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Effects of Substituents and Substitution Positions on Alkaline Stability of Imidazolium Cations and Their Corresponding Anion-Exchange Membranes

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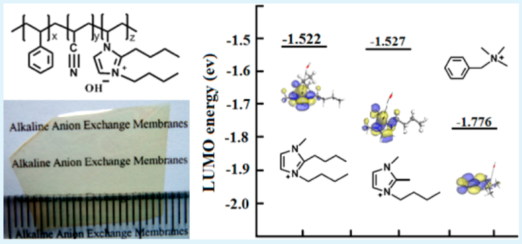
S Supporting Information



ABSTRACT: Imidazolium cations with butyl groups at various substitution positions (N1-, C2-, and N3-), 1-butyl-2,3-dimethylimidazolium ([N1-BDMIm]$^+$), 2-butyl-1,3-dimethylimidazolium ([C2-BDMIm]$^+$), and 3-butyl-1,2-dimethylimidazolium ([N3-BDMIm]$^+$), were synthesized. Quantitative ^{1}H NMR spectra and density functional theory calculation were applied to investigate the chemical stability of the imidazolium cations in alkaline solutions. The results suggested that the alkaline stability of the imidazolium cations was drastically affected by the C2-substitution groups. The alkaline stability of imidazolium cations with various substitution groups at the C2-position, including 2-ethyl-1-butyl-3-methylimidazolium ([C2-EBMIm]$^+$), 1,2-dibutyl-3-methylimidazolium ([C2-BBMIm]$^+$), and 2-hydroxymethyl-1-butyl-3-methylimidazolium ([C2-HMBMIm]$^+$), was further studied. The butyl group substituted imidazolium cation ([C2-BBMIm]$^+$) exhibited the highest alkaline stability at the elevated temperatures. The synthesized anion-exchange membranes based on the [C2-BBMIm]$^+$ cation showed promising alkaline stability. These observations should pave the way to the practical application of imidazolium-based anion exchange membrane fuel cells.

KEYWORDS: *imidazolium cations, substitution, anion exchange membranes, alkaline stability, theory calculation*

INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) have been extensively investigated due to their high energy-conversion efficiency, high power density, and low environmental pollution.[1−5] Proton exchange membrane fuel cells were a kind of PEFC, in which proton exchange membranes (PEMs) acted as the electrolytes for proton transportations.[6] However, the widespread application of PEFCs was hampered by the high cost of the noble metal catalysts (such as platinum) and the electrolytes.[7−9] Therefore, the alkaline anion exchange membrane fuel cell (AEMFC) has been receiving increased attention because of its enhanced oxygen reduction kinetics, increased tolerances to CO_2 impurities in gaseous feeds,[10] and the ability of using nonprecious metal based catalysts (such as cobalt, nickel, or silver).[1,11]

The alkaline anion exchange membrane (AEM) is one of the key components of the AEMFCs, which play an important role in anion transportations. An ideal AEM should possess good hydroxide ion conductivity, high mechanical strength, low swelling degree, and good chemical stability,[11,12] which are fundamentally influenced by the cationic groups.[13] To date, cationic species, including quaternary ammonium,[9,14−17] tertiary sulfonium,[13] guanidinium,[18,19] phosphonium,[20,21] imidazolium,[22−25] benzimidazolium,[26,27] phosphatranium,[28] and metal cations,[29] have been extensively studied and shown potential in AEMFCs. However, their alkaline stability under vigorous conditions (high pH environment and elevated temperatures) continues to be a major challenge for alkaline fuel cell applications. For example, as we know, quaternary ammonium cations are likely to degrade via Hofmann elimination (E2),[30] nucleophilic substitution (S_N2),[31] and (or) ylide formation[32] in high pH aqueous solution. Recently, some effective ways have been documented to improve the chemical stability of the cations.[21,27,33−35] For example, Yan and co-workers reported that trimethoxyphenyl substitutes could enhance the stability of the quaternary phosphonium cations and imidazolium cations due to their high electron density and steric bulk effect.[21,33,36] Holdcroft and co-workers recently demonstrated that installation of adjacent bulky groups around the reactive benzimidazolium C2-position could improve the stability of the cations.[27,34]

Among the cationic polymers studied, imidazolium cation based AEMs showed good alkaline stability and potential in AEMFCs.[30,37−39] For further improving the stability of the imidazolium cations, more recently, our group[40,41] and Price et al.[35] have been engaging in the study of C2- and N3-substitutions on the alkaline stability of imidazolium cations. These preliminary studies suggested that C2- and (or) N3-substituents can stabilize the imidazolium cations in alkaline solutions. However, the influence of substitution positions on the alkaline

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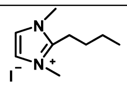
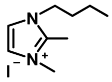
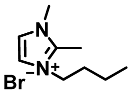
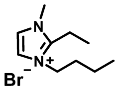
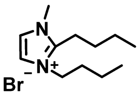
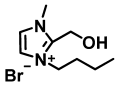
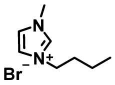
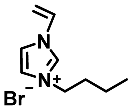
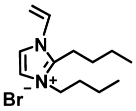
Table 1. Molecular Structures and Abbreviations of Imidazolium Cations Studied in This Work

Molecular structure	Name	Abbreviation
	2-butyl-1,3-dimethylimidazolium iodide	[C2-BDMIm][I]
	3-butyl-1,2-dimethylimidazolium iodide	[N3-BDMIm][I]
	1-butyl-2,3-dimethylimidazolium bromide	[N1-BDMIm][Br]
	2-ethyl-1-butyl-3-methylimidazolium bromide	[C2-EBMIm][Br]
	2,1-dibutyl-3-methylimidazolium bromide	[C2-BBMIm][Br]
	2-hydroxymethyl-1-butyl-3-methylimidazolium bromide	[C2-HMBMIm][Br]
	1-butyl-3-methylimidazolium bromide	[BMIm][Br]
	1-vinyl-3-butylimidazolium bromide	[VBIm][Br]
	1-vinyl-2, 3-dibutylimidazolium bromide	[VDBIm][Br]

stability of imidazolium cations has not been systematically investigated in detail as far as we know. These results encouraged us to investigate the effects of both substituents and substitution positions on the imidazolium cations and their corresponding AEMs in terms of the alkaline stability.

In the present work, a series of imidazolium cations with various substituents were synthesized and characterized. Both experimental studies and theoretical calculations were used to study the alkaline stability of imidazolium cations. Effects of substitution positions (at N1-, N3-, and C2-) on the alkaline stability of imidazolium cations were investigated. Furthermore, the influence of C2 substitutions on the imidazolium cationic rings was further confirmed, and a novel imidazolium cation ($[C2\text{-}BBMIm]^+$) and its corresponding AEMs with enhanced alkaline stability were designed and synthesized. The alkaline anion-exchange membranes were evaluated in this work, with respect to alkaline stability, thermal properties, and conductivity.

■ EXPERIMENTAL SECTION

Materials. *N*-Methylimidazole, 2-methylimidazole, styrene, ethylether, *N*-vinylimidazole, 1,2-dimethylimidazole, acrylonitrile, potassium hydroxide, divinylbenzene (DVB), 1-bromobutane, hydrochloric acid, bromoethane, iodomethane, benzoin ethyl ether, chlorobutane, benzyltrimethylammonium chloride, sodium hydroxide, paraformaldehyde, and acetonitrile were purchased from Acros and used as received. Distilled water was used for all the experiments.

Synthesis of Imidazolium Salts. Table 1 listed the molecular structures and abbreviations of the imidazolium cations synthesized in this work. The synthesis and the ^{1}H NMR characterization of the imidazolium cations are described in the Supporting Information.

Preparation of Imidazolium-Based Copolymer Membranes. A photocross-linking method was used for the preparation of the imidazolium-based copolymer membranes as described in our previous work:[42] [VDBIm][Br] (20−30 wt %), acrylonitrile/styrene (3:1 weight ratio, 70−80 wt %), photoinitiator (benzoin isobutyl ether, 1 wt %), and cross-linking agent (divinylbenzene, 4 wt %) were mixed and ultrasonicated to form a homogeneous solution. The prepared monomer solution was cast into a glass mold and irradiated at 25 °C with ultraviolet light (wavelength: 250 nm) for 40 min. Standard spacer bars (~60 μm in diameter) were used to control the thickness of the polymeric membranes. To prepare the membranes in OH^- form, the resulting polymeric membranes in Cl^- form were immersed in N_2-saturated 1 M KOH solution (in which the N_2 atmosphere could exclude the effect of CO_2 and prevent the exchange of the OH^- form to HCO_3^- and CO_3^- forms) at 60 °C for 24 h. To ensure a complete conversion displacement, such a process was repeated three times. The membranes were then washed with N_2-saturated deionized water until the pH of residual water reached 6−7. The polymeric membranes with various components could be prepared by changing the feed ratio of [VDBIm][Br].

CHARACTERIZATION

^{1}H NMR spectra were obtained from a Varian spectrometer at 400 MHz using D_2O (or CD_3OD/D_2O) as the solvent. The thermal analysis was carried out from 30 to 600 °C at a heating rate of 10 °C min^{-1} in nitrogen on a Universal Analysis 4000 thermogravimetric analyzer (TGA).

Hydroxide Ion Conductivity. The resistance value of the produced membranes was measured in a frequency range from 1 Hz to 1 MHz on an electrochemical workstation (Zahner IM6 EX) by a four-point probe alternating current (AC) impedance method. Before the conductivity measurement, the produced membranes were immersed in deionized water (N_2 saturated) until the membranes were fully hydrated. The membranes were equilibrated at a given temperature for at least 30 min. The time interval of the repeated measurements was at least 10 min. The hydroxide ion conductivity σ (S cm^{-1}) can be calculated as follows

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

where A is the membrane cross-sectional area (cm^2), which was determined from width/cm multiplied by thickness/cm; R is the resistance (Ω) of the membrane, and l (cm) is the interelectrode separation.

Water Uptake and Swelling Degree. The water uptake and the swelling degree of the membranes can be evaluated by weight analysis and linear expansion ratio, respectively: a sample of the produced membrane (width: 1 cm, length: 4 cm) was soaked in the N_2-saturated deionized water at 30 °C for 24 h. The adsorbed water on the surface could be removed by tissue papers. The hydrated polymeric membranes were weighed and then dried at 80 °C under vacuum until no weight loss was observed. The water uptake of the membrane (W) and the membrane swelling degree can be calculated from

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

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

where W_w and X_{wet} are the weight and lengths of the hydrated membranes, respectively, while W_d and X_{dry} are the the weight and lengths of the dry membranes, respectively.

Ion Exchange Capacity (IEC). The membrane ion exchange capacities can be measured using a back-titration method:[22] a produced membrane sample was soaked in 0.01 M HCl standard solution (100 mL) for 24 h. Then the resulting solution was titrated with a NaOH standard solution (indicator: phenolphthalein). The membrane ion exchange capacities can be obtained as follows

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

where m_{dry} is the weight of membranes in dry conditions; C_{NaOH} is the mol concentration of NaOH standard solution (titrated by oxalic acid standard solution); and $V_{x,\text{NaOH}}$ and $V_{0,\text{NaOH}}$ are the consumed NaOH solution volume in the titration with and without membranes, respectively. The test was conducted at least three times to reach an average value.

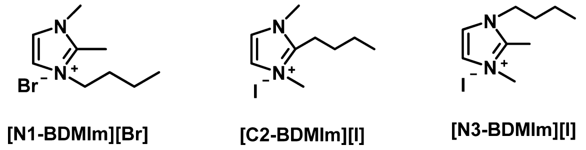
Alkaline Stability. The alkaline stability of ammonium and imidazolium cations was examined by NMR spectra in D_2O (or CD_3OD/D_2O) KOH solution (1, 4, and 6 M, respectively), which was performed in a sealed fluoropolymer lined vessel at 80 °C. The alkaline stability was evaluated by immersing the corresponding polymer membranes in N_2-saturated 1 M KOH solution at 80 °C.

Computational Details and Analysis. Theoretical calculations on the C2-substituted imidazolium molecules were performed by Dmol^3 available in Materials Studio (version 6.0) software package.[43] The GGA-BLYP functional and double numerical plus polarization basis set were employed for the calculations.[44] The single molecules are all fully optimized with a self-consistent field (SCF) convergence value of 10^{-6} Ha.[45] Considering the solution environment, solvent effect is added into the calculations (water, ε = 78.54).

RESULTS AND DISCUSSION

Effect of Substitution Positions on Alkaline Stability of Imidazolium Cations. In this work, ^{1}H NMR spectra were first used to investigate the effect of substitution positions on the alkaline stability of imidazolium cations. Scheme 1 shows the chemical structures of imidazolium cations with substituent groups at N1-, C2-, and N3- positions. The ^{1}H NMR spectra of [N1-BDMIm][Br], [C2-BDMIm][I], and [N3-BDMIm][Br] after exposure to 4 M KOH solution at 80 °C at various times were shown in Figure 1. It can be clearly seen that ^{1}H signals belonging to C-4, C-5, and α-protons of the C-2 substituents gradually disappeared during the testing periods due to the fast hydrogen/deuterium (H/D) exchange reactions of the imidazolium cations.[40,46−48] In addition, a new peak at around 1.88 ppm was observed after a certain testing period for all the synthesized imidazolium cations, suggesting the ring-opening reactions of imidazolium cations. The possible degradation mechanism of the substituted imidazolium cations at elevated temperatures in alkaline solution is shown in Scheme 2.[30,41,49] It should be noted that the imidazole rings were opened at the C2-position under the attack of OH^-. Therefore, the chemical shift observed at 1.88 ppm was likely ascribed to the protons belonging to the −NH− groups.

Scheme 1. Molecular Structures of Imidazolium Cations with Different Substitution Positions Investigated in This Work



The degradation degree of the imidazolium cations was investigated by quantitative ^{1}H NMR spectra, as shown in the Supporting Information. Table 2 summarized the results of the calculation. The degree of the degradation in 4 M KOH solution at 80 °C for 120 h was determined to be 17.0%, 23.65%, and 15.92% for [N1-BDMIm][Br], [C2-BDIm][I], and [N3-BDIm]-[I], respectively. It should be noted that the alkaline stability of the C2-substituted imidazolium cations with strong electron-donating groups (butyl groups) at the N1 and N3 positions (namely, $[\text{N1-BDMIm}]^+$ and $[\text{N3-BDMIm}]^+$) are better than the imidazolium cation with the same substituent at the C2 position ($[\text{C2-BDIm}]^+$).

It has already been demonstrated that the energy level of the lowest unoccupied molecular orbital (LUMO) of imidazolium cations determines their nucleophilic reactions. Under the

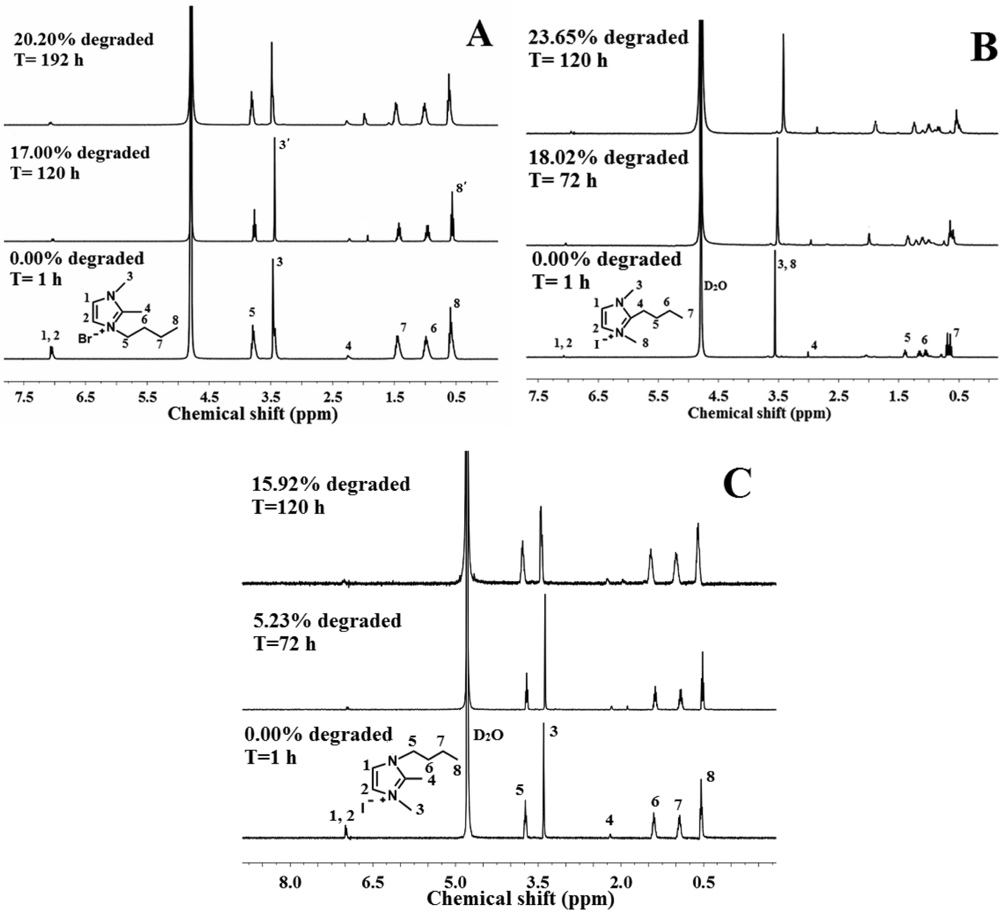
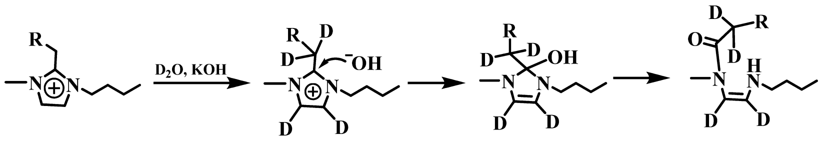


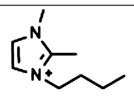
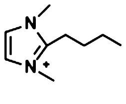
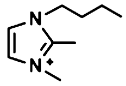
Figure 1. ^{1}H NMR spectra for (A) [N1-BDMIm][Br], (B) [C2-BDIm][I], and (C) [N3-BDIm][I] in 4 M KOH solution at 80 °C at various times.

Scheme 2. Possible Degradation Mechanism of the Substituted Imidazolium Cations in Alkaline Solution



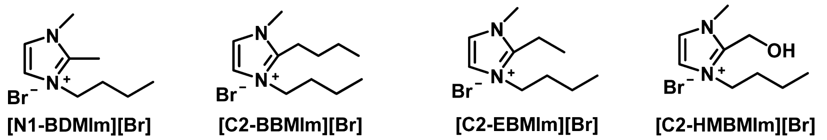
R=CH_3, $CH_2CH_2CH_3$, or OH

Table 2. Degree of the Degradation of Substituted Imidazolium Cations at 80 °C in Alkaline Solutions

Imidazolium cations	Molecular structure	KOH concentration (M)	Time (h)	Degradation (%)	LUMO energy (ev)
[N1-BDMIm]$^+$		4 M	120	17.00	-1.527
[C2-BDMIm]$^+$		4 M	120	23.65	-1.550
[N3-BDMIm]$^+$		4M	120	15.92	-1.527

conditions of high temperature and strong basicity, the lower the LUMO energy, the easier it is for imidazolium or quaternary ammonium cations to be assaulted by OH^-.[40,50,51] Here, the LUMO energy level of the cations was evaluated via density functional theory (GGA-BLYP) calculations, which are performed by the Materials Studio (Version 6.0) program

Scheme 3. Molecular Structures of Imidazolium Salts with Different C2-Substituent Groups Synthesized in This Work



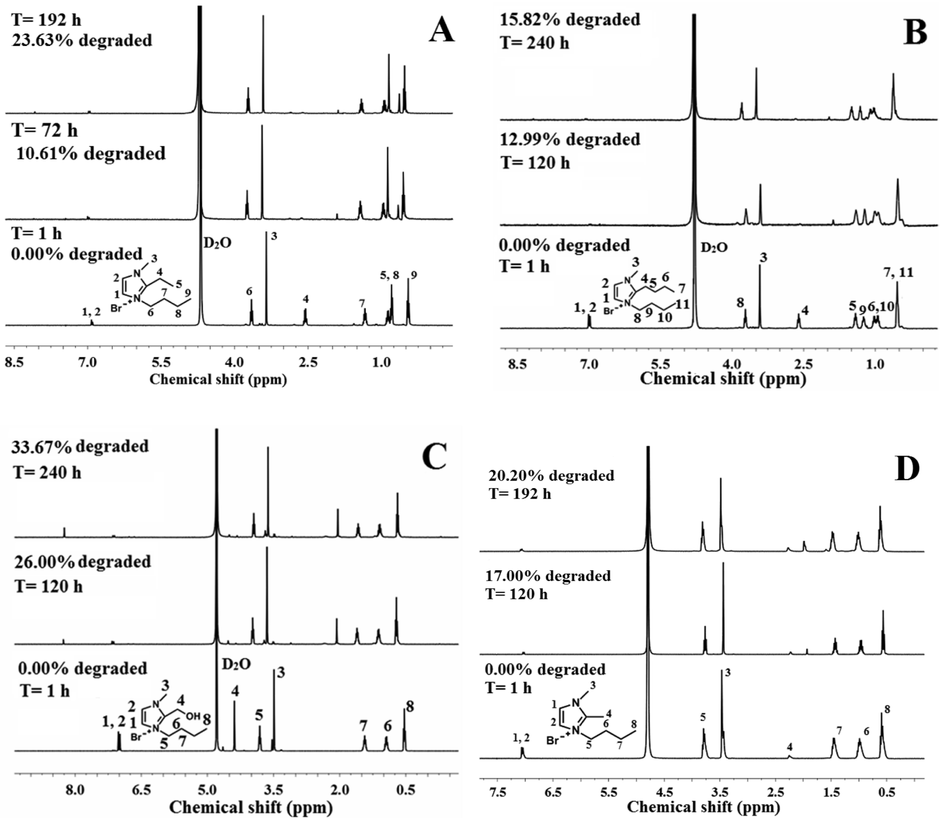


Figure 2. ^{1}H NMR spectra for (A) [C2-EBMIm][Br], (B) [C2-BBMIm][Br], (C) [C2-HMBMIm][Br], and (D) [N1-BDMIm][Br] in 4 M KOH solution at 80 °C for various times.

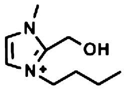
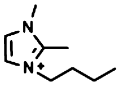
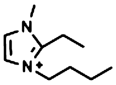
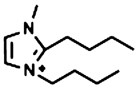
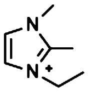
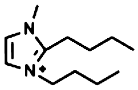
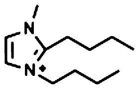
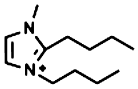
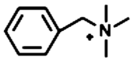
package. As we can see from Table 2, the LUMO energies of [N1-BDMIm]$^+$, [C2-BDIm]$^+$, and [N3-BDIm]$^+$ in aqueous solution are determined to be −1.527, −1.550, and −1.527 eV, respectively. Therefore, it is not surprising that [C2-BDIm]$^+$ shows the worst stability in alkaline solutions. The alkaline stabilities of butyl groups at the N1- and N3-position are almost the same, which were well consistent with the results of theoretical calculation (Table 2). The stability of imidazolium cations largely depends on the C2-functionality.[46] Here, the N1-position of the imidazolium cations was substituted with butyl groups, and the effect of C2-substituents on their alkaline stability was further studied.

Effect of C2-Substituents on the Alkaline Stability of Imidazolium Cations. To further study the effect of the different C2-substitutions on the alkaline stability of imidazolium cations and optimize the alkaline stability of their corresponding AEMs, various C2-substituted imidazolium salts, including [N1-BDMIm][Br], [C2-EBMIm][Br], [C2-BBMIm][Br], and [C2-HMBMIm][Br], were synthesized in this work (molecular structures are shown in Scheme 3). Their chemical stability at 80 °C in 4 M KOH solution was also studied by ^{1}H NMR spectra (Figure 2), and the results of the degradation degree were summarized in Table 3. The degradation degree of [C2-BBMIm]$^+$ was calculated to be 15.8% for a testing period of 240 h and 20.2% (192 h), 23.6% (192 h), and 26.0 % (120 h) for [N1-BDMIm]$^+$, [C2-EBMIm]$^+$, and [C2-HMBMIm]$^+$, respectively. Therefore, the order of the alkaline stability was determined to be [C2-BBMIm]$^+$ > [N1-BDMIm]$^+$ > [C2-EBMIm]$^+$ > [C2-HMBMIm]$^+$. This result was well consistent with the results of theoretical calculation (Figure 4 and Table 3). In addition, as the most stable imidazolium cation synthesized in this work, [C2-BBMIm]$^+$ was also stable even at 80 °C in 6 M KOH solution (4.68% degraded for 12 h) (Figure 3). It should also be noted that [C2-BBMIm]$^+$ was less stable in 4 M KOH solution (15.8% degraded for 240 h) than in 1 M KOH solution (0% degraded for 240 h), suggesting that high pH environment accelerates the degradation of imidazolium cations.

Quaternary trimethylammonium cation based AEMs have been extensively studied. Here, the stabilities of a quaternary ammonium cation, benzyltrimethylammonium ([BTMA]$^+$), and [C2-BBMIm]$^+$ were evaluated in 1 M KOH CD_3OD/D_2O solution (1 M KOH, V_{CD3OD}/V_{D2O} = 3:1). The methanol was added as a co-solvent for the alkaline stability test because it could accelerate the cation degradation and dissolve polyatomic cations better than pure aqueous solution (Figure 5).[20]

Table 3 shows the alkaline degradation degree of [C2-BBMIm]$^+$ and [BTMA]$^+$ in 1 M KOH CD_3OD/D_2O solution. It can be seen that about 6.08% and 23.08% of [C2-BBMIm]$^+$ and

Table 3. Degradation Degree of the Imidazolium Cations with C2-Substituent Groups after Exposing to Alkaline Solutions at 80 °C

Imidazolium cations	Molecular structure	Concentration (KOH) (M)	Time (h)	Degradation (%)	LUMO energy (ev)
[C2-HMBMIm]$^+$		4 M	120	26.00	-2.021
[N1-BDMIm]$^+$		4 M	192	20.2	-1.527
[C2-EBMIm]$^+$		4 M	192	23.63	-1.528
[C2-BBMIm]$^+$		4 M	240	15.82	-1.522
[EDMIm]$^{+}$ [33]		6 M	10	5.40	-1.668
[C2-BBMIm]$^+$		6 M	12	4.68	-1.522
[C2-BBMIm]$^+$		1 M	240	0.00	-1.522
[C2-BBMIm]$^+$		1 M[a]	192	6.08	-1.522
[BTMAM]$^+$		1 M[a]	192	23.08	-1.776

[a] A mixture of CD_3OD and KOH/D_2O solution (1 M KOH, V_{CD3OD}/V_{D2O} = 3:1), 1,4-dioxane was used as the internal standard.

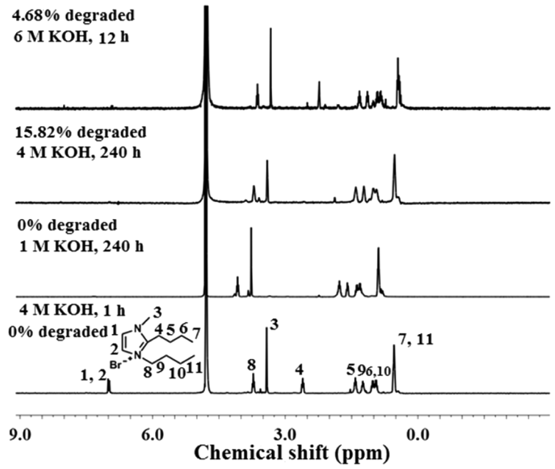


Figure 3. ^{1}H NMR spectra for [C2-BBMIm][Br] in KOH solutions at 80 °C for various times.

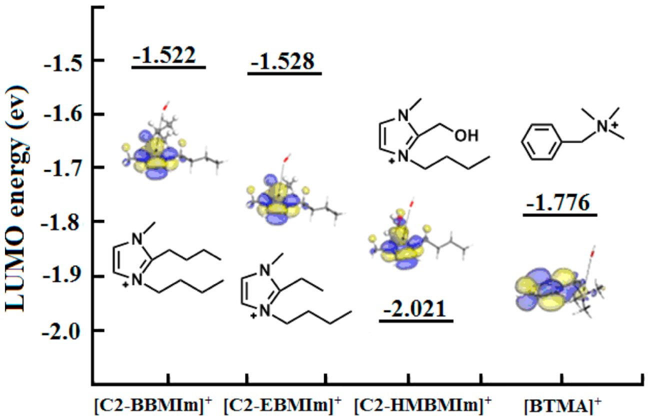


Figure 4. Isosurface and LUMO energy of the synthesized imidazolium cations. The color of atoms: red (O), blue (N), white (H), and gray (C). The black arrows indicate the nucleophilic attacking direction of OH⁻.

[BTMA]$^+$ degraded after 192 h at 80 °C, respectively, suggesting a better alkaline stability of [C2-BBMIm]$^+$, which should be a promising class of functional groups for AEMs. In addition, [C2-BBMIm]$^+$ was more stable in 1 M KOH solution (0% degraded for 240 h) than in 1 M KOH CD_3OD/D_2O solution (6.08% degraded for 192 h), which further confirmed that the presence of methanol could accelerate the cation degradation.

Characterization of Anion-Exchange Membranes. C2- and N1-substituted imidazolium cation-based AEMs were synthesized and characterized to assess the feasibility of the

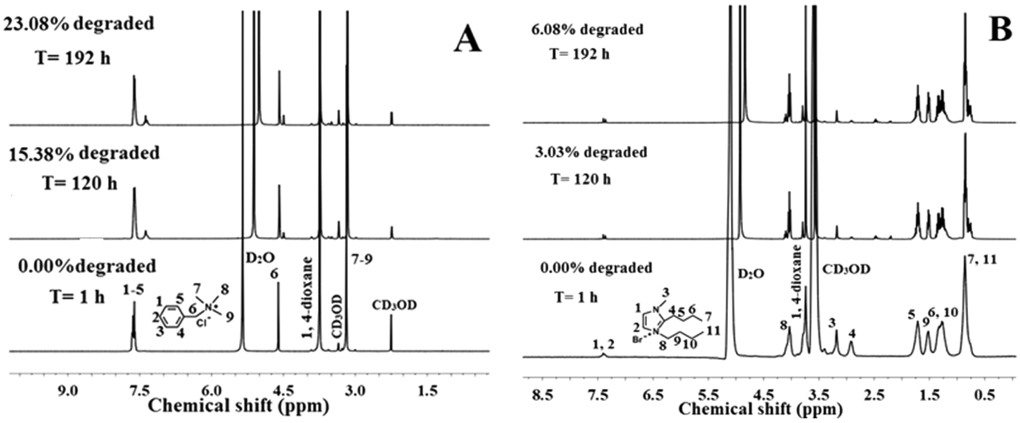


Figure 5. ^{1}H NMR spectra for (A) [BTMAM][Cl] and (B) [C2-BBMIm][Br] in 1 M KOH CD_3OD/D_2O solution (1 M KOH, V_{CD3OD}/V_{D2O} = 3:1, 1,4-dioxane was used as internal standard) at various times.

scheme that imidazolium cations are used in the AEMs. The imidazolium-based AEMs were prepared by photo-crosslinking as described in the Experimental Section. The obtained AEMs were denoted as $[PVDBIm]_x[OH]$ (here, the subscript x is 20 or 30, indicating that the feed weight ratio of [VDBIm][Br] was 20% and 30%, respectively). The produced polymeric membranes exhibit good mechanical properties and could be easily bent and cut to any sizes (Figure 6).

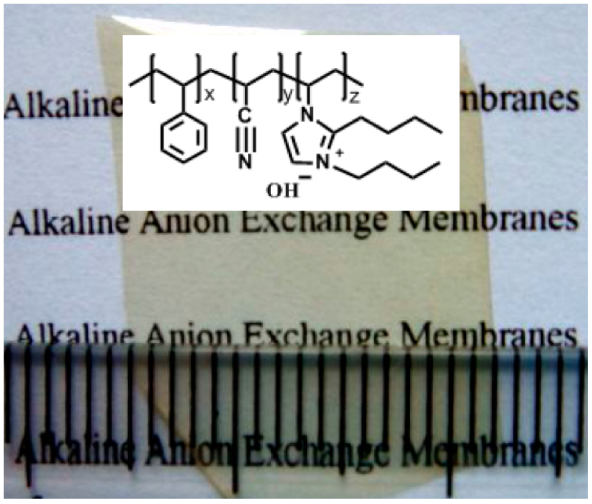


Figure 6. Photograph and chemical structure of the produced AEM.

Good thermal stability is essential for AEMs when they act as the electrolytes for AEMFCs, which was often assessed by a thermogravimetric analyzer (TGA). Figure 7 shows the typical TGA curves of the final membranes, which was recorded under a nitrogen flow from 30 to 600 °C (heating rate:10 °C min^{-1}). It should be noted that there is no weight loss observed below 200 °C, and the temperature was above 300 °C when there is 5% weight loss. The decomposition of imidazole rings could occur at about 200−390 °C. The main-chain degradation of polymers may take place at beyond 400 °C, which can be comparable to that of the phenyltrimethylammonium-functionalized polysulfone,[52] which fulfills the thermal stability requirement for the AEMFC applications.

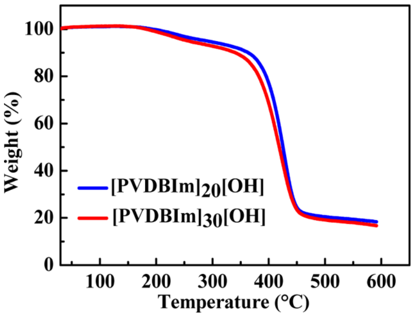


Figure 7. TGA curves of the produced membranes in nitrogen at a heating rate of 10 °C min^{-1}.

IEC which reflected the exchangeable groups in the membranes was related to the ion conductivity. Water uptake and swelling degree are essential factors which affect the membrane mechanical and morphologic stability. Table 3 shows the conductivity, IEC, water uptake, and swelling degree of the produced $[PVDBIm]_{20}[OH]$ and $[PVDBIm]_{30}[OH]$ membranes. The theoretical IEC values of $[PVDBIm]_{20}[OH]$ (0.87 meq g^{-1}) and $[PVDBIm]_{30}[OH]$ (1.22 meq g^{-1}) are close to the experimental results (0.93 and 1.39 meq g^{-1}, respectively). In addition, the swelling degree and water uptake of $[PVDBIm]_{20}[OH]$ are 24.5% and 53.6%, respectively, which are lower than those of $[PVDBIm]_{30}[OH]$ (35.4% and 81.9%, respectively).

The hydroxide conductivity is a key property for AEMs used in fuel cells. Figure 8 shows hydroxide ion conductivity of the AEMs at various temperatures (30−90 °C). It should be noted that the membrane hydroxide ion conductivities increased dramatically with the rising examining temperature. For example, the conductivity of $[PVDBIm]_{30}[OH]$ increases from 16.6 to 23.1

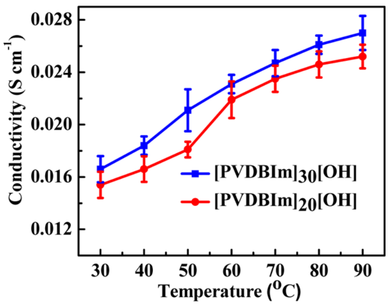


Figure 8. Temperature dependence of the hydroxide conductivity for $[PVDBIm]_{20}[OH]$ and $[PVDBIm]_{30}[OH]$.

Table 4. Conductivity, Ion Exchange Capacity (IEC), Water Uptake, and Swelling Degree of $[PVDBIm]_{20}[OH]$, $[PVDBIm]_{30}[OH]$, and [PTMVPMA][OH]

	IEC (meq g^{-1})						
		experimental[b]		water uptake (%)	swelling degree (%)	conductivity ($\times 10^{-2}$ S cm^{-1})	
membrane	theoretical[a]	before test	after test	30 °C	30 °C	30 °C	60 °C
$[PVDBIm]_{30}[OH]$	1.39	1.22 ± 0.09	1.17 ± 0.12	81.9 ± 6.4	35.4 ± 2.2	1.66 ± 0.10	2.31 ± 0.07
$[PVDBIm]_{20}[OH]$	0.93	0.87 ± 0.08	0.83 ± 0.05	53.6 ± 3.7	24.5 ± 3.4	1.54 ± 0.10	2.19 ± 0.14
[PTMVPMA][OH][54]	1.70	1.62	1.57	92.56	22.35	1.14	1.63

[a] Calculated from the monomer ratio. [b] Before and after immersion in N_2-saturated 1 M KOH solution at 80 °C for 100 h.

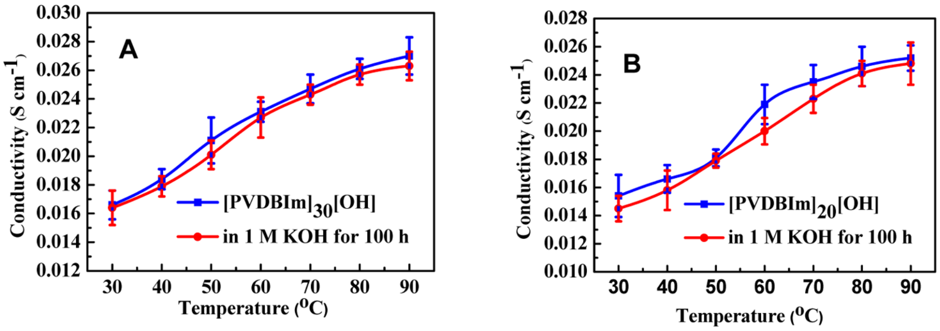


Figure 9. Temperature dependence of the hydroxide conductivity for (A) $[PVDBIm]_{30}[OH]$ and (B) $[PVDBIm]_{20}[OH]$ after immersion in N_2-saturated 1 M KOH solution at 80 °C for 100 h.

mS cm^{-1} on raising the temperature from 30 to 60 °C. In addition, the conductivities of all the produced membranes at 30 °C are above 1.5×10^{-2} S cm^{-1}, suggesting that the produced AEMs are suitable for the AEMFC applications in terms of the hydroxide conductivity.

The alkaline stability of the produced membranes $[PVDBIm]_x[OH]$ was characterized by measuring the changes of the membrane IEC values and hydroxide ion conductivity after conditioning them at 80 °C in N_2-saturated 1 M KOH solution for 100 h, which is currently a standard protocol for the examination of chemical stability.[53] It can be seen from Table 4 that the IEC values of produced membranes almost kept constant during the stability test. Figure 9 showed the changes of the membrane hydroxide ion conductivities with the alkaline stability test. The membrane conductivity remained almost unchanged, suggesting the substituted imidazolium-based AEMs are stable in the experimental conditions.

CONCLUSIONS

In summary, a series of substituted imidazolium cations were synthesized and characterized. The influence of substitution positions and C2-substituents on alkaline stability of imidazolium cations and imidazolium-based AEMs was systematically studied by GGA-BLYP calculations and ^{1}H NMR analysis. These studies showed that the alkaline stability of imidazolium cations with strong electron-donating groups at the N1(3) position is better than that at the C2-position. Furthermore, $[C2\text{-}BBMIm]^+$-based alkaline anion-exchange membranes possessed high chemical stability in alkaline solutions. These results may cast a new light on the design of high performance imidazolium-based AEMs.

ASSOCIATED CONTENT

Supporting Information

The synthesis details and ^{1}H NMR characterization of the imidazolium salts, and the calculation of the degradation degree of imidazolium cations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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