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Insight into the Alkaline Stability of N-Heterocyclic Ammonium Groups for Anion-Exchange Polyelectrolytes

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Abstract: The alkaline stability of N-heterocyclic ammonium (NHA) groups is a critical topic in anion-exchange membranes (AEMs) and AEM fuel cells (AEMFCs). Here, we report a systematic study on the alkaline stability of 24 representative *NHA* groups at different hydration numbers (λ) at 80°C. The results elucidate that *γ*-substituted NHAs containing electrondonating groups display superior alkaline stability, while electron-withdrawing substituents are detrimental to durable NHAs. Density-functional-theory calculations and experimental results suggest that nucleophilic substitution is the dominant degradation pathway in NHAs, while Hofmann elimination is the primary degradation pathway for NHA-based AEMs. Different degradation pathways determine the alkaline stability of NHAs or NHA-based AEMs. AEMFC durability (from $1 A cm^{-2}$ to $3 A cm^{-2}$) suggests that NHA-based AEMs are mainly subjected to Hofmann elimination under $1 \, A \, cm^{-2}$ current density for 1000 h, providing insights into the relationship between current density, λ value, and durability of NHAbased AEMs.

Introduction

Anion exchange membranes (AEMs) and anion exchange ionomers (AEIs) have received a surge of interest related to applications in AEM fuel cells (AEMFCs) and AEM water electrolyzers (AEMWEs) due to the feasibility of utilizing

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platinum-group-metal (PGM)-free catalysts.^[1-5] AEMFC technology has been rapidly advanced in the past four years, attributed to the discovery of high-performance AEMs and AEIs. AEMFCs have attained remarkable peak power densities (PPDs) $> 2 \text{ W cm}^{-2}$ in H₂-O₂ and $> 1 \text{ W cm}^{-2}$ in H₂-air so far, which is comparable to or even surpasses proton exchange membrane fuel cells (PEMFCs), which have dominated the field of low-temperature fuel cells for years.^[6-11] Recent studies suggest that the insufficient durability of AEMFCs has become the most critical issue, which is strongly associated with the chemistry of their AEMs and AEIs.^[1-14]

As key materials of AEMFCs, AEMs and AEIs consist of the polymer backbones and suspended cationic groups that are responsible for conducting OH⁻ ions. Although many cationic groups, such as quaternary ammonium (QA), imidazolium (IM), quaternary phosphonium (QP), and organometallic cations,^[15-22] have been explored as AEMs and AEIs, most of them are vulnerable to being exposed to alkaline media due to severe chemical degradations, such as nucleophilic substitution, Hofmann degradation, ring-opening reaction, and ylide degradation. Years of study have revealed that only a few cationic groups have exhibited promising alkaline stability (so-called ex-situ durability) under harsh alkaline conditions and elevated temperatures.^[18,22-27] For instance, 6azonia-spiro[5.5]undecane (ASU), N,N-dimethyl piperidinium (DMP), tetramethyl quaternary ammonium (TMA), large steric hindrance IMs, bulky OP, and substituted cobaltocenium groups have been reported to possess high and promising alkaline stability. Typically, some bulky IMs exhibited outstanding half-life time () over 10,000 h in 3 M NaOD/D₂O/CD₃OD at 80 °C under hydration number (λ) = 4.8 conditions.^[18] Bulky QP groups also displayed high alkaline stability in KOH/D2O/CD3OD at 80°C.[24] Unfortunately, the application of bulky IM and QP groups in AEMs and AEMFCs are limited at present by their complicated chemistry and synthesis.^[26-28] On the other hand, previous studies have suggested that ASU and DMP groups possessed much higher alkaline stability among QA groups in 6 M NaOH at 160°C due to the merits of their N-heterocyclic ring.^[23] Systematic studies on the comparison between these stable cationic groups (ASU, DMP, IMs, or QP) have not been reported yet.

To date, QA groups have been the most-studied cationic groups, possessing outstanding ion conductivity and AEMFC performance.^[3,29] The realm of AEMFCs has been greatly advanced by the discovery of high-performance QA-based AEMs in the past few years. Three types of QA groups-*N*-

heterocyclic ammonium (NHA), alkyl ammonium, and trimethylammonium benzyl (BTMA)-based AEMs^[1,4-9,12,30-32] currently dominate AEMFCs. Specifically, NHA-based AEMs were stable in 1 M NaOH at 80°C over 2,000 h.[1,7,12] Alkyl ammonium-based AEMs exhibited promising alkaline stability in 1 M NaOH at 80°C as well.^[33] However, some arguments have been raised in current QA and QA-based AEMs. For instance, (1) BTMA groups have been documented to possess poorer alkaline stability than NHA and bulky IM groups, while some reports indicated that the BTMA groups may have higher durability than ASU or bulky IM groups under low λ conditions ($\lambda < 4$).^[34] In addition, few BTMA-based AEMs^[31] (such as: BTMA-based high-density polyethylene-BTMA-HDPE) exhibited excellent AEMFC durability (so-called in situ durability) for 1,000 h at a 0.6 A cm⁻² current density at 60 °C. (2) Another typical example is that ASU groups have been preliminarily documented to possess the highest alkaline stability among current OA groups, while some DMP-based AEMs displayed higher alkaline stability than ASU-based AEMs.^[35,36] (3) Different λ values certainly show a significant effect on the alkaline stability of cationic groups, while the relationship between λ values, alkaline stability of QA and AEMs, and in situ durability still has not been well elucidated to date.^[34]

Here, we explored the of 24 representative QA groups in NaOD/D₂O/CD₃OD under different λ conditions (i.e., 4.8, 7.0 and 10.0), and present several durable and promising NHA groups for future design of AEMs for AEMFC and AEMWE research. The electronic effect of substituents on NHA groups and degradation mechanisms of NHA groups are systematically investigated by ¹H nuclear magnetic resonance (¹H NMR) and density functional theory (DFT) calculations. High-performance poly(aryl-co-aryl piperidinium) (c-PAP) AEMs and ionomers^[1,7] are used as an example to examine the *ex-situ* and in situ durability under different λ values and current densities, intending to disclose the relationship between λ values, and *ex-situ* and in situ durability.

Results and Discussion

Synthesis of ASUs and DMPs with different substituents was reported along with ¹H NMR analysis in Figures S1 to S19 and Schemes S1 to S4. The alkaline stability of these NHA groups was examined in air based on 3 M NaOD/D₂O/ CD₃OD solution that can effectively dissolve compounds with many different types of cationic groups.^[18,25,35] The molecular structures of 24 representative QAs along with abbreviations are shown in Table 1. BTMA and TMA were used as a benchmark, and benzyl DMP (B-DMP) and hexyltrimethyl ammonium (HTMA) were used for comparison. Sodium 3-(trimethylsilyl)propane-1-sulfonate (SDBS) was used as an internal standard for ¹H NMR measurement to calculate the degradation ratio (Figure S20). To confirm the alkaline stability of cationic compounds, three λ conditions- $\lambda = 4.8$, 7.0 and 10.0-were selected, and the measuring temperature was fixed at 80 °C to match typical AEMFC applications.^[1-7] ¹H NMR spectra, and possible degradation pathways of NHA groups are presented in Figures S21 to S85 and Schemes S5 to S25.

Alkaline Stability of NHA Groups

 $\lambda = 4.8$ conditions: Figure 1 a indicates the original ASU and DMP groups exhibit outstanding alkaline stability under $\lambda = 4.8$ conditions due to highly symmetric structure and special ring strain. of ASU is greater than 20,000 h (compared with 13,256 h for DMP), which is comparable to bulky IMs (> 10,000 h) and is higher than bulky QP compounds.^[18,24,25] This result is consistent with the discovery of Marino et al. that ASU and DMP possessed excellent alkaline stability in 6 M KOH ($\lambda = 9.25$) at 160 °C.^[23] Nevertheless, it is theoretically impossible to use the pristine ASU or DMP groups directly in polymeric AEMs without substitutions. Therefore, a study on the effect of substituents on the alkaline stability of NHA groups is a crucial topic for current AEMs. Using DMP as an example, the possible chemical structure of NHA-based AEMs is shown in Figure 1b.^[1-9,36-39]

NHAs (DM-IQ, O-DMP, IS-ASU, O-ASU) with electronwithdrawing substituents (such as phenyls or heteroatoms) presented in the α - or β -position exhibit much lower than those of the pristine DMP or ASU (Figure 1a). The electronwithdrawing substituents activate α -carbons and β -hydrogens in the NHA ring so as to accelerate the nucleophilic substitution and Hofmann elimination reactions, respectively, which dramatically decreases the alkaline stability of NHAs. Moreover, H-DMP (3,527 h), H-ASU (3,433 h), Bis-TP-DMP (2,078 h), Bis-TP-ASU (3,777 h) groups with electron-withdrawing substituents in the γ -position display significantly improved compared to the aforementioned NHAs with electron-withdrawing substituents in the α - or β -position (2) h-1,157 h) due to the weakening electron-withdrawing effect. Besides, of Bis-TP-DMP and Bis-TP-ASU are close to or even higher than the TMA benchmark (2,412 h). DMP or ASU series display much higher than BTMA (171.6 h), which is consistent with previous findings.

On the other hand, the of NHA groups containing electron-donating substituents (such as -CH2-, CH3-, benzyl, or aliphatic chain) surpasses that of the TMA benchmark, which is much higher than that of NHAs containing electronwithdrawing substituents. The electron-donating groups contribute to increasing the steric hindrance and electron density of N-heterocyclic ring and thus reducing the possibility of nucleophilic substitution and Hofmann degradation reactions. Moreover, NHAs with electron-donating substituents in the γ-position (4-M-DMP) exhibited much higher alkaline stability (\approx 14,000 h) than NHAs with electron-donating substituents in the α - or β -position (3-M-DMP: 5589 h; 2-M-DMP: < 2,000 h) due to the higher geometric symmetry, as shown in Figure 1 a. Recently, Pham et al.^[35,36,38] presented a series of B-DMP and B-ASU-based polyphenylene AEMs with electron-donating substituents in the γ -position. They found that the alkaline stability of these AEMs significantly increased compared to polyphenylene-based AEMs with electronwithdrawing substituents (phenyl groups) in the γ -position.





This phenomenon is well verified by the alkaline stability of B-DMP (3,460 h) and B-ASU (4,156 h) in this work.

Having said that, compared to the pristine ASU and DMP, most NHAs with electron-donating substituents still show slightly lower alkaline stability, which is assumed to the change in ring strain and symmetry. Multiple-substituted HMP groups only exhibit moderate alkaline stability (of \approx 1,570 h), indicating that the overladen substituents may not be a good choice for highly stable AEMs. Moreover, NHAs with a symmetric structure (such as: ASU, DMP, Bis-ASU, Bis-DMP) seem to possess higher alkaline stability than that of asymmetric NHAs, such as B-DMP and B-ASU. Consequently, linking NHA groups with the polymer backbone via y-position could be a rational design for highly stable AEMs, particularly using electrondonating substituents. Attention should be taken to avoid placing improper substituents in the wrong position of the NHA ring because this can be highly detrimental to the alkaline stability of AEMs.

 $\lambda = 7.0$ and $\lambda = 10.0$ conditions: The alkaline stability of NHA groups was explored under $\lambda = 7.0$ and 10.0 conditions as well, as shown in Figure 2. Basically, most NHAs show much longer under higher λ values, which is quite natural for QA groups. The electronic effect of substitutions on NHA groups under both $\lambda = 7.0$ and 10.0 conditions are almost the same as that of $\lambda = 4.8$. Again, NHAs containing electron-donating substituents exhibit much higher alkaline stability than that of NHAs containing electron-withdrawing substituents. Specifically, the of y-substituted NHA groups with electron-donating groups can reach > 10,000 h, and some of them can even reach the over 60,000 h under $\lambda = 10.0$ conditions. Unfortunately, Bis-TP-DMP and Bis-TP-ASU groups cannot be well dissolved in NaOD/D2O/CD3OD solvents when the λ value increases to 7.0 and 10.0.

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Figure 1. a) The of different QA groups under $\lambda = 4.8$ conditions in NaOD/D₂O/CD₃OD at 80 °C. b) The possible chemical structure of NHA-based polymers for AEMs. ¹H NMR spectra monitored total degradation ratios of NHAs. The degradation ratio of Bis-DMP and Bis-ASU with diammonium groups is twice that of the other NHA groups containing a single ammonium group. Therefore, the actual half-life time of Bis-DMP and Bis-ASU can be predicted by multiplying the first half-life by 2.

Currently, three types of AEMs have been mostly studied in AEMFCs: BTMA-based AEMs, HTMA-based AEMs, and DMP-based AEMs.^[1,4-9,12,30-32] Some of them displayed excellent AEMFC performance with power density over 1.5 W cm⁻² in H₂-O₂, such as BTMA-based HDPE,^[9,31] HTMA-based polynorbornene,^[8] HTMA-based polyphenylene,^[32] and poly(aryl piperidinium)s (PAPs).^[1,7,12,14] Some additional information can be obtained from this research. (1) BTMA and BMP exhibit acceptable over 1,100 h under $\lambda = 10.0$ conditions, and BMP possesses slightly higher alkaline stability than BTMA, implying that replacing BTMA into BMP will be helpful for benzyl ammonium-based AEMs (such as for the development of DMP-based HDPE). Note that Biancolli et al.^[40] has previously demonstrated BMPbased poly(ethylene-co-tetrafluoroethylene) (ETFE) ionomers showed higher alkaline stability and AEMFC durability than BTMA-based ETFE. (2) HTMA groups display comparable (2,046 h) to Bis-TP-DMP (2,078 h) groups under $\lambda =$ 4.8 conditions. HTMA shows higher over 6,000 h under $\lambda =$ 7.0 and 10.0 conditions, indicating that state-of-the-art ASU or substituted ASUs. All these phenomena can be explained by their different degradation pathways determined by ¹H NMR results and DFT calculation, as discussed below.

DFT was used to calculate the Gibbs free energy (ΔG , so called energy barrier) of degradation in DMP, ASU, diphenylsubstituted DMP (DP-DMP), and diphenyl-substituted ASU (DP-ASU) undergoing potentially different degradation pathways, as shown in Figure 4.^[41,42] Calculated results elucidate that the free energy of $S_N 2$ (ΔG_{SN2}) is lower than that of E2 (ΔG_{E2}) in DMP or ASU series under alkaline conditions, implying that the $S_{\ensuremath{N}}2$ is the dominant degradation pathway in these NHA groups, which is well matching with our ¹H NMR results. Notice that DMP displays free energy values of $15.4 \text{ kcal mol}^{-1}$, $46.36 \text{ kcal mol}^{-1}$, and 48.88 kcal mol^{-1} for S_N2 (1), S_N2 (2), and E2, respectively. Moreover, DP-DMP shows lower free energy in all degradation pathways ($S_N 2$ (1): 15.23 kcal mol⁻¹, $S_N 2$ (2): 22.44 kcal mol⁻¹, E2: 35.54 kcalmol⁻¹) compared to DMP, particularly in $S_N 2$ (2) and E2, meaning that electron-withdrawing substituents in

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HTMA and DMP-based AEMs are both promising for durable AEMFC applications. (3) DM-IQ and IS-ASU with quinoline structure possess poor alkaline stability; thus, these structures may not be a rational design for AEMs.

Degradation Mechanism of NHA Groups and NHA-Based AEMs

Several interesting findings have been noticed in this study. (1) Based on ¹H NMR investigation and analysis, we found that the $S_N 2$ reaction, instead of the ring-opening E2 reaction, dominates the degradation pathway of most NHA groups in NaOD/D₂O/ CD₃OD under different λ conditions, as shown in Figures 3a and 3b using B-DMP and B-ASU as examples. (2) Under lower λ conditions (4.8 or 7.0), ASU and substituted ASU groups exhibited higher alkaline stability than DMP or substituted DMPs. However, under higher λ conditions $(\lambda = 10.0)$, DMP and substituted DMPs display comparable alkaline stability to







Figure 2. The of different QA groups under $\lambda = 7.0$ and 10.0 conditions in NaOD/D₂O/CD₃OH at 80°C. ¹H NMR spectra monitored total degradation ratios of NHA groups. The degradation ratios of Bis-DMP and Bis-ASU with diammonium groups are twice that of the other NHA groups with a single ammonium group. Therefore, the actual of Bis-DMP and Bis-ASU can be predicted by multiplying the first half-life by 2.

the γ -position of NHA ring can accelerate the degradation reactions, particularly attacking the inside of the NHA ring. ASU and DP-ASU display similar degradation behavior to the DMP series. Note that ASU and DP-ASU show higher $\Delta G_{\rm SN2}$ (18.7 kcalmol⁻¹ and 17.8 kcalmol⁻¹) but lower $\Delta G_{\rm E2}$ (29.1 kcalmol⁻¹and 24.0 kcalmol⁻¹) compared to those of DMP and DP-DMP, implying that the ASU series possesses higher alkaline stability than the DMP series when $S_{\rm N2}$ is the dominant degradation pathway, while DMP may possess higher alkaline stability when E2 is the dominant degradation pathway.

According to the features of $S_N 2$ and E2 on QA groups, the $S_N 2$ reaction is triggered by the nucleophilic attack on α carbon (electron-poor) from the back side. The $S_N 2$ reaction rate is highly dependent on the concentration of nucleophilic reagent (electron-rich, OH⁻), followed by the reaction rate of primary carbon (1°C) > secondary carbon (2°C) > tertiary carbon (3°C) > quaternary carbon (4°C). On the other hand, E2 reaction starts from a β -hydrogen elimination through a trans and coplanar conformation, followed by the reaction rate: 1°C < 2°C < 3°C < 4°C. Note that ASU contains four 2° α -carbons in the spiro ring, whereas DMP possesses two 1° α carbons outside of the ring and two 2° α-carbons in the ring. Naturally, two 1° α-carbons outside of the DMP ring are more sensitive to S_N^2 degradation than 2° α -carbons, followed by $S_N 2$ (1) degradation pathway. Therefore, the ASU series reasonably possesses higher alkaline stability than the DMP series when S_N2 reaction is the dominant degradation pathway. However, the half-life time gap between ASU and DMP series becomes weakened under high λ values (or low OH⁻ concentration) because the S_N2 reaction rate decreases significantly at low OH- concentration according to the feature of S_N2 reaction.^[23,25] On the other hand, ASU series contains eight β -hydrogens, while the DMP series only contains four β -hydrogens, meaning that ASU series are more sensitive to E2. In other words, the alkaline stability of ASU and DMP series is not always the same, which is determined by their degradation pathways. Moreover, the reversibility of these degradation reactions was calculated^[41,42] in Table S1 based on DMP and ASU groups. The results show that the rate constant of reverse degradations is much slower than that of forward degradations, suggesting



Figure 3. a) Typical ¹H NMR spectra and of B-DMP in NaOD/D₂O/CD₃OH under $\lambda = 4.8$ conditions at 80°C. b) Typical ¹H NMR spectra and of B-ASU in NaOD/D₂O/CD₃OH under $\lambda = 4.8$ conditions at 80°C. The was estimated by exponential fitting via Origin software.



Figure 4. DFT calculation of a) DMP and DP-DMP and b) ASU and DP-ASU in different degradation pathways.

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that the effect of reverse degradation reactions on the alkaline stability of NHA groups can be neglected.

Interestingly, in the case of α -multi-substituted HMP, HMP groups contain two 4° α -carbons in the NHA ring; thus S_N2 reaction is significantly suppressed. However, monomolecular S_N1 reaction is aroused since the rate-determining step of the S_N1 reaction is the formation of carbocation (C⁺) intermediate. In addition, based on the features of the S_N1 reaction, the reaction rate of S_N1 is not related to the concentration of nucleophilic reagent (OH⁻), but strongly related with the stability of C⁺ intermediate. Under high λ value (or low OH⁻ concentration), there are more free water molecules, which can contribute to stabilizing C⁺ intermediates.^[23,25] Therefore, HMP groups exhibit depressed alkaline stability or when the λ value increases (λ = 4.8, 1,570 h; λ = 7.0, 440 h; λ = 10.0, 243 h), which is totally opposite to other NHA groups.

Degradation behavior in c-PAP AEMs: Notably, c-PAP AEMs mainly suffered from ring-opening $E2^{[1,7]}$ reaction, instead of S_N2 reaction, as shown in Figures S83 and S84. The of poly(diphenyl-co-terphenyl piperidinium) (PDTP) AEMs can be predicated under different λ values, as shown in Figure 5 a. Compared to the of Bis-TP-DMP (2,078 h, $\lambda = 4.8$), the alkaline stability of PDTP AEMs (<1,100 h, $\lambda =$

4.8) is much lower than that of phenyl-substituted DMPs. Recent discoveries^[7,35-38] found that DMP-based PAP AEMs possessed higher alkaline stability than ASU-based PAP AEMs, and E2 was always the dominant degradation pathway in PAP AEMs. Certainly, the alkaline stability behavior of NHA-based AEMs does not match well with that of NHAs due to different degradation pathways. The aforementioned DFT calculation in Figure 4 also indicates that ΔG_{F2} and $\Delta G_{\rm SN2}$ can be significantly influenced by substituents. In addition, Marino et al.^[23] pointed out that the balance between ring strain and transition state energy of the NHA ring may determine the degradation pathways. Based on the DFT calculation presented in Figure S85, bond angles near central γ -C (i.e., β - γ - β -Cs) of DP-DMP (105.152°) and DP-ASU (106.077°) are lower than those of DMP (110.47°) and ASU (110.821°), and the ring strain and total strain energy of diphenyl-substituted DMP or ASU compounds also has increased. These calculations give us a possible explanation that the decreased transition state energy and increased ring strain of NHA groups in PAP AEMs upon substitution, may contribute to accelerating E2 degradation.

Therefore, the alkaline stability of NHAs and NHA-based AEMs is not always stereotyped, which is related to specific degradation pathways. These fundamental discoveries and



Figure 5. a) The relationship between half-life of c-PAP AEMs and λ values. The Figure was plotted based on ¹H NMR spectra of c-PAP AEMs after alkaline treatment in NaOH/H₂O at 80 °C under different λ (55.5, 11.1, 5.5) conditions. b) *In-situ* durability of c-PAP-based AEMFCs under different current densities: H₂-O₂ 80 °C, 75/100% anode (A)/cathode (C) RH, 200/200 mLmin⁻¹ A/C flow rate, 0.6/0.6 bar A/C backpressure, Pt-Ru/C anode and Pt/C cathode along with 0.39 mg cm⁻² catalyst loading. c) and d) ¹H NMR spectra of CCMs after in situ durability testing. [D₆]DMSO was used as solvent, and 10% TFA was added to NMR sample to eliminate the effect of H₂O.

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understandings of DMP and ASU effectively answer the current argument associated with their alkaline stability, guiding the rational design of highly stable AEMs.

Relationship Between λ , Ex-Situ Durability, and In-Situ Durability

Meanwhile, insight into in situ durability of AEMs is still lacking to date. Determining the realistic alkaline conditions for operating AEMFCs is crucial for the development of durable AEMFCs. Previous research^[34] simulated the λ values of AEMFCs under different current densities (such as 0.5 A cm⁻², 1 A cm⁻², 2 A cm⁻² may be equal to the λ values of 7, 4, 2, respectively), while recent work hinted that these predictions may not well match with current AEMFCs. For instance, BTMA-based HDPE AEMs can be operated stably under 0.6 A cm⁻² at 60°C for 1,000 h.^[9] That is, the real alkalinity of AEMFCs and the degradation pathway of QA groups during in situ durability testing should be well verified by experiment.

Recently, we developed a series of high-performance c- $\ensuremath{\mathsf{PAPs}}^{[1,7]}$ for AEMs and AEIs, which can be operated under high current density in AEMFCs. Therefore, the short-term durability of c-PAP-based AEMFCs under super high current densities $(1 \text{ A cm}^{-2}, 1.5 \text{ A cm}^{-2}, 2 \text{ A cm}^{-2}, 3 \text{ A cm}^{-2})$ at 80 °C was tested in H₂-O₂, and the cells were continuously measured for ≈ 30 h, ≈ 10 h, ≈ 8 h, and ≈ 2 h, respectively. As shown in Figure 5b, the cell voltage was kept stable at a current density of 1 Acm⁻² for the initial 10 hours, whereas the voltage dropped quickly under high current densities, particularly in 3 A cm⁻². To confirm the chemical stability of AEMs and AEIs, all catalyst-coated membranes (CCMs) were detached from the cells and redissolved in [D₆]DMSO for ¹H NMR analysis (Figure 5 c). ¹H NMR spectra of CCMs indicate that no degradation signal can be detected under 1 A cm⁻², 1.5 A cm⁻², and 2 A cm⁻² current densities for short time, meaning that the alkaline environment of AEMFCs is not as harsh as previously predicted. Therefore, long-term durability of c-PAP-based AEMFCs was conducted under 1 A cm⁻² current density at 60°C for 1,000 h (Figure 5 d). Interestingly, three typical -C=C- signals (4.97 ppm, 5.35 ppm, 6.35 ppm) derived from Hofmann degradation reaction were detected under 1 A cm^{-2} after 1,000 h ($\approx 12\%$ piperidinium group degradation in AEMs), suggesting that the Hofmann degradation is the dominant pathway of NHA-based AEMs and AEIs during in situ durability testing. The detailed information of long-term durability under 1 A cm⁻² current density will be presented in our separate publication. These discoveries hint that S_N2-dominated AEMs or ionomers may have advantages in the durability of AEMFCs, which may answer the reason why the aforementioned BTMA-HDPE^[9] can be operated stably under 0.6 $A cm^{-2}$ for 1,000 h.

Conclusion

In summary, we systematically investigated the alkaline stability of 24 representative NHAs at different λ values (λ =

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4.8, 7.0 and 10.0) in NaOD/D2O/CD3OD at 80°C. (1) NHA groups with electron-donating substituents exhibited outstanding alkaline stability among current cationic groups, whereas electron-withdrawing substituents displayed a detrimental effect on the stability of NHA groups. (2) ysubstituted NHAs possess much higher alkaline stability than α - or β -substituted NHAs. (3) DFT calculation and experimental results demonstrated that different degradation pathways determine the alkaline stability of NHAs or NHA-based AEMs. The S_N^2 reaction is the dominant degradation pathway in NHAs, while E2 reaction is the primary degradation pathway for PAP-based AEMs. In-situ durability of c-PAP-based AEMFCs suggests that E2 is the dominant degradation pathway of aryl ether-free NHA-based AEMs under 1 A cm⁻² current density at 60 °C for 1,000 h. We believe that the present work provides insights into current NHAs and NHA-based AEMs and presents a clear guideline for design of highly stable AEM or ionomer, contributing to promoting the development of durable AEMFCs.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: anion-exchange-membrane fuel cells · ex-situ durability · in-situ durability · N-heterocyclic ammonium

- [1] N. J. Chen, C. Hu, H. H. Wang, S. P. Kim, H. M. Kim, W. H. Lee, J. Y. Bae, J. H. Park, Y. M. Lee, *Angew. Chem. Int. Ed.* **2021**, 60, 7710-7718.
- [2] W. E. Mustain, M. Chatenet, M. Page, Y. S. Kim, *Energy Environ. Sci.* 2020, 13, 2805–2838.
- [3] N. J. Chen, Y. M. Lee, Prog. Polym. Sci. 2021, 113, 101345.
- [4] D. Li, E. J. Park, W. Zhu, Q. Shi, Y. Zhou, H. Tian, Y. Lin, A. Serov, B. Zulevi, E. D. Baca, C. Fujimoto, H. T. Chung, Y. S. Kim, *Nat. Energy* **2020**, *5*, 378–385.
- [5] P. Chen, X. Hu, Adv. Energy Mater. 2020, 10, 2002285.

- [6] S. T. Thompson, D. Peterson, D. Ho, D. Papageorgopoulos, J. Electrochem. Soc. 2020, 167, 084514.
- [7] N. J. Chen, H. H. Wang, S. P. Kim, H. M. Kim, W. H. Lee, C. Hu, J. Y. Bae, E. S. Sim, Y.-C. Chung, J.-H. Jang, S. J. Yoo, Y. B. Zhuang, Y. M. Lee, *Nat. Commun.* **2021**, *12*, 2367.
- [8] N. Ul Hassan, M. Mandal, G. Huang, H. A. Firouzjaie, P. A. Kohl, W. E. Mustain, *Adv. Energy Mater.* **2020**, *10*, 2001986.
- [9] X. Peng, D. Kulkarni, Y. Huang, T. J. Omasta, B. Ng, Y. Zheng, L. Wang, J. M. LaManna, D. S. Hussey, J. R. Varcoe, I. V. Zenyuk, W. E. Mustain, *Nat. Commun.* **2020**, *11*, 3561.
- [10] C. H. Park, S. Y. Lee, D. S. Hwang, D. W. Shin, D. H. Cho, K. H. Lee, T. W. Kim, T. W. Kim, M. Lee, D. S. Kim, C. M. Doherty, A. W. Thornton, A. J. Hill, M. D. Guiver, Y. M. Lee, *Nature* **2016**, *532*, 480–483.
- [11] D. W. Shin, M. D. Guiver, Y. M. Lee, Chem. Rev. 2017, 117, 4759–4805.
- [12] J. Wang, Y. Zhao, B. P. Setzler, S. Rojas-Carbonell, C. Ben Yehuda, A. Amel, M. Page, L. Wang, K. Hu, L. Shi, S. Gottesfeld, B. Xu, Y. Yan, *Nat. Energy* **2019**, *4*, 392–398.
- [13] J. S. Olsson, T. H. Pham, P. Jannasch, Adv. Funct. Mater. 2018, 28, 1702758.
- [14] H. Peng, Q. Li, M. Hu, L. Xiao, J. Lu, L. Zhuang, J. Power Sources 2018, 390, 165–167.
- [15] N. J. Chen, C. Long, Y. Li, C. Lu, H. Zhu, ACS Appl. Mater. Interfaces 2018, 10, 15720-15732.
- [16] Z. Yang, R. Guo, R. Malpass-Evans, M. Carta, N. B. McKeown, M. D. Guiver, L. Wu, T. Xu, Angew. Chem. Int. Ed. 2016, 55, 11499–11502; Angew. Chem. 2016, 128, 11671–11674.
- [17] X. Liang, M. A. Shehzad, Y. Zhu, L. Wang, X. Ge, J. Zhang, Z. Yang, L. Wu, J. R. Varcoe, T. Xu, *Chem. Mater.* **2019**, *31*, 7812– 7820.
- [18] J. Fan, S. Willdorf-Cohen, E. M. Schibli, Z. Paula, W. Li, T. J. G. Skalski, A. T. Sergeenko, A. Hohenadel, B. J. Frisken, E. Magliocca, W. E. Mustain, C. E. Diesendruck, D. R. Dekel, S. Holdcroft, *Nat. Commun.* **2019**, *10*, 2306.
- [19] J. Fan, A. G. Wright, B. Britton, T. Weissbach, T. J. G. Skalski, J. Ward, T. J. Peckham, S. Holdcroft, ACS Macro Lett. 2017, 6, 1089–1093.
- [20] S. Gu, R. Cai, T. Luo, Z. Chen, M. Sun, Y. Liu, G. He, Y. Yan, Angew. Chem. Int. Ed. 2009, 48, 6499–6502; Angew. Chem. 2009, 121, 6621–6624.
- [21] N. J. Chen, H. Zhu, Y. Chu, R. Li, Y. Liu, F. Wang, *Polym. Chem.* 2017, 8, 1381–1392.
- [22] T. Zhu, S. Xu, A. Rahman, E. Dogdibegovic, P. Yang, P. Pageni, M. P. Kabir, X. D. Zhou, C. Tang, *Angew. Chem. Int. Ed.* **2018**, 57, 2388–2392; *Angew. Chem.* **2018**, *130*, 2412–2416.
- [23] M. G. Marino, K. D. Kreuer, ChemSusChem 2015, 8, 513-523.
- [24] B. Zhang, R. B. Kaspar, S. Gu, J. Wang, Z. Zhuang, Y. Yan, *ChemSusChem* 2016, 9, 2374–2379.

- [25] K. M. Hugar, H. A. Kostalik IV, G. W. Coates, J. Am. Chem. Soc. 2015, 137, 8730–8737.
- [26] W. You, E. Padgett, S. N. MacMillan, D. A. Muller, G. W. Coates, Proc. Natl. Acad. Sci. USA 2019, 116, 9729–9734.
- [27] W. You, K. M. Hugar, G. W. Coates, *Macromolecules* 2018, 51, 3212–3218.
- [28] A. G. Wright, J. Fan, B. Britton, T. Weissbach, H.-F. Lee, E. A. Kitching, T. J. Peckham, S. Holdcroft, *Energy Environ. Sci.* 2016, 9, 2130–2142.
- [29] W. You, K. J. T. Noonan, G. W. Coates, Prog. Polym. Sci. 2020, 100, 101177.
- [30] L. Wang, J. J. Brink, Y. Liu, A. M. Herring, J. Ponce-González, D. K. Whelligan, J. R. Varcoe, *Energy Environ. Sci.* 2017, 10, 2154–2167.
- [31] L. Wang, X. Peng, W. E. Mustain, J. R. Varcoe, *Energy Environ. Sci.* 2019, *12*, 1575–1579.
- [32] S. Maurya, S. Noh, I. Matanovic, E. J. Park, C. Narvaez Villarrubia, U. Martinez, J. Han, C. Bae, Y. S. Kim, *Energy Environ. Sci.* 2018, *11*, 3283–3291.
- [33] W.-H. Lee, Y. S. Kim, C. Bae, ACS Macro Lett. 2015, 4, 814-818.
- [34] D. R. Dekel, S. Willdorf, U. Ash, M. Amar, S. Pusara, S. Dhara, S. Srebnik, C. E. Diesendruck, *J. Power Sources* 2018, 375, 351– 360.
- [35] T. Zhu, Y. Sha, H. A. Firouzjaie, X. Peng, Y. Cha, D. M. M. M. Dissanayake, M. D. Smith, A. K. Vannucci, W. E. Mustain, C. Tang, J. Am. Chem. Soc. 2020, 142, 1083–1089.
- [36] T. H. Pham, J. S. Olsson, P. Jannasch, J. Mater. Chem. A 2018, 6, 16537–16547.
- [37] T. H. Pham, J. S. Olsson, P. Jannasch, J. Mater. Chem. A 2019, 7, 15895–15906.
- [38] T. H. Pham, J. S. Olsson, P. Jannasch, J. Am. Chem. Soc. 2017, 139, 2888–2891.
- [39] J. S. Olsson, T. H. Pham, P. Jannasch, *Macromolecules* 2020, 53, 4722–4732.
- [40] A. L. Gonçalves Biancolli, D. Herranz, L. Wang, G. Stehlíková, R. Bance-Soualhi, J. Ponce-González, P. Ocón, E. A. Ticianelli, D. K. Whelligan, J. R. Varcoe, E. I. Santiago, *J. Mater. Chem. A* 2018, 6, 24330–24341.
- [41] L. Zhao, H. J. Liu, Y. Liu, X. Han, J. Xu, W. Xing, W. Guo, ACS Appl. Mater. Interfaces 2020, 12, 40248–40260.
- [42] H. J. Liu, L. Zhao, Y. H. Liu, J. Xu, H. Zhu, W. Guo, *Catal. Sci. Technol.* 2019, 9, 5301–5314.

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