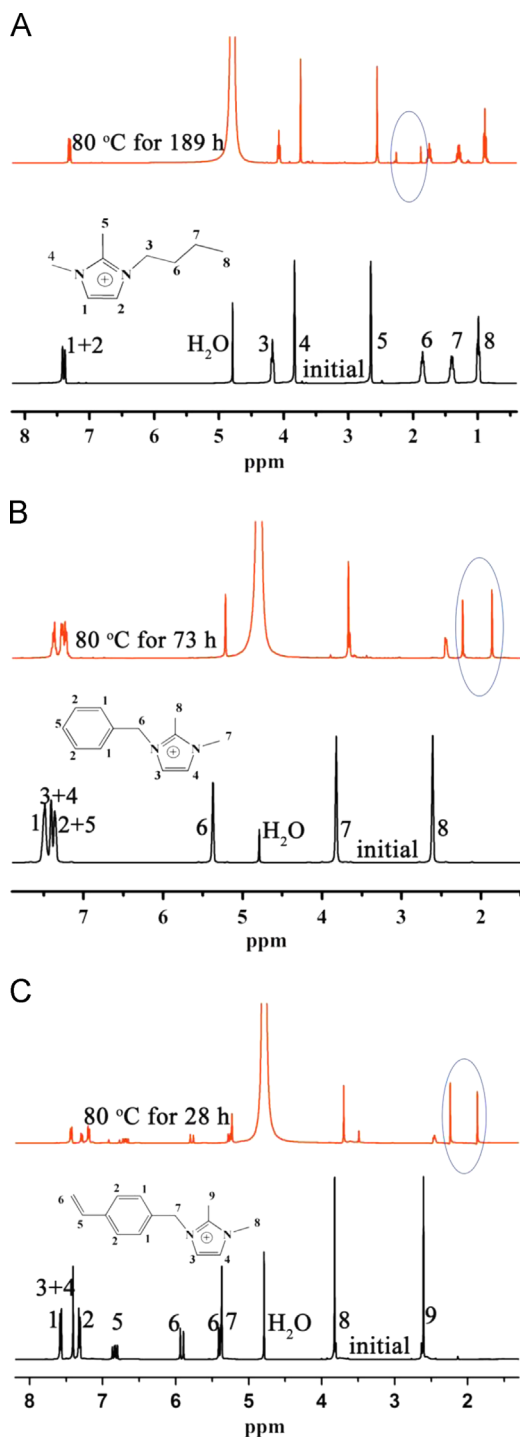


Fig. 2. <sup>1</sup>H NMR spectra of quaternary ammonium cations before and after being exposed to 3 M KOH solution at 80 °C: (A) [BUTMA]<sup>+</sup>; (B) [BETMA]<sup>+</sup>; (C) [VBTMA]<sup>+</sup>.

Compared to quaternary ammonium, though 1,2-dimethylimidazolium cations are stable at 25 °C (Fig. S10), two new peaks emerged in the  $^1\text{H}$  NMR spectra of  $[\text{DMBEIM}]^+$  and  $[\text{DMVBIM}]^+$  after being treated at either 60 °C (Fig. S11B and S11C) or 80 °C (Fig. 3B and C) and of  $[\text{DMBUIM}]^+$  treated at 80 °C (Fig. 3A), indicating new matter forms in 1,2-dimethylimidazolium/3 M KOH solution treated at 60 or 80 °C.

Accordingly, an obvious peak was observed at high frequency (about 180 ppm) in the  $^{13}\text{C}$  NMR spectra (Figs. S12 and S13),



**Fig. 3.**  $^1\text{H}$  NMR spectra of 1,2-dimethylimidazolium cations before and after the exposure to 3 M KOH solution at 80 °C: (A)  $[\text{DMBUIM}]^+$ ; (B)  $[\text{DMBEIM}]^+$ ; (C)  $[\text{DMVBIM}]^+$ .

further confirming that 1,2-dimethylimidazolium salts would be degraded in 3 M KOH at 60 or 80 °C.

The NMR and FT-IR results show that 1,2-dimethylimidazolium cations are much less stable than quaternary ammonium salts in 3 M KOH solution at elevated temperature, especially at 80 °C.

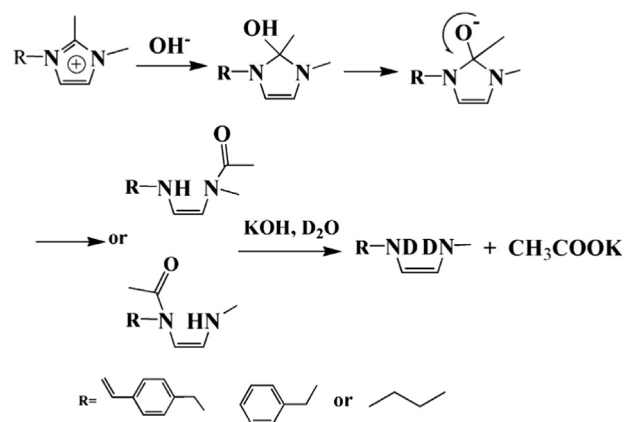
The degradation mechanism of 1,2-dimethylimidazolium cations was systemically proved in Supporting information. According to the proposed degradation mechanism of 1,2-dimethylimidazolium cations (Scheme 2), the degradation degree of 1,2-dimethylimidazolium cations could be calculated by the ratio of the H peak area (Table 1). From the degradation degree results, it can be found that the alkaline stability of the 1,2-dimethylimidazolium cations would be influenced by the experiment temperature and the N3-substitutions.  $[\text{DMBUIM}]^+$  is more stable than  $[\text{DMBEIM}]^+$  and  $[\text{DMVBIM}]^+$ . The reason might be that the electron-withdrawing effect of the aromatic ring weakens the average distribution of the positive charge of the imidazolium ring and makes C2-position of imidazolium prone to be attacked by  $\text{OH}^-$ . However, due to the steric hindrance effect of butyl substitution and the hyperconjugative effect between the substitutions (for example, C–H ( $\sigma$  bond) of methyl group) and the  $\pi$ -conjugated imidazole ring, N3-butyl substituted imidazolium cation ( $[\text{DMVBIM}]^+$ ) shows a better alkaline stability.

### 3.2. Characterization of the membranes

According to the alkaline stability results of the small molecule compounds, 1,2-dimethylimidazolium- and quaternary ammonium-based AAEMs, denoted as  $[\text{DMVImPS}][\text{X}]$  and  $[\text{QAPS}][\text{X}]$ , were further prepared to determine the alkaline stability of the resultant membranes. X is OH for the IEC test and Cl for the other tests, such as SEM, WU, SD, conductivity, TGA, mechanical strength and the fuel cell test.

#### 3.2.1. SEM of the membranes

Visually, the membranes are flexible, transparent, and can be cut into any sizes or be bent at any degrees in wet condition. The



**Scheme 2.** The degradation mechanism of 1,2-dimethylimidazolium cations.

**Table 1**

Degree of ring-opening degradation of 1,2-dimethylimidazolium salts after exposure to 3 M KOH solution at different temperatures.

	Temperature (°C)	Time (h)	Degradation degree (%)
$[\text{DMBUIM}]^+$	60	357	0
	80	189	8.0
$[\text{DMBEIM}]^+$	60	264	16.8
	80	73	29.2
$[\text{DMVBIM}]^+$	60	119	50.0
	80	28	50.0

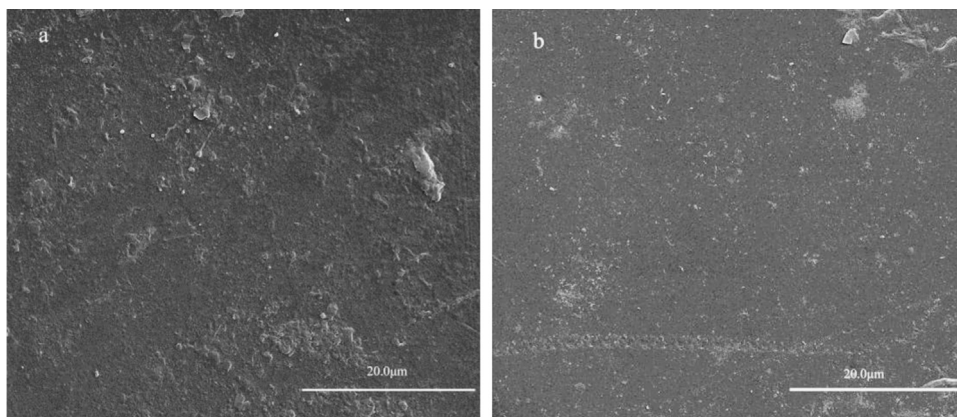


Fig. 4. SEM images of the plane views of [QAPS][Cl] and [DMVImPS][Cl] membranes: a) [QAPS][Cl] membrane; b) [DMVImPS][Cl] membrane.

Table 2

IEC, SD and WU values of the [DMVImPS][X] and [QAPS][X] membranes at room temperature.

Samples	SD (%)	WU (%)	IEC (mmol g <sup>-1</sup> )
[QAPS][X]	5.9 ± 2.48%	2.2 ± 0.14%	1.34
[DMVImPS][X]	0	3.3 ± 0.71%	0.48

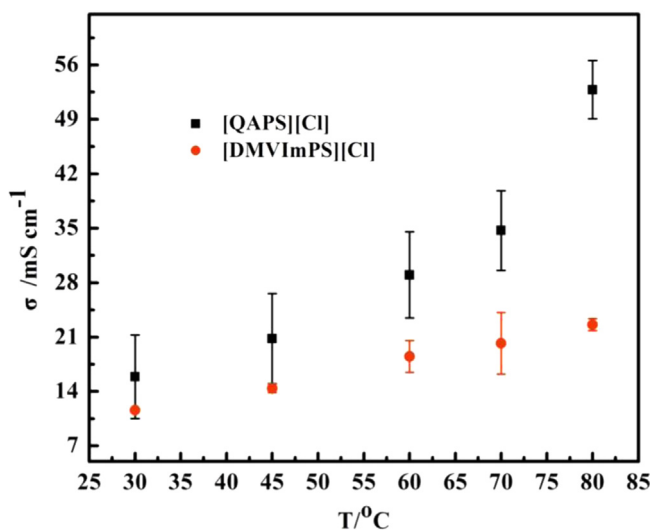


Fig. 5. Ion conductivities of the [DMVImPS][Cl] and [QAPS][Cl] membranes as a function of temperature.

Table 3

The change of conductivity and IEC of [DMVImPS][OH] as the membrane-treating time in 1 M KOH at 60 °C.

	Treating time (h)	Conductivity <sup>a</sup> (mS cm <sup>-1</sup> )	IEC <sup>b</sup> (mmol g <sup>-1</sup> )
[DMVImPS]	0	11.6	0.48
[OH]	90	6.3	0.035

<sup>a</sup> Tested at 30 °C.

<sup>b</sup> Tested at room temperature.

morphologies of the [QAPS][Cl] and [DMVImPS][Cl] membranes are characterized by SEM as shown in Fig. 4. Fig. 4a and b is the plane view of the membranes. It can be seen that the surface of the membrane is relatively smooth and compact without obvious defects or cracks on surface.

### 3.2.2. IEC, WU and SD of the membranes

IEC value reflects to a certain extent the properties of the membranes, such as WU, SD, and ionic conductivity. The IEC, WU and SD of the [DMVImPS][X] and [QAPS][X] membranes are listed in Table 2. From the results in Table 2, it can be found that the IEC value of the [QAPS][OH] membrane is much higher than that of the [DMVImPS][OH] membrane, though the ratio of the functional groups (quaternary ammonium and 1,2-dimethylimidazolium) is the same in the membranes. It may be due to the molecular mass of 1,2-dimethylimidazolium is much higher than that of quaternary ammonium. The SD the [DMVImPS][Cl] membrane is much lower than that of the [QAPS][Cl] membrane, indicating the dimension stability of the [DMVImPS][Cl] membrane is better than that of the [QAPS][Cl] membrane. The WU value of the [DMVImPS][Cl] membrane is close to that of the [QAPS][Cl] membrane. However, the SD and WU values of the [QAPS][Cl] membrane are greatly influenced by the temperature (the values shown in Table S1). With the temperature increasing from room temperature to 60 °C, the SD is from 5.9% to 11.1%, and the WU is from 2.2% to 13.6%. However, the WU and SD of the [DMVImPS][Cl] membrane is not obviously influenced by the temperature (compared in Table 2 and Table S1).

### 3.2.3. Ion conductivity of the membranes

The conductivities of the membranes are tested in deionized water, and the results are shown in Fig. 5. From Fig. 5, it can be seen that the conductivity of the [QAPS][Cl] membrane is much higher than that of the [DMVImPS][Cl] membrane, especially at high temperature. In addition, the conductivity of the [QAPS][Cl] membrane would increase more obvious than that of the [DMVImPS][Cl] membrane as the increase of temperature. It is deduced that there are two explanations. One reason might be that the IEC value of the [QAPS][OH] membrane is instinctively higher than that of the [DMVImPS][OH] membrane. The other reason is the increase of WU and SD of the [QAPS][Cl] membrane as the increase of the temperature. These factors are all in favor of the enhancement of the ion conductivity of the [QAPS][Cl] membrane.

### 3.2.4. Alkaline stability of the membranes

To investigate the alkaline stability of the [DMVImPS][OH] and [QAPS][OH] membranes, the membranes were immersed in 1 M KOH solution at 60 °C for a certain time. The change of ion conductivities and IEC were used to estimate the alkaline stability of the membranes. The results are shown in Table 3 and Table 4, respectively. It can be found that the conductivity and IEC of the [DMVImPS][OH] membrane decrease largely after being treated in

1 M KOH at 60 °C for 90 h, indicating that this membrane is unstable in this alkaline condition. It should be noted that the degradation degree of the [DMVImPS][OH] membrane was much higher than those 1,2-dimethylimidazolium small molecular cations. This may be due to an effect of the polymer backbone [6,27,28], which decreases the alkaline stability of the membrane.

**Table 4**  
The change of conductivity and IEC of [QAPS][OH] as the membrane-treating time in 1 M KOH at 60 °C.

	Treating time (h)	Conductivity <sup>a</sup> (mS cm <sup>-1</sup> )	IEC <sup>b</sup> (mmol g <sup>-1</sup> )
[QAPS][OH]	0	18.9	1.34
	342.5	21.7	1.27
	820	16	1.35

<sup>a</sup> Tested at 30 °C.

<sup>b</sup> Tested at room temperature.

**Table 5**  
Mechanical properties of the [QAPS][OH] and [DMVImPS][OH] membranes at 30 °C.

Samples	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
[QAPS][OH]	12.4 ± 1.12	6.87 ± 1.40	291 ± 49.1
[DMVImPS][OH]	14.2 ± 2.05	2.63 ± 0.57	646 ± 98.0

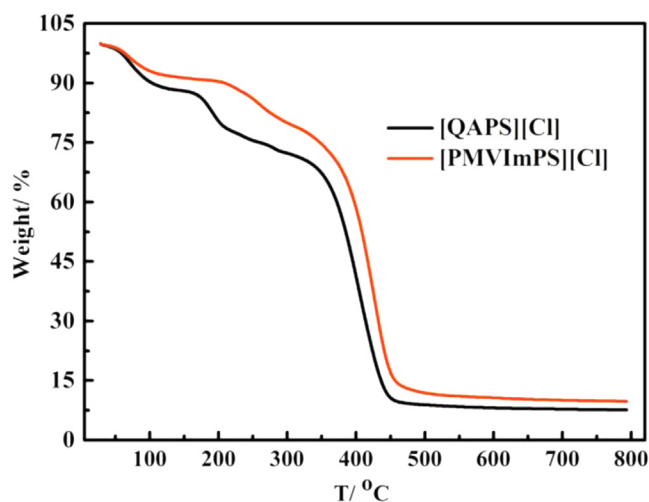


Fig. 6. TGA curves of the [DMVImPS][Cl] and [QAPS][Cl] membranes.

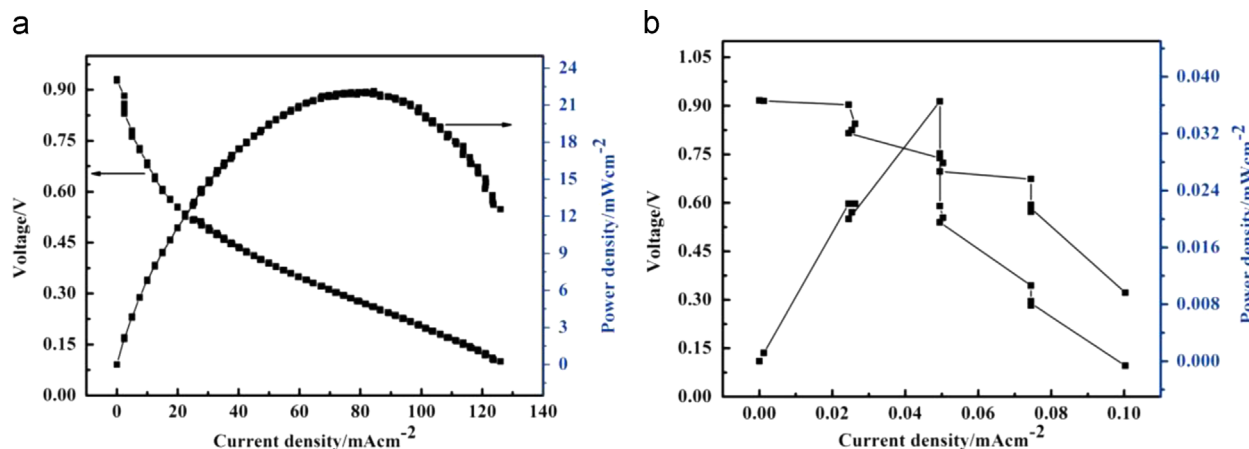


Fig. 7. Performance of the alkaline direct methanol fuel cell with [QAPS][Cl] and [DMVImPS][Cl] membranes at 60 °C : A) [QAPS][Cl]; B) [DMVImPS][Cl].

However, the [QAPS][OH] membrane could be stable enough in 1 M KOH at 60 °C for more than 800 h, which can be confirmed by the constant conductivity and IEC before and after being treated in KOH solution (seen as Table 4). The results show that the [QAPS][OH] membrane is much more stable than the [DMVImPS][OH] membrane with the same polymer backbone in 1 M KOH at 60 °C.

### 3.2.5. TGA and mechanical strength

Thermal and mechanical stabilities are another important parameters of the membrane. TGA curves of the [DMVImPS][Cl] and [QAPS][Cl] membranes are presented in Fig. 6. Though the membranes were dried before the TGA test, there is a slight weight loss (< 10%) of the membranes below 100 °C due to the evaporation of water, which could indicate that the membranes could absorb the water in the air as soon as possible and [QAPS][Cl] membrane absorbs water more easily than that of [DMVImPS][Cl] membrane. The weight loss between 200–300 °C is ascribed to the degradation of the functional groups. It can be seen that the quaternary ammonium functional group is slightly less thermally stable than the 1,2-dimethylimidazolium functional group. The sharp weight loss at about 375 °C is due to the decomposition of the phenyl groups, which is the main chain of the membranes. The TGA result indicates that the [DMVImPS][Cl] and [QAPS][Cl] membranes are both stable below 200 °C, which can meet the demand of AAEMFCs.

Table 5 shows the mechanical properties of the [QAPS][OH] and [DMVImPS][OH] membranes. From Table 5, it can be seen that the tensile strength of the [DMVImPS][OH] is close to that of the [QAPS][OH] membrane, but the flexibility of the [DMVImPS][OH] membrane is much worse than that of the [QAPS][OH] membrane (from the elongation at break and the tensile modulus results of the membranes). This may be due to that the crystallinity of the 1,2-dimethylimidazolium functional group is much higher than that of the quaternary ammonium, attributing to the presence of the  $\pi$ -conjugated structure in the imidazole ring.

### 3.2.6. Single cell tests

The [DMVImPS][Cl] and [QAPS][Cl] membranes are used for MEA fabrication. Fig. 7 shows the polarization curves of the alkaline direct methanol fuel cell using [QAPS][Cl] and [DMVImPS][Cl] membranes at 60 °C. From Fig. 7, it can be seen that a peak power density of 22 mW cm<sup>-2</sup> is obtained at a current density of 82 mA cm<sup>-2</sup> (Fig. 7A) for the fuel cell with the [QAPS][Cl] membrane, which is much higher than that of the cell with the [DMVImPS][Cl] membrane (peak power density of 0.03 mW cm<sup>-2</sup> as shown in Fig. 7B). It may be attributed to the higher conductivity of the [QAPS][Cl] membrane.

#### 4. Conclusions

In this work, the alkaline stability of quaternary ammonium and 1,2-methylimidazolium functional groups was systematically investigated. The quaternary ammonium small molecular compounds are much more stable than the 1,2-dimethylimidazolium small molecular compounds with different N3-substitutions in 3 M KOH at 60 °C and 80 °C. In addition, the quaternary ammonium-based membrane ([QAPS][Cl]) is much more stable than the 1,2-dimethylimidazolium-based membrane ([DMVImPS][Cl]) in 1 M KOH at 60 °C. Additionally, the performance of the alkaline direct methanol fuel cell with the [QAPS][Cl] membrane is much better than that of the fuel cell with the [DMVImPS][Cl] membrane. Therefore, it can be concluded that the quaternary ammonium functional group is much more stable than the 1,2-dimethylimidazolium function group in the alkaline environment at elevated temperature (> 60 °C). In order to boost the alkaline stability of imidazolium function group, some substitutions, which could form the steric hindrance and hyperconjugative effects on the C2-position of the imidazole ring, should be introduced to the N1, N3 or C2-position of the imidazole ring. List of symbols

IEC	ion-exchange capacity (mmol g <sup>-1</sup> )
N <sub>0HCl</sub>	moles of HCl before titration
N <sub>iHCl</sub>	moles of HCl after titration
m	the weight of dry membrane in Cl <sup>-</sup> form
WU	water uptake (wt%)
W <sub>wet</sub>	the weights of hydrated membranes (g)
W <sub>dry</sub>	the weights of dry membranes (g)
SD	swelling degree (%)
L <sub>wet</sub>	the lengths of hydrated membranes (cm)
L <sub>dry</sub>	the lengths of dry membranes (cm)
L	the distance between the working electrode and reference electrode (cm)
W	the width of the membranes (cm)
T	the thickness of the membranes (cm)
R	the resistances of the membranes (Ω)
σ	ion conductivity (S cm <sup>-1</sup> )

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.memsci.2015.03.067>.

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