

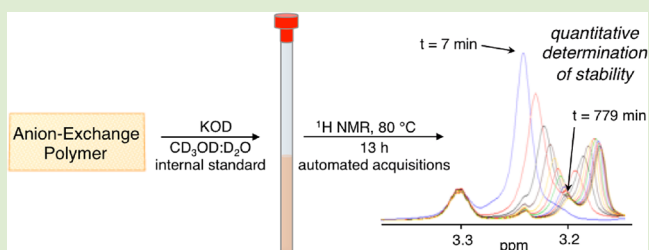
Quantitative ^1H NMR Analysis of Chemical Stabilities in Anion-Exchange Membranes

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Supporting Information

ABSTRACT: We compared the alkaline stability of three classes of anion exchange membranes that are leading candidates for applications in platinum-free fuel cells. A methodology is presented for the study of chemical stability of anion-exchange polymers in alkaline media that provides clear and quantitative ^1H NMR spectroscopic data of dissolved polymers containing benzyltrimethylammonium functionalities. Recent studies have investigated the stabilities of benzimidazolium- and alkylimidazolium-bearing polymers using periodic ^1H NMR sampling. These studies included varying alkaline concentrations, external heating sources, and excessive processing and contained no internal standard for absolute measurements. Key aspects of our time-resolved ^1H NMR method include in situ heating and sampling *within the spectrometer*, fixed stoichiometric relationships between the benzyltrimethylammonium functionalities of each polymer and potassium deuteroxide (KOD), and the incorporation of an internal standard for the absolute measurement of the polymer degradation. In addition, our method permits the identification of the degradation products to find the underlying cause of chemical lability. Our results demonstrate that a styrene-based polymer containing benzyltrimethylammonium functional groups is remarkably stable when exposed to 20 equivalents per cation of KOD at 80 °C with a half-life ($t_{1/2}$) of 231 h. Under these standard conditions, functionalized poly(phenylene oxide) and poly(arylene ether sulfone) copolymers, both bearing benzyltrimethylammonium functionalities were found to degrade with a half-lives of 57.8 and 2.7 h, respectively.



Anion-exchange membranes (AEMs) have attracted interest for their operation in platinum-free fuel cells¹ and electrolyzers² that feature carbon-free supports,³ increased tolerances to CO₂ impurities in gaseous feeds,⁴ and conductivities that rival proton exchange membranes.⁵ However, the use of AEMs in a wide range of devices has been limited due to the polymers' poor stability in the highly alkaline environment required for fuel cells that necessitates generation of hydroxide anions and transport through the solid polymer membrane. Recent studies have determined the chemical stabilities of AEMs using measurements of ion-exchange capacities,⁶ ionic conductivities,⁷ and FT-Raman⁸ and ^1H NMR spectroscopy⁹ that sought to address the change in chemical composition of materials during degradation processes. FT-Raman studies of AEM degradation are typically conducted on films with varying levels of humidity but only provide relative data of chemical stability due to varying absorption coefficients of specific functional groups among different polymers. Current ^1H NMR methods investigate benzimidazolium-^{9b} and imidazolium^{9a}-bearing polymers but lack an internal standard for absolute measurements,¹⁰ use external heating sources,⁹ involve multiple steps⁹ (i.e., exposure to alkali, evaporation of the solvent, and characterization), and generally ignore the stoichiometric relationship between the ion-conducting functional group and the concentration of the alkali. These variations in methods and other factors in measuring degradation, as meticulously

discussed by Varcoe,⁸ in assessing the stability of AEMs have made it difficult for the community to come to a consensus on the most promising directions for highly stable, highly conductive AEMs.

To date, few researchers^{9a,b} have employed a standardized methodology to determine the rate of degradation in AEMs that include a coherent *stoichiometric relationship* between the concentration of alkali and the concentration of ion-conducting functional groups within the polymer. The established mechanisms of degradation in quaternary ammonium (QA)-based AEMs occur as a result of hydrolysis in aqueous alkaline solutions.¹¹ We postulate that fixing this *stoichiometric relationship* is essential to accurately measure and describe the stabilities of these polymers—thereby establishing a precedent for describing the stability of QA AEMs in the field.

This Letter describes a simple methodology and provides clear ^1H NMR spectroscopic data to quantitatively study the stability and degradation pathways of *dissolved* AEMs under standardized conditions. We chose four benzyltrimethylammonium-functionalized compounds consisting of a model small molecule, pMeBTMA, and three polymers, QA-PAES, QA-

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PPO, and QA-PS (Figure 1). These polymers represent three major AEM candidates based on widely accessible polymer

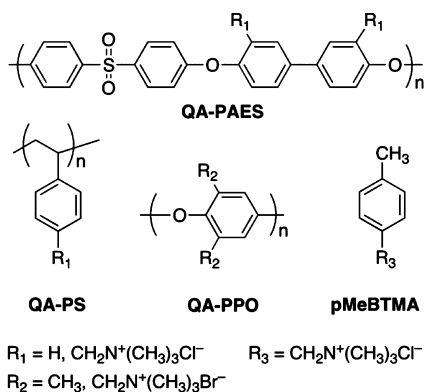


Figure 1. Chemical structures of QA-based compounds studied.

backbones. This new methodology should guide others to easily and accurately determine the stability of dissolved AEMs for meaningful comparisons.

We studied ^1H NMR degradation of AEMs under alkaline conditions. Since quaternary-ammonium functionalities are susceptible to degradation under alkaline conditions, we sought to investigate the stabilities of AEMs with potassium deuteroxide (KOD) at elevated temperatures to provide an accelerated assessment of the stability of these molecules. One initial challenge was finding a suitable deuterated solvent system to dissolve the selected QA AEM, the alkali (KOD), an

internal standard, and the resulting products of degradation. After considering a number of single- and mixed-solvent systems, we determined that a 3:1 $\text{CD}_3\text{OD}-\text{D}_2\text{O}$ mixed-solvent system was suitable to solvate the components throughout the duration of the experiment. The samples consisted of the selected AEM (30 mM)¹² in 3:1 $\text{CD}_3\text{OD}-\text{D}_2\text{O}$ with an excess of KOD (0.6 M, 20 equiv) and 1,4-dioxane¹³ (internal standard). The resulting sample solutions were transferred to a standard NMR tube and heated in situ at 80 °C within the spectrometer. Under these conditions, quaternary ammonium decomposition was measured by the deconvoluted peak area of the methyl groups of the QA (i.e., $\text{N}^+(\text{CH}_3)_3$) relative to 1,4-dioxane in the ^1H NMR spectrum. Figure 2 reveals a stacked overlay of QA-PAES spectra taken over 779 min (12.9 h) in ~64 min intervals. The signal corresponding to the methyl groups of the benzyltrimethylammonium and the covalently bonded benzylic methylene (i.e., CH_2) decreases in agreement against the fixed internal standard concentration. Additionally, the ^1H NMR spectrum revealed two products of degradation: a benzylmethyl ether (i.e., CH_2OCH_3 ; 3.17 ppm, 3, see Supporting Information) and a benzyltrimethylammonium (i.e., $\text{N}^+(\text{CH}_3)_3$; 3.29 ppm, 4, see Supporting Information). We hypothesized the benzylmethyl ether (3) and benzyltrimethylammonium (4) functionalities arose from the dealylation of a benzyltrimethylammonium moiety followed by the substitution of methoxide (i.e., CH_3O^-) generated at a separate QA site. These results are consistent with the reported pathways of degradation for QA-based AEMs.¹¹

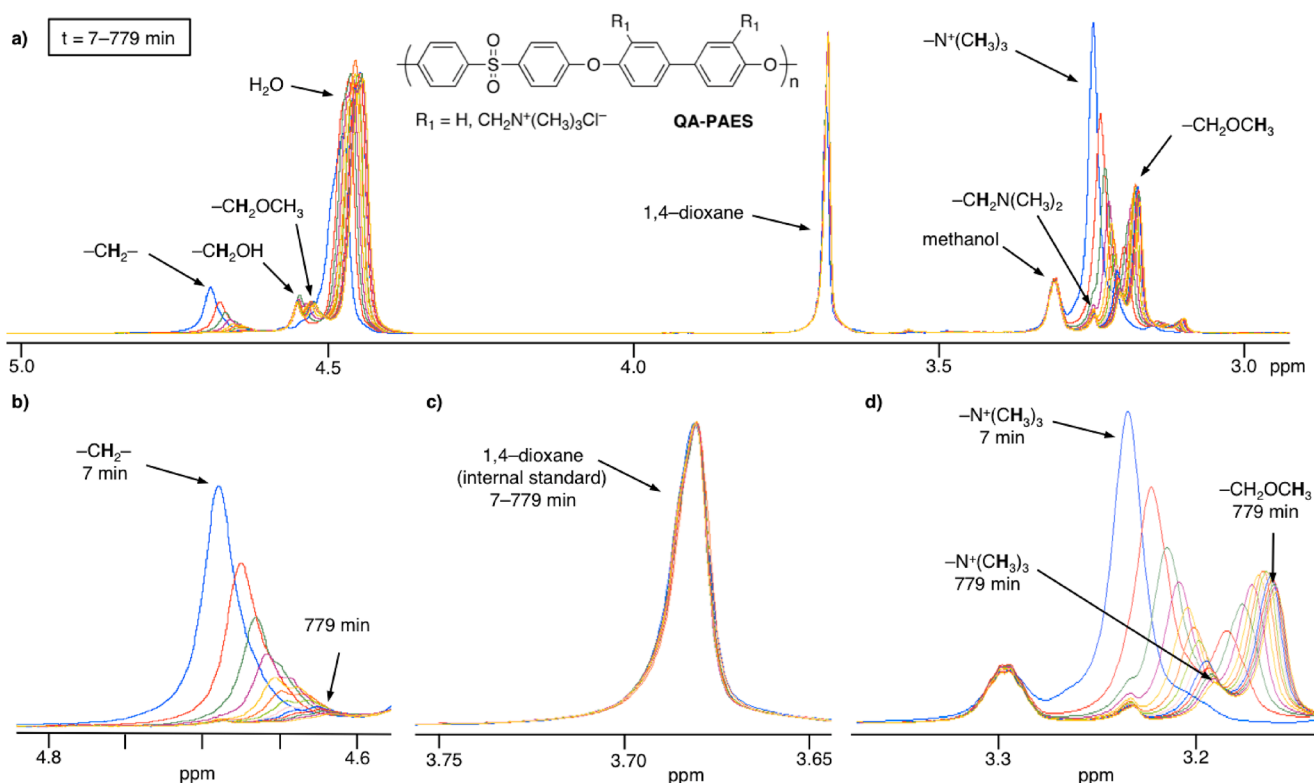


Figure 2. Stacked overlay of ^1H NMR spectra of QA-PAES in $\text{CD}_3\text{OD}-\text{D}_2\text{O}$ (3:1), 1,4-dioxane (internal standard), and KOD (20 equiv), from 7 to 779 min in ~64 min intervals at 80 °C: (a) overlay of the aliphatic region, (b) overlay of benzyl methylene decaying, (c) overlay of 1,4-dioxane (internal standard), (d) overlay showing the decay of QA over the course of the study and the evolution of a benzylmethyl ether product (i.e., CH_2OCH_3). Note: ^1H NMR signal movement in aqueous solutions is a commonly observed phenomenon.¹⁴

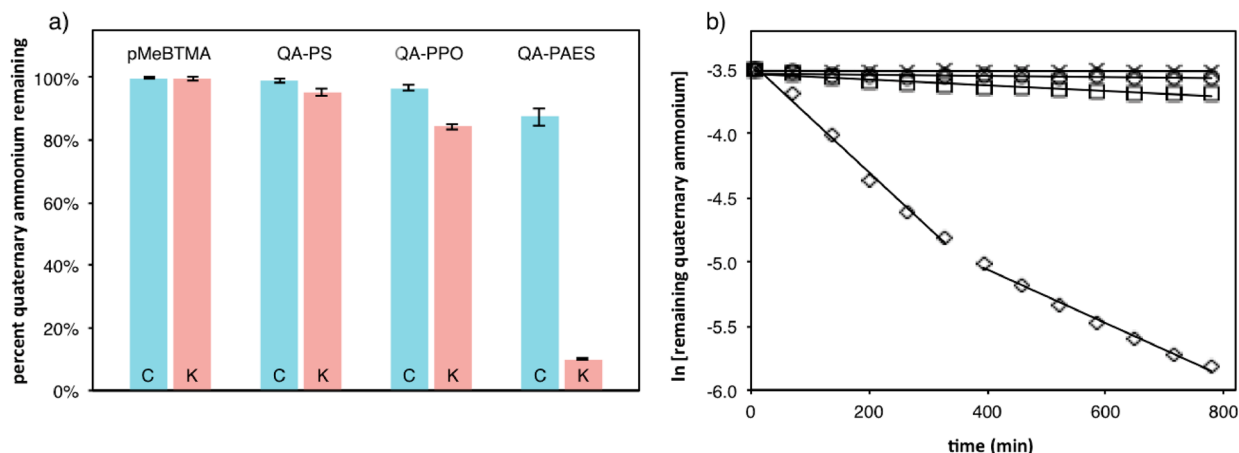


Figure 3. Rates of degradation of selected QA-AEMs: (a) Measurements of the absolute degradation of the indicated QA-AEM in the presence of 20 equiv of KOD (K) and in the absence of KOD (C) after 779 min of exposure to a 3:1 $\text{CD}_3\text{OD}-\text{D}_2\text{O}$ at 80 °C. (b) Linear plot showing rates of degradation of the remaining QA concentration of each polymer in 3:1 $\text{CD}_3\text{OD}-\text{D}_2\text{O}$ with the addition of 20 equiv of KOD at 80 °C over 779 min: \times = pMeBTMA; \circ = QA-PS; \square = QA-PPO; \diamond = QA-PAES. The data were normalized to the concentration of the internal standard. The solid lines indicate the linear regression of each data set used to determine a rate constant. The experiments were performed in triplicate, and the error bars reflect the standard deviation from the average values.

We also studied quantitative analysis of QA-AEM degradation by ^1H NMR. The stabilities of 30 mM solutions of QA-PAES, QA-PPO, QA-PS, and pMeBTMA dissolved in 3:1 $\text{CD}_3\text{OD}-\text{D}_2\text{O}$ at 80 °C in the presence of 20 equiv of KOD (0.6 M) were evaluated in triplicate. Hydrolysis of QA head groups is accelerated under basic conditions but is possible in the absence of highly alkaline conditions; thus, a control experiment under the exact same conditions, but in the absence of KOD, was performed. In all cases with KOD, we observed the decomposition of the polymers by solely monitoring the disappearance of the QA (i.e., $\text{N}^+(\text{CH}_3)_3$) peak in the ^1H NMR spectrum relative to a fixed internal standard, 1,4-dioxane (Figure 3a). Under these conditions, pMeBTMA showed virtually no signs of degradation in the presence of KOD (i.e., $99.5\% \pm 0.9\%$ remaining QA) with a negligible rate of hydrolysis in the absence of KOD (i.e., $99.8\% \pm 0.6\%$ remaining QA) after 779 min, as shown in Figure 3a. Similarly, QA-PS showed comparable stability to pMeBTMA (i.e., $95.2\% \pm 1.1\%$ remaining QA) in the presence of KOD and had minimal hydrolysis (i.e., $98.0\% \pm 0.8\%$ remaining QA) in the absence of KOD. The slightly poorer stability of QA-PS compared to pMeBTMA could be due to better solvation of the small molecule which would bolster its stability. QA-PPO showed considerable hydrolysis with only $84.2\% \pm 0.9\%$ of the QA remaining after 779 min in the presence of KOD and $96.6 \pm 0.9\%$ of the QA remaining in the absence of KOD.

Finally, QA-PAES showed significant degradation in the presence of KOD with only $9.9\% \pm 0.3\%$ of the QA remaining after 779 min and equally significant hydrolysis in the absence of KOD with only $87.3\% \pm 2.8\%$ of the QA remaining.

The rates of degradation were determined from the linear regression plot of the natural log of polymer concentration versus time using a pseudo-first-order approximation (Figure 3b). The concentration of base (i.e., 20 equiv) with respect to the quaternary-ammonium group on the degraded species is in significant excess to assume a constant base concentration and pseudo-first-order kinetics. Table 1 summarizes the ^1H NMR-determined experimental kinetic rates of degradation for our selected QA-AEMs in 3:1 $\text{CD}_3\text{OD}-\text{D}_2\text{O}$ with 20 equiv of KOD at 80 °C. pMeBTMA, QA-PS, and QA-PPO, show the

Table 1. ^1H NMR Experimental Rates and Half-Lives of Selected QA AEMs in 3:1 $\text{CD}_3\text{OD}-\text{D}_2\text{O}$ with 20 equiv of KOD at 80 °C

	K ($\text{M}^{-1} \text{s}^{-1}$) 10^{-3}	$t_{1/2}$ (h)	QA remaining at $t_{779 \text{ min}}$ (%)
QA-PAES:			
primary	4.3	2.7	—
secondary	2.1	5.5	9.9 ± 0.1
QA-PPO	0.2	57.8	84.2 ± 0.9
QA-PS	0.05	231	95.2 ± 1.1
pMeBTMA	0.004	2887	99.5 ± 0.6

greatest stability with half-lives of 2887, 231, and 57.8 h, respectively.

The small molecule, pMeBTMA, and QA-PS showed considerable stability with pMeBTMA displaying higher half-life stability by an order of magnitude. However, styrene-based ion-containing membranes generally have poor mechanical properties, especially when hydrated. Thus, strategies to reinforce the mechanical properties of functionalized styrene-based AEMs are required.¹⁵

The data for QA-PAES did not fit a single constant first-order rate expression. We found that the initial rate of degradation (primary) was significantly greater than the rate after 328 min (secondary). Further analysis revealed that assigning two separate first-order rates resulted in agreement with the primary half-life of 2.7 h and the secondary half-life of 5.5 h. This change in the rate of degradation could be due to functionalization distribution or a change in solubility (see Supporting Information for a detailed discussion).

Comparing the kinetic rates of degradation and half-lives of the samples, we have concluded the stability of the sulfone-containing QA-PAES was greatly reduced compared to its poly(phenylene oxide) analogue, QA-PPO. To explain the differences in the stability of QA-PAES, we reason that the electron-withdrawing sulfone exerts a long-range inductive effect, thereby reducing the electron density of the benzyl carbon. It has been previously noted that poly(sulfone) backbones are not stable under basic conditions,¹⁶ but in the present study we directly assess the stability of the quaternary ammonium cation and not scission of the backbone chain.

Thus, there appears to be an influence by the backbone type on the stability of the quaternary ammonium group.

In QA-PAES, the inductive effect of the sulfone moiety may increase the electrophilic character of the benzylic methylene, increasing its susceptibility to nucleophilic attack.^{11c} This increased electrophilicity of the benzylic methylene protons in the QA-PAES is manifested in the higher chemical shift of this moiety compared to the other compounds studied. Additional information to explain the reduced stability of QA-PAES using steric arguments with molecular modeling of a small molecule analogue is offered in the Supporting Information.

This Letter demonstrates a spectroscopic method to systematically measure AEM stability under controlled and reproducible test conditions, thereby consistently affording knowledge of the cationic quaternary-ammonium stabilities. Our results indicate the *para*-substituted styrenic AEM, QA-PS, offers a significant increase in stability over quaternary-ammonium functionalized poly(phenylene oxide), QA-PPO, and the *ortho*-substituted poly(arylene ether sulfone), QA-PAES. The QA-PAES showed surprisingly low stability and calls into question the suitability of benzyltrimethyl quaternary-ammonium cations on poly(sulfone) backbones for long-lived devices. The standardized approach presented here offers a powerful method to compare AEM stabilities and identify the products of degradation, while also identifying the underlying cause of degradation. Using this systematic investigation will help build a consistent and uniform database of knowledge that can be applied in the search for new, stable AEMs. While our study primarily focused on benzyltrimethylammonium groups, we envision our method could be extended to other AEMs that contain ionic groups such as imidazolium, guanidinium, and phosphonium moieties.

EXPERIMENTAL METHODS

General Procedure for Measuring the Rates of QA Degradation Using ¹H NMR.¹⁷ A 300 MHz spectrometer equipped with a variable-temperature probe was heated to 80 °C, programmed to acquire 32 scans for each sample with a relaxation time of 5 s, and programmed to acquire acquisitions at intervals of 3600 s (1 h). ¹H NMR spectra were acquired *exactly* 5 min after sample preparation. The time intervals reported indicate the average concentration of peak signals determined by using the median acquisition time for each spectrum. Peak area deconvolution of the ¹H NMR signals corresponding to the methyl groups of the quaternary ammonium within the polymer and the methylenes of 1,4-dioxane (internal standard) were used to calculate the percentage of quaternary ammonium remaining.

Example Procedure for Sample Preparation.¹⁷ To a QA-PAES sample (19.6 mg) was added CD₃OD (750 μL), and to the resulting suspension were sequentially added D₂O (178.8 μL) and a 1.8 M solution of 1,4-dioxane (internal standard) in D₂O (16.6 μL). The vial was capped and vortexed until the polymer was completely dissolved (~60 s). To the resulting solution was added a 40% wt/v solution of KOD in D₂O (57.6 μL), and the vial was recapped and briefly vortexed (~5 s). A portion (600 μL) of the solution was transferred into a standard 5 mm NMR tube. The tube was capped and sealed with PTFE tape and inserted into the heated spectrometer immediately after preparation.

ASSOCIATED CONTENT

Supporting Information

Experimental details of synthetic procedures, characterization data, degradation data, pictures of samples, reasoning for

kinetics, and modeling studies. 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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