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Relative Chemical Stability of Imidazolium-Based Alkaline Anion Exchange Polymerized Ionic Liquids

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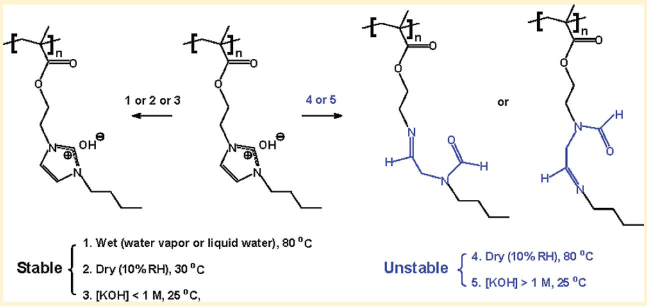
Supporting Information

ABSTRACT: We thoroughly investigate and quantify the chemical stability of an imidazolium-based alkaline anion exchange polymerized ionic liquid (PIL), poly(1-[(2-methacryloyloxy)ethyl]-3-butylimidazolium hydroxide) (poly(MEBIm-OH), over a broad range of humidities, temperatures, and alkaline concentrations using the combined techniques of electrochemical impedance spectroscopy and nuclear magnetic resonance spectroscopy. High chemical stability was observed under dry conditions (10% RH) at 30 °C, humid and saturated conditions up to 80 °C, and even in mild alkaline conditions ([KOH] < 1 M) at 25 °C. Degradation was only observed under more vigorous conditions: dry conditions (10% RH) at 80 °C or at higher alkaline concentrations ([KOH] > 1 M). Under these conditions, we suggest an imidazolium ring-opening mechanism as the primary degradation pathway, based on a detailed analysis of the ^{1}H NMR spectra. Similar to poly(MEBIm-OH), other alkaline anion (carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-)) exchange PILs were also synthesized in this study via salt metathesis of the PIL precursor, poly(1-[(2-methacryloyloxy)ethyl]-3-butylimidazolium bromide) (poly(MEBIm-Br)). The thermal and ion conductive properties of each PIL in this study were characterized. The ionic conductivity of the hydroxide conducting PIL, poly(MEBIm-OH), was the highest of these PILs investigated at 9.6 mS cm^{-1} at 90% RH and 30 °C with an Arrhenius activation energy of 17.1 kJ mol^{-1} at 90% RH.



INTRODUCTION

Recently, advances in alkaline anion exchange membranes (AEMs)[1,2] have significantly renewed interest in alkaline fuel cells (AFCs). AEMs not only circumvent problems encountered with liquid-based alkaline electrolytes (i.e., rapid AFC performance degradation due to carbonate precipitation), but more importantly, a long-lasting AFC provides a significant advantage over the well-adopted proton exchange membrane fuel cell (PEMFC) with the ability to produce high power densities at low temperatures (<200 °C) with a wide range of less expensive non-noble metal catalysts due to their facile oxygen reduction electrokinetics in basic environments.[3] In other words, a solid-state (AEM) AFC holds the promise of a low-cost, long-lasting, high power density fuel cell. In principle, an ideal AEM candidate should possess the following properties: excellent alkaline ion conductivity, chemical stability, mechanical strength, and durable, long-lifetime AFC performance. To date, various AEMs have been synthesized and characterized, including grafted polymers,[4,5] cross-linked copolymers,[6,7] random copolymers,[8−10] and block copolymers.[11,12] Note that despite different AEM chemical structures, the covalently attached cations in all of these polymers were based on ammonium. So far, among all the cations investigated, the quaternary ammonium cation has received the most attention. Other cations in AEMs have also been recently investigated, including phosphonium,[13] sulfonium,[14] guanidinium,[15] and imidazoilum.[16−18]

Despite the recent advances in the development of new AEMs, only a few AEMs have actually been tested in an AFC.[19−21] Therefore, there is a limited understanding regarding the relationship between AEM chemistry (and their resulting thermal, mechanical, and transport properties) and long-lifetime AFC performance. Furthermore, one of the critical issues that limits the use of AEMs in AFCs is the chemical stability of AEMs in hydroxide (OH^-) form. Because of the nucleophilicity and basicity of OH^- ions, the attack of OH^- ions can lead to a number of known degradation pathways for the countercation as well as the polymer backbone. For example, well-known degradation pathways for the tetraalkyl quaternary ammonium cation coupled with the OH^- ion, include β-hydrogen (Hofmann or E2) elimination,[22] direct nucleophilic substitution (S_N2),[23] and ylide formation.[24] In particular, in the absence of water, OH^- ions are not well solvated and can lead to faster degradation of the countercation.[23] As a consequence, AEMs are usually stored in the presence of water to prevent fast degradation. Depending on the nature of an AEM, the degradation of the polymer backbone may also occur under certain conditions (e.g., poly(vinylidene fluoride)-based AEM under alkaline conditions).[25] Of course, the chemical stability of an AEM is strongly dependent on the nature of the cation group as well. In general, compared to the quaternary ammonium cation, quaternary phosphonium and tertiary sulfonium cations undergo even faster degradation rates in

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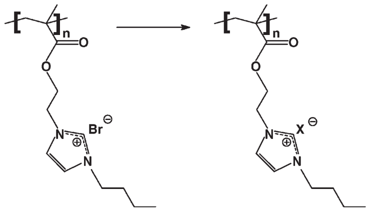
Scheme 1. Synthesis of Imidazolium-Based Alkaline Anion Exchange PILs: Poly(MEBIm-X) (X = OH, CO_3, HCO_3)



a) X = OH

(1) 1-propanol, KOH ($[OH^-]/[Br^-]$ = 1.5/1), room temperature, 48 h

(2) Dialysis, DI water, room temperature, 24 h

b) X = CO_3, HCO_3

(1) K_2CO_3 ($[CO_3^{2-}]$ = 0.5 M) or $KHCO_3$ ($[HCO_3^-]$ = 1 M), DI water, room temperature, 24 h

(2) Repeat (1) 3 times

(3) Dialysis, DI water, room temperature, 24 h

vinylbenzyl-based AEMs.[26] However, it was also reported that a novel poly(ether sulfone)-based AEM with quaternary phosphonium cation exhibited improved chemical stability due to the strong electron-donating groups (*o*-methoxy (*o*-OCH_3) and *p*-methoxy (*p*-OCH_3)) in the phenyl ring and the steric hindrance of the bulky trimethoxyphenyl group in the cation.[13] Recently, a guanidinium-based poly(ether sulfone) AEM showed no change in conductivity after immersion in 1 M NaOH solution at 60 °C for 48 h.[15] In addition, enhanced chemical stability for imidazolium-based AEMs[16,17] has been reported based on conductivity results. Specifically, the conductivity of a 1-allyl-3-methylimidazolium-based random copolymer reduced by only 8% after immersion in 6 M NaOH solution at 60 °C for 120 h,[16] and a 1-vinyl-3-methylimidazolium-based block copolymer retained its conductivity after immersion in 1 M KOH solution at 60 °C for 400 h.[17]

The enhanced chemical stability of imidazolium-based AEMs is largely attributed to the five-membered heterocyclic ring structure. The steric hindrance and the presence of the π-conjugated structure reduce the S_N2 substitution and Hofmann elimination reactions. The stable structure of imidazolium cations has also been demonstrated with a number of hydroxide-based ionic liquids (ILs) that have been synthesized and dried for use as catalysts (i.e., stable under dry conditions), such as 1-butyl-3-methylimidazolium hydroxide[27] and 1-butyl-2,3-dimethylimidazolium hydroxide.[28] As a comparison, ammonium counterparts, such as tetrabutylammonium hydroxide, are commercially available but always stored in a liquid form at a low concentration (<40 wt %) (i.e., requires solvation for stability).[29] More recent work has shown that a hydroxide-based imidazolium IL can slowly degrade into ring opened products (~3 months to full conversion.), but its stability increased with increasing amount of water.[30] In contrast to the work on quaternary ammonium cations, fundamental studies on the stability of imidazolium cations are relatively scarce. The degradation of purines, compounds that consist of a pyrimidine ring fused to an imidazole ring, appears to be the only relevant work reported. For example, several studies[31,32] reported that 7-methylguanosine undergoes ring-opening reactions in a strong aqueous base due to a nucleophilic attack by OH^- ions. To the best of our knowledge, however, no fundamental studies on the chemical stability of imidazolium-based AEMs exist in the literature. Such studies will be beneficial for the design of future AEMs for AFCs.

In this study, an imidazolium-based alkaline anion exchange polymerized ionic liquid (PIL), 1-[(2-methacryloyloxy)ethyl]-3-butylimidazolium hydroxide (poly(MEBIm-OH)), was synthesized via metathesis (anion exchange) of the precursor PIL (poly(MEBIm-Br): the Br^- ion form of the PIL). As a comparison to poly(MEBIm-OH), other alkaline anion exchange AEMs in the carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) forms (poly(MEBIm-CO_3) and poly(MEBIm-HCO_3)) were also prepared. The thermal and ion conductive properties of these anion exchange PILs were characterized and compared with ammonium-based AEMs. In contrast to previous studies, the ionic conductivity was combined with chemical structure analysis using nuclear magnetic resonance (NMR) spectroscopy to comprehensively characterize and quantify the chemical stability of poly(MEBIm-OH) over a broad range of humidity, temperature, and alkaline concentration conditions. This study shows enhanced chemical stability of poly(MEBIm-OH) at 30 °C under dry conditions (i.e., 10% RH). In hydrated conditions, poly(MEBIm-OH) is relatively stable even at 80 °C. Also, it is stable in mild alkaline conditions (i.e., [KOH] < 1 M) at a low temperature (25−30 °C). Chemical degradation appears to only significantly occur under more vigorous conditions (e.g., dehydrated (<10% RH) at high temperature (80 °C) or higher alkaline concentrations ([KOH] > 1)). The ^1H NMR analyses suggest that the degradation of poly(MEBIm-OH) under these conditions undergoes a ring-opening reaction as its primary degradation mechanism.

■ EXPERIMENTAL SECTION

Materials. 1-Propanol (anhydrous, ≥99.7%), potassium hydroxide (KOH, ACS reagent, ≥90%), potassium carbonate (K_2CO_3, ACS reagent, ≥99%), potassium bicarbonate ($KHCO_3$, ACS reagent, ≥99.7%), *N,N*-dimethylformamide (DMF, HPLC grade, 99.9%), lithium bromide (LiBr, anhydrous, ≥99.9%), methanol-d_4 (CD_3OD, 99.8 atom % D), and deuterium oxide (D_2O, 99.98 atom % D) were purchased from Sigma-Aldrich and used as received. Dialysis tubing (Spectra/Por biotech membrane, molecular weight cutoff (MWCO) = 500) was purchased from Fisher Scientific. Ultrapure deionized (DI) water (resistivity ∼16 MΩ cm) was used as appropriate.

Synthesis of Poly(MEBIm-OH). Poly(MEBIm-OH) was synthesized by anion exchange from the precursor PIL, poly(MEBIm-Br) (Scheme 1). The synthesis of poly(MEBIm-Br) has been documented in detail elsewhere.[33] A typical procedure for the exchange of the bromide anion (Br^-) form of the PIL, poly(MEBIm-Br), to the hydroxide anion form of poly(MEBIm-OH), is given as follows. 0.867 g of poly(MEBIm-Br) ($Br^- = 2.73 \times 10^{-3}$ mol) and 0.230 g of KOH ($OH^- = 4.10 \times 10^{-3}$ mol) were dissolved in 20 and 10 mL of 1-propanol at room temperature, respectively. Under nitrogen environment, the KOH solution was added dropwise to the poly(MEBIm-Br) solution. The mixture was stirred in a sealed vessel at room temperature for 48 h. After phase separation, the liquid portion was transferred into a tubular dialysis bag and purified extensively with nitrogen-saturated DI water for 24 h to remove excessive KOH and residual potassium bromide (KBr). After dialysis, water was removed by drying under vacuum at room temperature for 24 h. Yield: 0.306 g solid particles (44% yield). ^{1}H NMR (UNITYINOVA 500 MHz, D_2O, ppm) and elemental analysis: 7.62 (s, 2H, N−CH═CH−N), 4.28−4.58 (d, 6H, N−CH_2−CH_2−O, N−CH_2−CH$_2$−CH$_2$), 1.88 (s, 4H, CH_2−C(CH$_3$), N−CH$_2$−CH_2−CH$_2$−CH$_3$), 1.34 (s, 5H, N−CH$_2$−CH$_2$−CH_2−CH$_3$, CH$_2$−C(CH_3)), 0.95 (s, 6H, N−CH$_2$−CH$_2$−CH$_2$−CH_3, CH$_2$−C(CH_3)), 0.41−0.73 (m, 3H, CH$_2$−C(CH_3)). Anal. Calcd: C, 61.38; H, 8.74; O, 18.87; N, 11.02; Br, 0. Found: C, 58.79; H, 7.81; O, 24.34; N, 8.72; Br, 0.00.

Synthesis of Poly(MEBIm-HCO$_3$). Different from the synthesis of poly(MEBIm-OH), the anion exchange of poly(MEBIm-HCO$_3$) was performed in a dialysis bag at room temperature using DI water as a solvent (Scheme 1). 1.273 g of poly(MEBIm-Br) was dissolved in 20 mL of DI water, and the solution was transferred into a tubular dialysis bag. The exchange reaction was carried out in the dialysis bag against 1 M $KHCO_3$ aqueous solution. To ensure the complete metathesis of the bromide anion, three consecutive exchange reactions were carried out. After anion exchange, the polymer solution in the dialysis bag was purified extensively with nitrogen-saturated DI water for 24 h. This included at least six batches of fresh DI water. After dialysis, water was removed by drying under vacuum at room temperature for 24 h. Yield: 0.077 g solid particles (6.4% yield). ^{1}H NMR (UNITYINOVA 500 MHz, D_2O, ppm) and elemental analysis: 7.63 (s, 2H, N−CH═CH−N), 4.28−4.58 (d, 6H, N−CH_2−CH_2−O, N−CH_2−CH$_2$−CH$_2$), 1.88 (s, 4H, CH_2−C(CH$_3$), N−CH$_2$−CH_2−CH$_2$−CH$_3$), 1.34 (s, 5H, N−CH$_2$−CH$_2$−CH_2−CH$_3$, CH$_2$−C(CH_3)), 0.94 (s, 6H, N−CH$_2$−CH$_2$−CH$_2$−CH_3, CH$_2$−C(CH_3)), 0.40−0.73 (m, 3H, CH$_2$−C(CH_3)). Anal. Calcd: C, 56.35; H, 7.45; O, 26.81; N, 9.39; Br, 0. Found: C, 55.84; H, 8.22; O, 27.49; N, 7.76; Br, 0.00.

Synthesis of Poly(MEBIm-CO$_3$). The synthesis of poly(MEBIm-CO$_3$) was similar to poly(MEBIm-HCO$_3$) with the exception of using 0.5 M K_2CO_3 aqueous solution instead. Yield: 0.084 g solid particles (7.1% yield). ^{1}H NMR (UNITYINOVA 500 MHz, D_2O, ppm) and elemental analysis: 7.63 (s, 2H, N−CH═CH−N), 4.27−4.58 (d, 6H, N−CH_2−CH_2−O, N−CH_2−CH$_2$−CH$_2$), 1.88 (s, 4H, CH_2−C(CH$_3$), N−CH$_2$−CH_2−CH$_2$−CH$_3$), 1.33 (s, 5H, N−CH$_2$−CH$_2$−CH_2−CH$_3$, CH$_2$−C(CH_3)), 0.94 (s, 6H, N−CH$_2$−CH$_2$−CH$_2$−CH_3, CH$_2$−C(CH_3)), 0.51−0.78 (m, 3H, CH$_2$−C(CH_3)). Anal. Calcd: C, 60.64; H, 7.93; O, 20.95; N, 10.48; Br, 0. Found: C, 59.53; H, 8.66; O, 23.66; N, 7.18; Br, 0.00.

Characterization. The molecular weight of poly(MEBIm-Br) was determined by gel permeation chromatography (GPC) using poly(ethylene glycol)/poly(ethylene oxide) (PEG/PEO) standards. The measurement was performed at 40 °C using a Waters GPC system (breeze 2) equipped with two Styragel columns (Styragel@HR 3 and Styragel@HR 4) and a 2414 reflective index (RI) detector. A mixture of DMF and 0.05 M LiBr was used as a mobile phase at a flow rate of 1.0 mL/min. The chemical structures of alkaline anion exchange PILs were characterized by ^{1}H NMR using a UNITYINOVA 500 MHz spectrometer operated at 23 °C with D_2O used as the solvent. The chemical shifts were referenced to water at 4.79 ppm. The chemical stability of poly(MEBIm-OH) before and after conductivity measurements (described below) was analyzed by ^{1}H NMR using CD_3OD as the solvent. The chemical shifts were referenced to tetramethylsilane (TMS). The stability study under alkaline conditions was performed in NMR tubes. Poly(MEBIm-OH) was exposed to water and different KOH solutions (1, 6, and 10 M) at a concentration ∼10 wt % at 30 or 80 °C for a designated period of time followed by ^{1}H NMR experiments using CD_3OD as the solvent. The amount of residual bromide anion in the alkaline anion exchange PILs was determined by elemental analysis (Atlantic Microlab, Inc., Norcross, GA). Thermal degradation temperatures (T_d) of the PILs were determined by a thermal gravimetric analyzer (TGA, TA Instruments, Q50) at a heating rate of 10 °C/min under nitrogen environment. T_d was reported at 5% weight loss of a PIL sample. Glass transition temperatures (T_g) were measured by a differential scanning calorimeter (DSC) (TA Instruments, Q2000) with a temperature range of −10 to 200 °C at a heating/cooling rate of 10 °C/min under nitrogen environment using a heat/cool/heat method. T_g was determined using the midpoint method on the second heating cycle thermogram. The ionic conductivities of the alkaline anion exchange PILs were measured in film form with electrochemical impedance spectroscopy (EIS) (Solartron, 1260 impedance analyzer, 1287 electrochemical interface, Zplot software) using a four-electrode method over a frequency range of $1-10^6$ Hz at 200 mV. During conductivity experiments, the temperature and relative humidity (RH) were controlled with an environmental chamber (Tenney, BTRS model). Polymer films were solution cast from DI water at a 10 wt % polymer solution on a glass surface and dried under nitrogen environment overnight. The in-plane conductivities of the PIL films were measured in a cell with four-parallel electrodes, where an alternating current was applied to the outer electrodes and the real impedance or resistance, R, was measured between the two inner reference electrodes. The resistance was determined from a high x-intercept of the semicircle regression of the Nyquist plot. Conductivity was calculated by using the following equation: $\sigma = L/AR$, where L and A are the distance between two inner electrodes and the cross-sectional area of the polymer film ($A = Wl$; W is the film width and l is the film thickness), respectively. The film thicknesses, ranging between 80 and 200 μm, were measured with a Mitutoyo digital micrometer accurate to ±0.001 mm. Samples were allowed to equilibrate for 2 h at each measurement condition followed by at least six measurements at the equilibrium condition. The values reported are an average of these steady-state measurements.

■ RESULTS AND DISCUSSION

Anion Exchange Reactions. A series of alkaline anion exchange PILs, poly(MEBIm-X) (X = OH, CO$_3$, HCO$_3$), with the same degree of polymerization and molecular weight distribution, were synthesized via metathesis of the precursor PIL, poly(MEBIm-Br) ($M_w = 29\,900$, PDI = 2.2). A single batch of poly(MEBIm-Br) was polymerized from IL monomer, MEBIm-Br, using conventional free radical polymerization, and the syntheses of MEBIm-Br and poly(MEBIm-Br) have been detailed elsewhere.[33] The preparation of poly(MEBIm-OH) was conducted in 1-propanol, where the byproduct, KBr, precipitated resulting in an efficient metathesis of poly(MEBIm-Br) to

Table 1. Thermal Properties of Imidazolium-Based Alkaline Exchange PILs: Poly(MEBIm-X) (X = Br, OH, CO_3, HCO_3)

PIL	T_d (°C)[a]	T_g (°C)[b]
poly(MEBIm-Br)	265	110
poly(MEBIm-OH)	211	147
poly(MEBIm-CO_3)	205	154
poly(MEBIm-HCO_3)	196	–[c]

[a] Measured at 5% weight loss (under N_2 environment). [b] Determined by the midpoint of the second heating cycle in DSC thermograms (under N_2 environment). [c] The glass transition temperature was not observed.

poly(MEBIm-OH). The excess KOH and residual KBr in solution were removed by dialysis with extensive washing with nitrogen-saturated DI water. The resulting alkaline anion exchange poly(MEBIm-OH) was soluble in many polar protic solvents, such as water and various alcohols.

Compared to the metathesis of the PIL precursor from Br^- to OH^- form, a complete anion exchange of Br^- form to HCO_3^- or CO_3^{2-} form was more challenging. For example, only a fraction of Br^- could be exchanged to HCO_3^- using an alcohol as a solvent (e.g., ~0.32 in 1-propanol and ~0.61 in methanol). This is related to the low solubility of $KHCO_3$ in alcohols (e.g., the solubility of $KHCO_3$ in methanol at 25 °C is 0.012 g per 100 g of methanol).[34] Therefore, for efficient anion exchange, poly(MEBIm-HCO_3) and poly(MEBIm-CO_3) were prepared via metathesis of poly(MEBIm-Br) in water using dialysis against an aqueous K_2CO_3 or $KHCO_3$ solution, respectively.

The chemical structures of poly(MEBIm-OH), poly(MEBIm-CO_3), and poly(MEBIm-HCO_3) were characterized by ^1H NMR in D_2O. The hydrogen/deuterium (H/D) exchange reaction at position 2 of the imidazolium group resulted in the signal disappearance of the C(2) proton and a change of the C(4,5) signal from a doublet into a singlet. The anion exchange reactions were confirmed by chemical shifts of the C(4,5) protons (e.g., from 7.70 ppm (N–*CH*=*CH*–N of poly(MEBIm-Br)) to 7.62 ppm (poly(MEBIm-OH))). Elemental analysis further confirmed that there was no residual bromide anions present in these alkaline anion exchange PILs. The residual water content in these highly hydroscopic PILs resulted in slight deviations between measured elemental analysis results and theoretically calculated H, C, and N weight values.

Thermal Properties. The thermal degradation temperatures (T_d) and glass transition temperatures (T_g) of the alkaline anion exchange PILs were measured by TGA and DSC, respectively. The measured values of T_d and T_g are listed in Table 1. The TGA and DSC thermograms are provided as Supporting Information (see Figures S1 and S2). Table 1 shows that among these PILs, poly(MEBIm-Br) has the highest T_d (265 °C), and the relative thermal stability follows the order $Br^- > OH^- > CO_3^{2-} > HCO_3^-$. The reduction in thermal stability after anion exchange from the bromide anion to alkaline anions is mainly due to the increased nucleophilicity of these alkaline anions. All PILs exhibited a multistep degradation mechanism; however, the bromide PIL differs from the other alkaline anion PILs. For poly(MEBIm-Br), the predicted first degradation event should be triggered by a nucleophilic attack of bromide anions on the α carbon via S_N2 reaction, resulting in an alkyl leaving group, and this should be followed by main chain degradation in a subsequent event.[35] This would result in a ~39% weight loss in the first step corresponding to 1-butylimidazole with ~61% remaining corresponding to poly(2-bromoethyl methacrylate) (PBEMA). However, the thermogram (see Figure S1) of poly(MEBIm-Br) shows ~70% weight loss in the first degradation event. This additional weight loss may be attributed to a simultaneous degradation of PBEMA to poly(methacrylic acid) since the degradation temperature of PBEMA (~245 °C) is similar to poly(MEBIm-Br)) (see Table 1).[36] If the degradation of PBEMA is also considered in the first degradation event and PBEMA undergoes inter- and intramolecular degradation pathways,[36] the theoretical weight loss is calculated to be ~69%, which is in excellent agreement with the observed TGA data. For poly(MEBIm-OH)), if the first degradation event is caused by the nucleophilic displacement, the cleavage of 1-butylimidzole will correspond to a predicted 49% weight loss. However, the TGA data show only ~25% weight loss for the first degradation event, suggesting a different degradation mechanism for poly(MEBIm-OH)). The NMR results in this study show an imidazolium ring-opening reaction due to the attack of the hydroxide anion at the C(2) position at elevated temperatures (see Degradation Mechanism of Poly(MEBIm-OH) section). This suggests that the thermal degradation of poly(MEBIm-OH)) may be initiated by a ring-opening reaction and followed by further degradation of the side chain. Similarly, the ~35% observed weight loss during the first degradation event for poly(MEBIm-CO_3) and poly(MEBIm-HCO_3) also suggests a ring-opening mechanism at high temperatures. The ring-opening reaction significantly complicates thermal degradation analysis of alkaline anion exchange PILs, which may be contributed to the multistep degradation stages observed in the TGA thermograms.

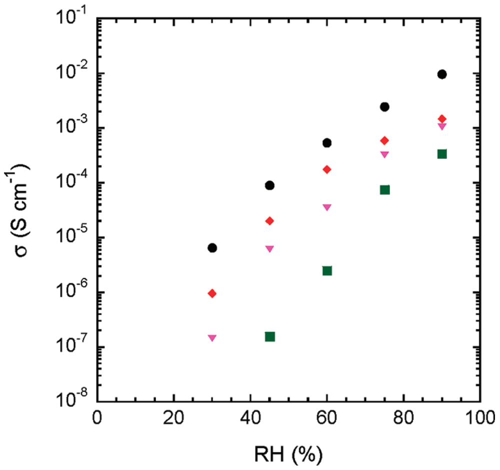


Figure 1. Humidity-dependent ionic conductivity of poly(MEBIm-X) at 30 °C (X = Br (red diamond), OH (black circle), CO_3 (magenta triangle), HCO_3 (green square)).

In contrast to the T_ds, the T_gs of the PILs follow the reverse order: $Br^- < OH^- < CO_3^{2-}$ (Table 1). The increase of T_g after anion exchange from bromide to alkaline anions may be due to the difference in anion size and ion pair coordination strength. In this study, the T_g of poly(MEBIm-HCO_3) was not observed, which may be due to the fact that the degradation of the bicarbonate anion occurs at a similar temperature.[37]

Ionic Conductivity. Figure 1 shows the ionic conductivity of the alkaline anion exchange PILs as a function of humidity at 30 °C. The results show an increase in humidity-dependent conductivity by 3–4 orders of magnitude from 30% RH to 90%

Table 2. Comparison of Ionic Conductivities of Representative Ammonium- and Imidazolium-Based AEMs

	ionic conductivity (mS cm^{-1})							
	quaternary ammonium-based AEMs					imidazolium-based AEMs		
	LW[a]				WV[b]	WV	LW	WV
anion	22 °C	20 °C	30 °C	20 °C	30 °C[c]	30 °C[c]	30 °C	30 °C[d]
OH^-	68.7	40	28–48	27	9.2	13.8–33.3	1.6–38.8	9.6
CO_3^{2-}	14	12	6.5–27.3	11.7				1.1
HCO_3^-	8.9							0.3
Br^-	1.8							1.5
reference	7	39	9	40	6	16	17	this work

[a] LW = liquid water. [b] WV = water vapor. [c] 100% RH. [d] 90% RH.

RH. Conductivity follows the order $OH^- > Br^- > CO_3^{2-} > HCO_3^-$, which (with the exception of the bromide anion) is similar in order to other AEMs reported in literature (see Table 2). At 90% RH and 30 °C, the conductivities of OH^-, Br^-, CO_3^{2-}, and HCO_3^- based PILs are 9.6, 1.5, 1.1, and 0.34 mS cm^{-1}, respectively. The conductivity of poly(MEBIm-OH) at 90% RH and 30 °C is comparable with other quaternary ammonium-based and imidazolium-based AEMs measured at similar conditions (Table 2).

Note that, in addition to the chemical stability of cations, another issue of concern is the conversion of OH^- to HCO_3^- and/or CO_3^{2-} ions in the presence of trace amount of carbon dioxide (CO_2) in air. However, there is no agreement on the kinetics of conversion of AEMs from OH^- form to CO_3^{2-} and/or HCO_3^- forms and the effect CO_2 on the cell performance. For example, it was reported that the time scale for the conversion of a commercially available ammonium-based AEM from OH^- to HCO_3^- form was 30 min,[38] while it took 4 days for an ammonium-based poly(ester sulfone).[9] The variation in reaction kinetics may be dependent on the chemistry of the polymer, covalently attached cation, as well as contact environment (e.g., liquid water, water vapor, etc.). Interestingly, Figure 1 shows a significant difference in conductivity among alkaline anion exchange PILs with experimental time of 18 h for each sample, suggesting that imidazolium-based alkaline AEMs may have a good tolerance to the deleterious effect of CO_2. However, a significant amount of work remains to investigate the effect of CO_2 on imidazolium-based AEMs and other AEMs under different conditions.

Figure 2 shows the temperature-dependent ionic conductivity of poly(MEBIm-OH) and poly(MEBIm-Br) at 90% RH. Different from the ionic conductivities of hydrophobic PILs, which exhibit Vogel–Fulcher–Tammann (VFT) behavior,[33] the ionic conductivity of hydrophilic PILs follow typical Arrhenius behavior,[41] which is similar to water-assisted ion transport in proton exchange membranes, such as Nafion. The activation energies determined from the Arrhenius regressions were 17.1 and 24.1 kJ mol^{-1} for poly(MEBIm-OH) and poly(MEBIm-Br), respectively. The activation energy of poly(MEBIm-OH) obtained in this study is in a good agreement with other imidazolium-based AEMs (e.g., 13.20–16.37 kJ mol^{-1} at 100% RH[16] and 11.99–15.46 kJ mol^{-1} in liquid water[17]) and quaternary ammonium-based AEMs (e.g., 15.1–18.9 kJ mol^{-1} at 100% RH[42]).

Stability of Poly(MEBIm-OH). In this study, we examined the effects of relative humidity, temperature, and alkaline concentration on the chemical stability of the polymer and the imidazolium cation with the use of EIS and ^1H NMR. An AEM that is chemically stable under low humidity is desired in order to sustain a long AFC lifetime under a variety of conditions (e.g., humidity oscillations, rapid startup and shutdown). Therefore, the chemical stability of poly(MEBIm-OH) under dry conditions is of great interest. A conductivity/stability test under humidity cycling conditions is shown in Figure 3. Figure 3a shows ionic conductivity of poly(MEBIm-OH) exposed to oscillating wet (90% RH)–dry (10% RH) humidity cycling conditions at 30 °C over 3000 min. It is clear that the conductivity of rehydrated poly(MEBIm-OH) recovers after each dehydration cycle (10 h at 10% RH), and the full recovery of conductivity was observed after multiple repeated hydration–dehydration cycles over a 3000 min period. Furthermore, it should be noted that poly(MEBIm-OH) was synthesized and dried under vacuum and then dissolved in water and solution cast into a film prior to conductivity measurements. The ^1H NMR spectra shown in Figure 3b also indicated that the chemical structure of poly(MEBIm-OH) were nearly identical before and after the humidity cycling test, confirming that poly(MEBIm-OH) is chemically stable under the test.

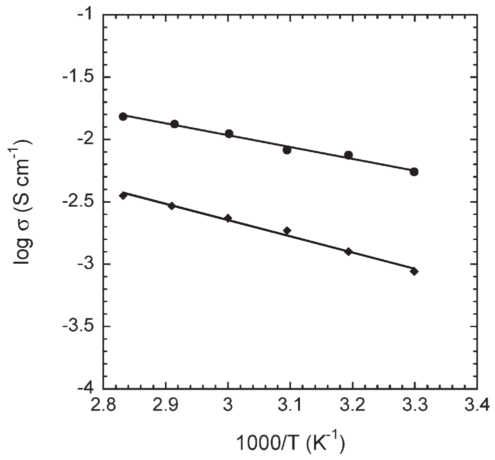


Figure 2. Temperature-dependent ionic conductivity of poly(MEBIm-X) at 90% RH (X = Br (diamond), OH (circle)).

The chemical stability of poly(MEBIm-OH) at dry conditions can be related to the steric hindrance of the imidazolium ring and

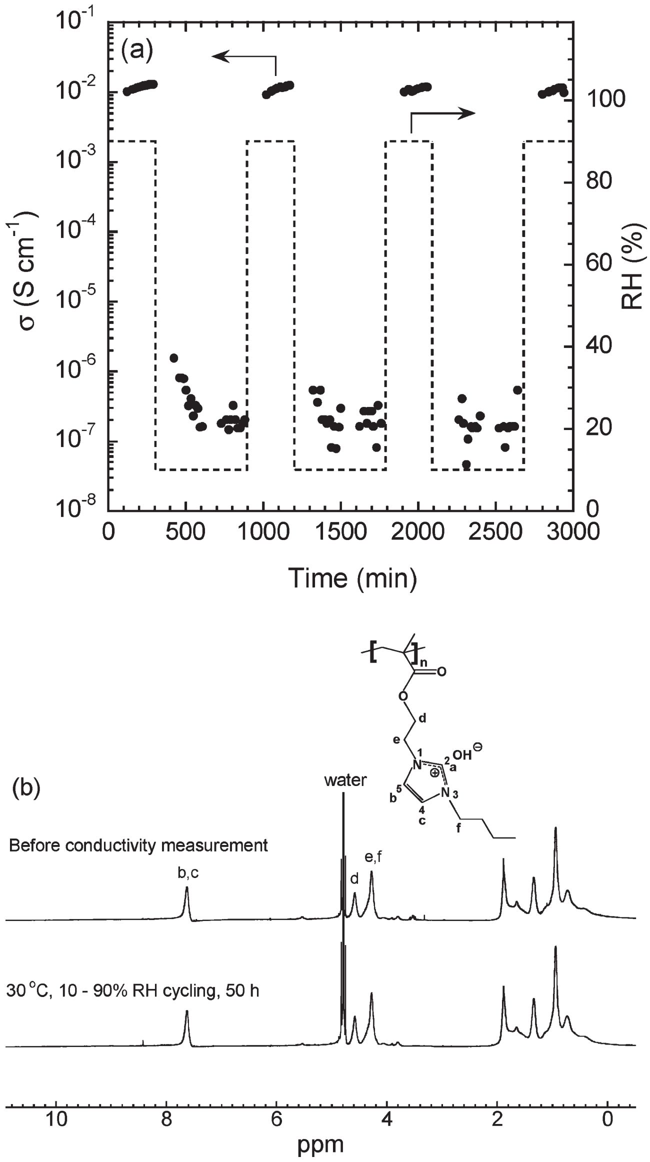


Figure 3. Conductivity/stability test of poly(MEBIm-OH) under oscillating humidity cycling conditions (90% RH−10% RH) at 30 °C: (a) ionic conductivity and (b) ^{1}H NMR spectra before and after conductivity measurement.

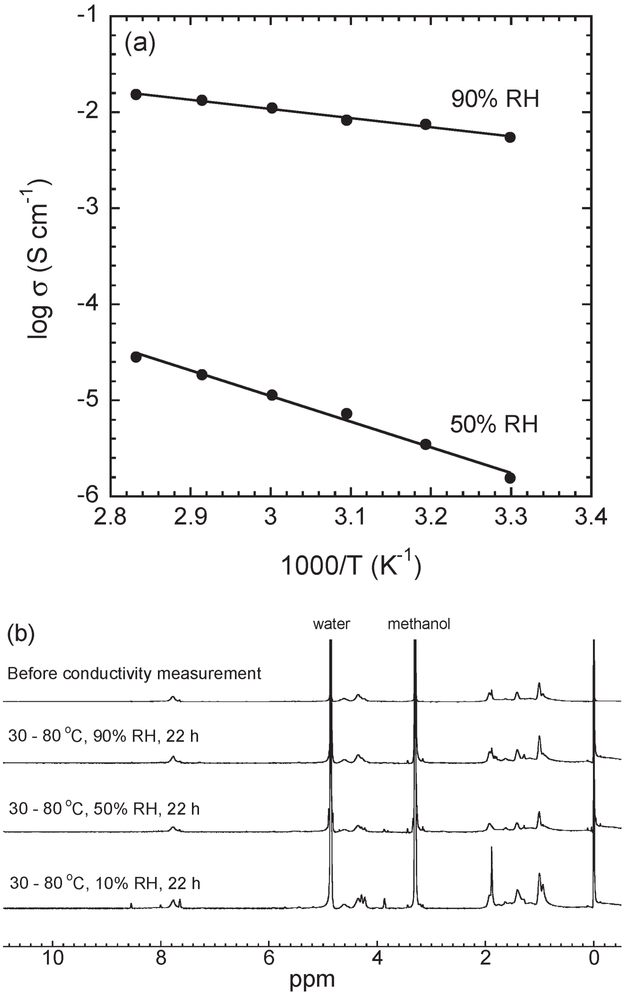


Figure 4. Conductivity/stability tests of poly(MEBIm-OH) under elevated temperatures at 90% RH, 50% RH, and 10% RH: (a) ionic conductivity and (b) ^{1}H NMR spectra before and after conductivity measurements.

the π-conjugated structure that delocalizes the positive charge. Furthermore, for the extreme case, the deprotonation of a 1,3-alkyl-substituted imidazolium hydroxide can result in a relatively stable carbene compared to ammonium-based AEMs. For example, stable imidazolium-based carbenes, such as 3-bis-(adamantyl)imidazol-2-ylidene, have been synthesized and isolated by others.[43] More importantly, the stable alkyl-substituted imidazol-2-yl carbenes resulting from deprontonation can be reversely protonated by water.[44,45] As a result, the conductivity can be retained through the hydration−dehydration process. As a comparison, deprotonation of the tetraalkyl quaternary ammonium cation has been shown to result in the formation of a relatively unstable ylide, and the ylide pathway becomes more prevalent under dry conditions.[23]

The chemical stability of an AEM at higher temperatures is also of interest for the AFC, where operating at these temperatures (up to 80 °C) is desired since it can enhance the reaction kinetics at both electrodes and ion transport in the AEM, thereby improving AFC performance. Thus, we also investigated the stability of poly(MEBIm-OH) at elevated temperatures under different humidity conditions (90%, 50%, and 10% RH). Conductivity/stability tests under elevated temperatures are shown in Figure 4. Figure 4a shows ionic conductivity of poly(MEBIm-OH) exposed to stability tests under elevated temperatures ranging from 30 to 80 °C at 90% RH and 50% RH for 22 h (3.6 h hold at each temperature). Similar to conductivity data at 90% RH (Figure 2), the data at 50% RH also follows an Arrhenius behavior with an activation energy of 59.4 kJ mol^{-1}. The conductivity data at 10% RH are not shown here. ^{1}H NMR spectra shown in Figure 4b indicates that there was no appreciable degradation in the temperature range between 30 and 80 °C at 90% RH and 50% RH. However, at 10% RH, additional peaks appeared after the conductivity measurement, suggesting some degree of degradation occurred at dry conditions and elevated temperatures.

In addition to investigating the stability of poly(MEBIm-OH) as a function of humidity and temperature, we also explored the effect of alkaline concentration (i.e., high pH), although it is unclear what the local pH of an AEM is in an operating AFC.

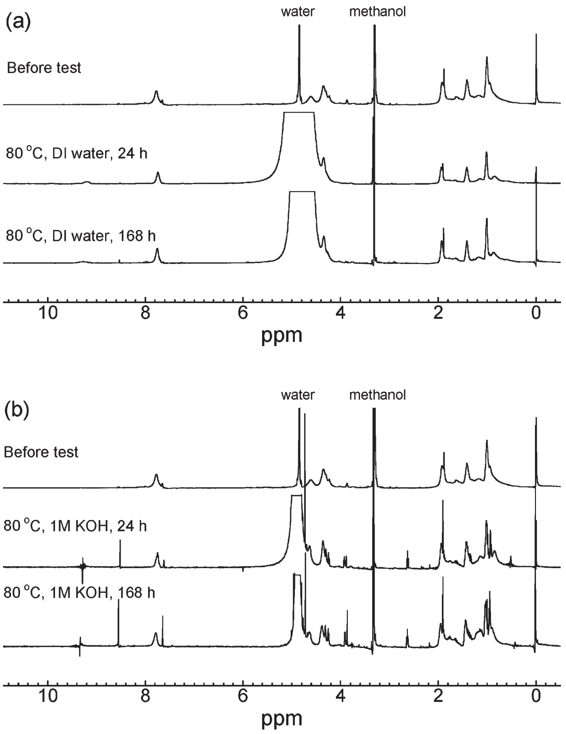


Figure 5. Stability tests (^{1}H NMR spectra) for poly(MEBIm-OH) (~10 wt % polymer in solution) at 80 °C in (a) DI water and (b) 1 M KOH for 24 and 168 h.

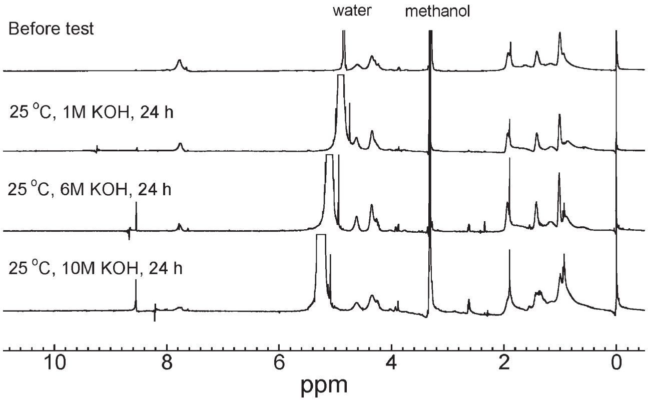


Figure 6. Stability tests (^{1}H NMR spectra) for poly(MEBIm-OH) (~10 wt % polymer in solution) in 1 M, 6 M, and 10 M KOH at 25 °C for 24 h.

To investigate the chemical stability under alkaline conditions, a NMR tube, where poly(MEBIm-OH) dissolved in a KOH aqueous solution at a polymer concentration ~10 wt %, was heated for a designated period of time. Figure 5 shows ^{1}H NMR spectra of poly(MEBIm-OH) after exposure to 1 M KOH at 80 °C for 24 and 168 h. The ^{1}H NMR spectra of polymer exposed to just neutral DI water at the same temperature and times are also shown in Figure 5 as a control. Figure 5a indicates that there was almost no change for the chemical structure of the polymer after exposure to DI water at 80 °C for both the 24 and 168 h times. As mentioned before, the C(2) proton peak disappeared due to the H/D exchange reaction. Interestingly, the C(2) proton peak appeared in DI water, suggesting that the presence of water suppresses the H/D exchange reaction. Figure 5b shows that with higher pH the imidazolium cation in the PIL becomes less stable evidenced by the appearance of additional peaks in the NMR spectra. This degradation became more pronounced with increasing time from 24 to 168 h.

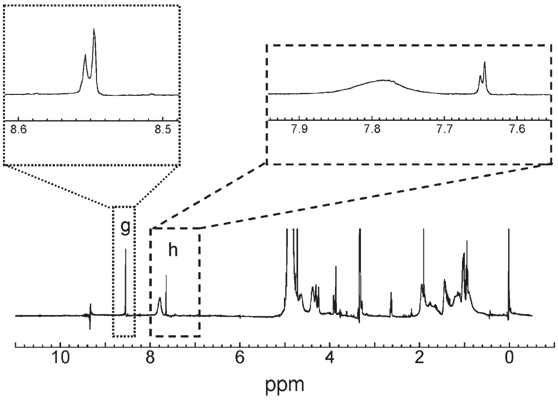


Figure 7. A typical ^{1}H NMR spectrum of a degraded poly(MEBIm-OH) sample (case 8 in Table 2, see Scheme 2 for peak assignment).

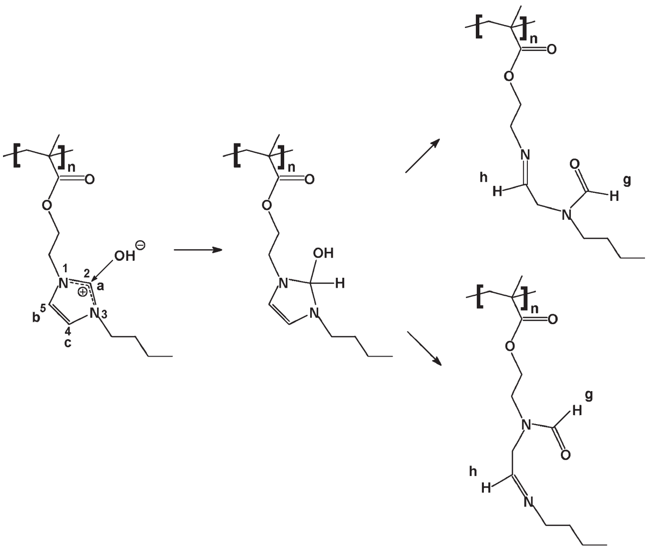
The stability of poly(MEBIm-OH) under a higher alkaline concentrations (e.g., 1−10 M) at a low temperature (25 °C) was also investigated. Figure 6 shows the ^{1}H NMR spectra of poly(MEBIm-OH) in 1, 6, and 10 M KOH at 25 °C. No significant degradation was observed for the polymer exposed to 1 M KOH at 25 °C for 24 h. However, in 6 and 10 M KOH, the degradation of poly(MEBIm-OH) was noticeable and became more significant with increasing alkaline concentration.

Degradation Mechanism of Poly(MEBIm-OH). The stability study indicated that poly(MEBIm-OH) is stable under dry environments and in relatively weak alkaline conditions (e.g., ≤1 M) at low temperatures (e.g., 25−30 °C). Poly(MEBIm-OH) is even chemically stable at higher temperatures when exposed to higher humidities. However, at a low humidity and elevated temperatures or at a higher pH, the polymer begins to chemically degrade as evidenced by NMR spectral analysis. Thus, it is also important to understand the degradation mechanism. However, the degradation of 1,3-substituted imidazolium cations under alkaline conditions is not well studied.

Because of the similarity of chemical structures between imidazole and purine, the degradation of purines and purine derivatives may be helpful to understand the degradation pathways for the imidazolium cation. Findings on the degradation of purine compounds suggest that the imidazolium cation may degrade via a ring-opening mechanism.[31,32] The opening of the imidazolium ring is triggered by the nucleophilic attack of OH^- on the imidazolium ring at the C(2) position (α carbon with respect to both nitrogen atoms), which is also analogous to the direct nucleophilic displacement of α carbons in the degradation of quaternary ammonium cations.[23] When examining the ^{1}H NMR spectra of all the degraded poly(MEBIm-OH) samples (shown in Figures 5−7), they all exhibit additional peaks around 8.55 ppm, which is not apparent in the nondegraded samples. With the knowledge of the degradation of purines, this data suggests an opening of imidazolium ring yielding formyl groups (−CHO). The literature findings on the formyl groups at 8.7,[32] 8.36,[46] and 8.15 ppm[47] confirm the assignment of the formyl group in ^{1}H NMR spectra of the degraded poly(MEBIm-OH) samples. The enlarged view of the formyl proton signal shown in

Figure 7 indicates that it actually consists of two peaks (i.e., 8.55 and 8.54 ppm), which can be attributed to the isomers of formyl groups due to the opening of the imidazolium ring at two possible sites (Scheme 2). This is also in agreement with the degradation of purine derivatives.[47] Another functional group resulting from the ring-opening reaction is the −CH═N− group, which is evidenced by the 7.65 and 7.64 ppm peaks in the NMR, where these two peaks also correspond to two isomers shown in Figure 7. The formation of −CH═N− is in good agreement with the ring-opening degradation of 1,3-di-*tert*-butylimidazol-2-ylidene.[48] It should be noted that the ring-opening reaction may also result in the double bond structure of −CH═CH−, which has been evidenced in the ^{1}H NMR spectrum at 5.56 and 4.66 ppm by others; however, it has been experimentally and theoretically shown that the formation of −CH═N− at 7.76 ppm is more thermodynamically stable.[30] It was also reported that the formation of −CH═N− can occur via the isomerization of −CH═CH−.[30] However, the isomerization was not reported in the ring-opening degradations of purines probably due to the constraint of the pyrimidine ring that is fused to the imidazole ring in a purine molecule. Additionally, in the experimental conditions we investigated in this study, there was no evidence to support the attack on the two α carbons located outside and next to the imidazolium ring (e and f positions shown in Figure 3), forming either 1-butylimidazole or 1-butanol (see Support Information for more details). Thus, the degree of ring-opening degradation of the imidazolium cations can be estimated by the relative integrations of the indicated ^{1}H resonances (i.e., g/((b + c)/2 + g) shown in Scheme 2). Table 3 lists these calculated degrees of degradation for poly(MEBIm-OH) for all the conditions examined in this study. In the temperature range between 30 and 80 °C at 10% RH, only 9.9% of the imidazolium cation degraded. In 1 M KOH solution for 24 h, 3.8% of the imidazolium cation degraded at 25 °C, while 18% at 80 °C. With increasing KOH concentration from 1 to 6 to 10 M at 25 °C, degradation increased from 3.8% to 41.9% and 49.7%, respectively. In summary, poly(MEBIm-OH) is relatively stable in hydrated conditions (at a high humidity (50%, 90% RH), in liquid water) at temperatures ranging between 25 and 80 °C and in mild alkaline conditions (i.e., [KOH] < 1 M) at a low temperature (25 −30 °C). However, the degradation becomes more significant under vigorous conditions (dehydrated (<10% RH) and high temperature (80 °C) and a high alkaline concentration ([KOH] > 1 M)). Infrared spectra collected on these samples confirm the ring-opening mechanism observed by NMR (see Supporting Information for more details).

Scheme 2. Ring-Opening Reaction of Poly(MEBIm-OH)



In addition, it should be noted that for a methacylate-based polymer the carboxylate ester linkage may also undergo a hydrolysis degradation reaction under alkaline conditions. Although the hydrolysis of the carboxylate ester linkage has often been observed in a saponification process of a small molecule ester, the hydrolysis of a polymeric ester has also been reported, and it typically occurs at a much slower rate compared to small molecule esters.[49] For a polymeric ester, the degradation rate is also significantly dependent on the structure of a polymer and the alkaline condition (e.g., concentration, temperature, etc.). For example, the hydrolysis of poly(methyl acrylate) was observed to be complete within 30 min in a 0.8 M NaOH solution of benzene and methanol at 80 °C, while only ∼9% hydrolysis of poly(methyl methacrylate) occurred after 100 h in the same condition.[50] The NMR spectra of the degraded

Table 3. Degree of Ring-Opening Degradation of Poly(MEBIm-OH) after Conductivity Measurements and Exposure to Alkaline Solutions

case[a]	*T* (°C)	rel humidity (%) or KOH concn (M)	*t* (h)	NMR spectrum	MR[b]	degradation (%)[c]
1	30	RH = 10%−90%	50	Figure 3	0	0
2	30−80	RH = 90%	22	Figure 4	0	0
3	30−80	RH = 50%	22	Figure 4	0	0
4	30−80	RH = 10%	22	Figure 4	0.11	9.9
5	80	[KOH] = 0 M	24	Figure 5	0	0
6	80	[KOH] = 0 M	168	Figure 5	0	0
7	80	[KOH] = 1 M	24	Figure 5	0.22	18
8	80	[KOH] = 1 M	168	Figure 5	0.62	38.3
9	25	[KOH] = 1 M	24	Figure 6	0.04	3.8
10	25	[KOH] = 6 M	24	Figure 6	0.72	41.9
11	25	[KOH] = 10 M	24	Figure 6	0.99	49.7

[a] Cases 1−4 are the results after conductivity measurements, and cases 5−11 are the results after exposure to alkaline solutions. [b] MR = mole ratio of the formyl group to the imidazolium group (i.e., 2 g/(b + c)). [c] The degree of degradation was estimated by the relative integration of the ^{1}H resonances (i.e., g/((b + c)/2 + g), or 1/(1 + 1/MR)) in Scheme 2).

poly(MEBIm-OH) also suggest that hydrolysis may occur after the ring-opening mechanism, where both covalently attached and cleaved ring-opening imidazoliums may be present (see Scheme S3 in Supporting Information). In other words, hydrolysis or cleavage of the C−O ester bond in alkaline conditions results in a ring-opened random copolymer with carboxylic acid salt and a small molecule ring-opened alkoxide salt as byproducts. NMR analysis suggests that ~30% of the ring-opened byproducts may be cleaved from the polymer (see Support Information for more details), which is in good agreement with the hydrolysis of poly(methyl methacrylate) under a similar condition studied by ^{14}C labeling.[50] However, the ring-opened polymer (Scheme 2) appears to be the primary degradation mechanism. Infrared data collected on these samples also suggest that a possible hydrolysis reaction may occur (see Supporting Information). Other possible degradation mechanisms were investigated; however, neither NMR nor IR provided any proof of these alternative mechanisms (see Supporting Information).

CONCLUSIONS

In this study, imidazolium-based alkaline anion exchange PILs, poly(MEBIm-X) (X = OH, CO_3, HCO_3), were synthesized via salt metathesis with the precursor PIL, poly(MEBIm-Br).The thermal and ion conductive properties of these PILs were characterized. The ionic conductivity of poly(MEBIm-OH) is comparable with other ammonium- and imidazolium-based AEMs reported in the literature. The chemical stability of poly(MEBIm-OH) was investigated and quantified over a wide range of humidities, temperatures, and alkaline concentrations. High chemical stability was evidenced by the sustained ionic conductivity and unchanged ^{1}H NMR spectra under dry conditions (10% RH) at 30 °C, humid and saturated conditions up to 80 °C, and even in mild alkaline conditions ([KOH] < 1 M) at 25 °C. Degradation was only observed under more vigorous conditions: dry conditions (10% RH) at 80 °C or at higher alkaline concentrations ([KOH] > 1 M). The analysis of ^{1}H NMR spectra suggests a ring-opening degradation pathway for the imidazolium cation, and the degree of degradation was also quantified. Compared to the ammonium and phosphonium cations, relatively high chemical stability of the imidazolium cation in a wide range of alkaline conditions suggests a promising future for the development of solid-state imidazolium-based AEMs for use in AFCs.

ASSOCIATED CONTENT

S Supporting Information. Additional data include TGA, DSC, NMR, and IR and a discussion on other possible degradation pathways. This material is available free of charge via the Internet at http://pubs.acs.org.

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