In this work, we investigate the performance and degradation of polyphenylene oxide (PPO) based AEMs in a solid-alkaline water electrolyzer at 50°C using electrochemical testing and 1-D and 2-D NMR spectroscopy. The PPO AEMs were derivatized with trimethylamine (TMA) and quinuclidine (ABCO) to yield AEMs with TMA+ and ABCO− cations. The AEMs underwent chemical degradation during electrolysis. The cell voltage at 0.2 A/cm² for BrPPO-ABCO+ and BrPPO-TMA+ increased by 0.4 V and 0.2 V respectively after 5 hours of operation at 0.1 A/cm². Postmortem analysis of the membrane and AEM binder recovered from the electrodes using 1D and 2D NMR spectroscopy revealed degradation via the backbone hydrolysis mechanism. The degradation occurred preferentially in the vicinity of the oxygen evolution electrode. Backbone hydrolysis resulted in loss of AEM mechanical integrity as well as solubilization and loss of binder in the electrodes. Impedance spectroscopy revealed an increase both in the high frequency resistance (from 0.41 to 0.53 Ohm·cm⁻² for BrPPO-TMA+ and from 0.83 to 1.86 Ohm·cm⁻² for BrPPO-ABCO+) and in the charge transfer resistance (from 0.26 to 1.47 Ohm·cm⁻² for BrPPO-TMA+ and from 0.28 to 6.77 Ohm·cm⁻² for BrPPO-ABCO+) over the course of the experiment. Stability of Poly(2,6-dimethyl 1,4-phenylene)Oxide-Based Anion Exchange Membrane Separator and Solubilized Electrode Binder in Solid-State Alkaline Water Electrolyzers

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Hydrogen production using solid alkaline water electrolyzers has recently attracted much interest as an alternative to traditional (liquid electrolyte) alkaline water electrolyzers, proton exchange membrane (PEM) water electrolyzers, and solid oxide water electrolyzers. Solid alkaline electrolyzers provide an efficient, modular, and reliable method to produce hydrogen from water and renewable electricity sources, for energy storage and/or grid-scale load leveling during spikes in electricity production or periods of low demand. One advantage in contrast with PEM electrolyzers arises from the fact that the alkaline environment facilitates better oxygen evolution reaction (OER) kinetics and allows the use of non-platinum group catalysts for the OER, which in turn can reduce capital expenditure. This must of course be tempered with the fact that the hydrogen evolution reaction is quite sluggish in alkaline environments and, based on the current state-of-the-art, will likely require a PGM electrocatalyst. In a solid alkaline water electrolyzer, the anion exchange membrane (AEM) electrolyte provides separation between the positive and negative electrodes, precluding the use of corrosive liquid electrolytes (and accompanying shunt currents) while permitting operation at high differential pressures. The production of hydrogen at intermediate pressures (15–30 bar) while releasing oxygen at atmospheric pressure is highly desirable as it facilitates hydrogen storage and delivery to applications requiring pressurized hydrogen.

Electrolysis of water in alkaline conditions proceeds according to the half-cell reactions shown in Equations 1 and 2. The ideal solid alkaline water electrolyzer should operate with pure water, without the addition of salts or bases to the water (as conductivity enhancers) to ensure simple operation, minimal maintenance and to produce ultra-pure hydrogen. Typically the same (or very similar) anion exchange material used in the AEM is also used in solubilized form as the binder and ion conducting phase in the electrodes, to permit hydroxide ion conduction pathways and maintain alkaline conditions for the electrolysis reactions at each electrode.

(Cathode) \[ 4 \text{H}_2\text{O} + 4e^- \rightarrow 2\text{H}_2 + 4\text{OH}^- \] \[ E_{\text{Cathode}} = -0.828 \text{ V vs. SHE} \] \[ (\text{Anode}) \quad 4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \] \[ E_{\text{Anode}} = 0.401 \text{ V vs. SHE} \] \[ \text{[1]} \]

A few recently published studies on solid alkaline electrolyzers are noteworthy in this context. Leng and coworkers23 reported a current density of 400 mA/cm² at 1.8 V in an electrolyzer prepared with a polysulfone-based AEM containing benzyl trimethyl ammonium fixed cations. They used Pt black and iridium oxide as electrocatalysts at the cathode and anode respectively. This performance is significantly lower than state-of-the-art PEM electrolyzers, which can be operated at current densities as high as 1300 mA cm⁻² at 1.9 V.2,6 Some of the reasons for the wide gap in performance between PEM-based water electrolyzers and AEM-based water electrolyzers are the larger overpotentials for the hydrogen evolution reaction in alkaline versus acidic environments, the significantly higher ionic conductivity of PFSA membranes over PSF-TMA⁺, the use of electrodes with non-optimized architectures,24 and the degradation of the membrane and/or binders during operation under alkaline conditions. During stability experiments reported in the aforementioned studies, dramatic increases in overpotentials were observed and were attributed to the degradation of the solubilized AEM binder in the electrodes and/or loss of adhesion between membrane and electrode, giving rise to contact resistances.

Xiao and coworkers25 demonstrated the operation of a solid alkaline electrolyzer using a self-crosslinking quaternary ammonium polysulfone (xQAPS) as the AEM and electrode binder. This material was developed and characterized by the same research group in a previous study.26 They used non-precious metal catalysts (Ni–Fe alloy as the oxygen evolution electrocatalyst and Ni–Mo alloy as the hydrogen evolution electrocatalyst) and were able to attain cell voltages as low as 1.80–1.85 V at 0.4A cm⁻² for the electrolysis of ultrapure water (without the addition of any salt to boost the electrode conductivity). Their short-term stability experiments yielded stable MEA operation for approximately 8 hours.

Finally, Faraj and coworkers27 synthesized an AEM by radiation grafting of vinylbenzyl chloride functional monomers followed by conversion into quaternary ammonium sites with 1,4-diazabicyclo(2.2.2)octane. The electrolysis of a potassium carbonate doped water solution (1 wt% carbonate was used to boost the ionic conductivity in the electrodes) resulted in a cell voltage of 2.1–2.2 V at 0.5 A cm⁻².

Developing highly stable AEMs28–31 and non-PGM electrocatalysts2,21,24–26,30,31 with superior performance and lower cost for solid alkaline electrolyzers and alkaline membrane fuel cells is a current research priority. It is crucial to synthesize membranes that are stable during electrolyzer operation to match the excellent efficiencies...
and high stability of PEM electrolyzers. Breakthrough developments are especially needed in solubilized binder materials to increase ionic conductivity, mechanical integrity and stability of the electrodes. To achieve such a breakthrough, one must first probe and understand the modes of AEM degradation during electrolyzer operation. To our best knowledge, there are no reports of in-depth studies to probe degradation mechanisms in solid alkaline electrolyzers.

The mechanism of AEM degradation under alkaline conditions is related to the different modes under which the tethered cation groups degrade. Quaternary ammonium groups can degrade under alkaline conditions through the following known mechanisms: (1) Hofmann elimination, where the quaternary amine is cleaved, leaving as tertiary amine, and resulting in the formation of an alkene at the carbon where the ammonium was bonded (carbon in the polymer backbone); 2) a direct nucleophilic (Sn2) reaction where the cation is completely cleaved too, resulting in the formation of a tertiary amine and an alcohol at the carbon where the ammonium was bonded; and 3) through another Sn2 reaction where the adjacent organic moiety to the inorganic atom (usually a methyl or alkyl group) is cleaved resulting in the formation of a tertiary amine and an alcohol.33–36 There are other less frequently observed degradation pathways, that involve the formation of ylide intermediates, known as Sommelet–Hauser rearrangement and Stevens rearrangement.37,38 All these mechanisms involve the presence of a strong base and cause the formation of tertiary amines (or other leaving groups depending on the cation used) with the subsequent loss of ion exchange capacity and ionic conductivity.39–42

Arges and coworkers,40,42 recently proposed that polysulfone and polyphenylene oxide based AEMs could undergo backbone hydrolysis when immersed in alkaline solutions at 60°C. They suggested the reactions are triggered by the presence of quaternary ammonium cations in close proximity to the aromatic rings. The fact that the same degradation products (identified using 1D and 2D NMR spectroscopic techniques) were found for several bases (trimethylamine, 1-methylimidazole, 1,4-dimethylpiperazine or trimethylphosphine)29,39

The 1H NMR spectra of pristine PPO and brominated PPO polymers are shown in the ESI section (Figures S1-S2). 1H NMR and 13C HMQC spectra of pristine BrPPO-TMA+Cl− and BrPPO-ABCO+Cl− (for comparison purposes) are shown in Figures S3-S6 of the ESI section. For PPO, we only observed two kinds of protons, whether it was more pronounced at the anode or the cathode. We investigated the stability of the electrode binders during electrolyzer operation over a period of 5 hours (this period was sufficient to induce degradation). We also studied degradation in the AEM membrane separator over longer periods of time (24–48 hours). We are well aware that these time-periods are too short for these experiments to be considered “durability tests”. The fact however was that these timeframes were adequate to induce degradation and study degradation phenomena at a fundamental level, which was the primary objective of this work.

Results and Discussion

Poly (2,6-dimethyl-p-phenylene oxide (PPO) has been suggested as a promising candidate for alkaline electrochemical cells26,32,43–45 and was selected as the base polymer to synthesize the AEMs. PPO produces mechanically strong films, is relatively inexpensive, has good oxidative stability, and can be readily functionalized into AEMs by bromination followed by reaction with base to yield fixed cation groups. Figure 1 illustrates the chemical structure of PPO and the different steps involved in AEM synthesis. The details of the bromination reaction with n-bromosuccinimide (NBS), and the quaternization reaction with either trimethylamine (TMA) or 1-azabicyclo[2.2.2]octane (ABCO) are briefly outlined in the experimental section. More details can be found under electronic supporting information (Sections 1 & 2) and in our previous paper.42 We selected these bases because it has been shown in our previous work that AEMs derivatized with these bases yielded films with higher ionic conductivity and alkaline stability than with alternative bases such as pentamethylguanidinium, N-methylimidazole, 1,4-dimethylpiperazine or trimethylphosphine.

The 1H NMR spectra of pristine PPO and brominated PPO polymers are shown in the ESI section (Figures S1-S2). 1H NMR and 13C HMQC spectra of pristine BrPPO-TMA+Cl− and BrPPO-ABCO+Cl− (for comparison purposes) are shown in Figures S3-S6 of the ESI section. For PPO, we only observed two kinds of protons,

Figure 1. Synthesis of AEMs by bromination of PPO followed by Sn2 reaction with tertiary amine.
at 2.1 ppm and 6.5 ppm, which were assigned as the protons in the methyl (6 protons per polymer repeat unit) and aromatic rings (2 protons per polymer repeat unit), respectively; the ratio of the $^1$H NMR integrated peaks were within ±5% of the expected value. After bromination of the PPO, both these peaks split. Three peaks corresponding to the aromatic protons were observed at 6.5, 6.7 and 6.2 ppm. These peaks correspond to the protons in the non-functionalized aromatic rings, protons in the aromatic rings with bromine in the benzyl position, and protons in the aromatic rings with bromine in the aryl position (bromine in the backbone). The peak at 2.1 ppm also split into two peaks with one peak corresponding to the methyl groups in the non-functionalized portion and in the units functionalized at the benzyl position (2.1 ppm), and another peak (at 2.3 ppm) corresponding to the polymer units containing bromine in the aryl position. Another peak corresponding to the protons in the –CH$_2$-Br group was observed at 4.3 ppm. The position of these protons remained unchanged after substitution of bromine by the base (Figures S3-S6).

Figure 2 shows the initial electrolysis polarization curves obtained on MEAs prepared with BrPPO-TMA$^+$ OH$^-$ and BrPPO-ABCO$^+$ OH$^-$ . The performance of the solid alkaline water electrolyzer using the BrPPO-TMA$^+$ OH$^-$ membrane and binder was slightly lower than the performances reported by Hickner and co-workers$^{23}$ and Xiao and coworkers$^{26}$ for polysulfone based MEAs, where current densities of 400 mA cm$^{-2}$ at 1.8 V were achieved. The lower performance compared with polysulfone-based MEAs was attributed to the lower ionic conductivities of BrPPO-TMA$^+$ and BrPPO-ABCO$^+$ when compared with the corresponding polysulfone-based AEMs. Chloride ion conductivity at 50 $^\circ$C for trimethylammonium functionalized polysulfone was 35 mS cm$^{-1}$, compared to 20 mS cm$^{-1}$ for trimethylammonium functionalized PPO (this comparison was made for AEMs having approximately the same ion exchange capacity of 2 mmol g$^{-1}$)$^{39,42}$. A second factor responsible for the lower performance was the use of non-optimized GDEs instead of catalyzed membranes;$^{23}$ the catalyst utilization within these GDEs was likely to be lower. The lower performance of the electrolyzer prepared with the BrPPO-ABCO$^+$ AEM compared with that prepared with the BrPPO-TMA$^+$ AEM was attributed to the lower ion conductivity of BrPPO-ABCO$^+$. In our previous work$^{42}$ we reported a chloride ion conductivity at 50 $^\circ$C of 15 mS cm$^{-1}$ for BrPPO-ABCO$^+$, 25% lower than for BrPPO-TMA$^+$.

To study AEM and solubilized AEM binder degradation during electrolyzer operation, each MEA was held at a current density of 0.1 A cm$^{-2}$ for 5 hours. During these stability experiments, the cell voltage was recorded at regular intervals (Figure 3a). Electrochemical impedance spectroscopy (EIS) (Figure 3b & 3c) was also performed. In the case of BrPPO-ABCO$^+$ the post-mortem $^1$H NMR spectra of BrPPO-TMA$^+$ demonstrated the absence of any degradation of the quaternary ammonium groups in the AEM. In the case of BrPPO-ABCO$^+$ (See Figure 5) the comparison of peaks before and after this current hold experiment to monitor changes in high frequency resistance ($HFR$) and charge transfer resistance ($R_{ct}$); the EIS experiments were performed 50 $^\circ$C and open circuit, by applying an AC perturbation of 15 mV in the frequency range 40,000 to 0.1 Hz. During the stability experiment, we observed an increase in cell voltage during the first hour of the experiment, with subsequent stabilization of the performance. Concomitant increases in both $HFR$ and $R_{ct}$ were observed (Figures 3b & 3c). The increase in $HFR$ was attributed to AEM degradation in the electrolyte (membrane) and subsequent loss in conductivity, and to possible increase in contact resistances due to degradation and loss of AEM binder in the electrodes. The increase in $R_{ct}$ was attributed entirely to the degradation of AEM binder in the electrode, which resulted in loss of hydroxide ion conductivity (the hydroxide ion is a reactant). To further investigate the exact mechanism of AEM degradation in the AEM separator and in the AEM binder present in the electrodes, postmortem NMR spectroscopic analyzes of the separator and electrode AEM materials were performed.

Samples of the membrane separator and the AEM binder were recovered from the tested MEAs and used for postmortem NMR spectroscopy analysis. Details of how to recover the binder or NMR analysis can be found in the experimental section. Figures 4 & 5 show the post-mortem $^1$H NMR spectra of BrPPO-TMA$^+$ and BrPPO-ABCO$^+$ membrane separators, and cathode and anode binders. We first probed the degradation of the quaternary ammonium groups in BrPPO-TMA$^+$ (Figure 4) by evaluating the ratio between the areas for the peaks corresponding to the protons “g” and “d” (see Figure 1 to map these peaks to the polymer structure). The peak “g” overlapped with water peak, making it difficult to obtain an accurate estimate of the area, but the ratio ([Area of “g”]/[Area of “d”]) obtained was reasonably close to the theoretical value of 4.5 (expected for quaternary benzyl trimethylammonium) demonstrating the absence of any degradation of the quaternary ammonium groups in the AEM.
Figure 4. $^1$H NMR spectra of a) BrPPO-TMA$^+$ membrane, b) cathode AEM binder and c) anode AEM binder after electrolyzer operation at 0.1 A cm$^{-2}$ for 5 hours. The NMR spectra of the BrPPO-TMA$^+$ Cl$^-$ AEM before the stability test are shown in Figures S3-S4).

“i” (6 protons) and peak d (2 protons) resulted in a similar conclusion, namely that the cation group did not degrade. The absence of degradation of the cation groups involved in ionic conduction gave rise to added questions regarding the reasons for the observed loss in the performance. Physical observation of the GDEs after the current hold experiment showed significant deterioration of the catalyst layer (see figures S11-S18 in the ESI). Most of the catalyst (especially at the anode side) was lost and the remaining catalyst had poor adherence, suggesting the loss and/or reduction of the molecular weight for the binder in the electrodes.

Figure 5. $^1$H NMR spectra of a) BrPPO-ABCO$^+$ membrane, b) cathode AEM binder and c) anode AEM binder after electrolyzer operation at 0.1 A cm$^{-2}$ for 5 hours. The NMR spectra of the BrPPO-ABCO$^+$ Cl$^-$ AEM before the stability test are shown in Figures S3-S4).
The 1H NMR spectra of the AEM membrane and binders after testing in the electrolyzer (Figures 4 & 5) for 5 hours (at 0.1 A/cm²) displayed two new peaks (A1 and A2) at approximately 1.2 and 0.9 ppm, which increased in height for samples exhibiting larger degradation extent. The peaks A1 and A2 in the spectra in Figures 4 and 5, were larger for the binder in the anode than for the binder in the cathode. In our previous studies of AEM alkaline stability (in KOH solutions) we assigned these peaks to backbone degradation products.40,42 Due to their upfield shift, the two new peaks were believed to correspond to protons in alkyl chains far from carbonyls, aromatic rings or any other electron withdrawing groups. Another indirect confirmation that these peaks were related to backbone degradation was the presence of the same peaks for both BrPPO-TMA+ and BrPPO-ABCO+, despite them having very different cation site structures. Moreover, both PSF and PPO based AEMs yielded similar peaks after alkaline stability tests.40,42 The most probable mechanism for the backbone degradation reaction was ether hydrolysis (leading to chain scission) followed by a ring opening reaction.40,42 The backbone degradation mechanism was further supported by the brittleness of the membranes after stability experiments, the reduction in their tensile strength,42 and by the poor adherence of the catalyst to the GDE that we observed during our experiments.

We also observed that the binder in the electrodes degraded on a faster timescale than the AEM separator (the binder degraded almost completely in around 5 hours, but the membrane underwent minimal degradation in this timeframe). To independently investigate AEM separator degradation over a longer period of time, we performed a new independent electrolyzer experiments using the BrPPO-TMA+ membrane at higher current density (1A.cm⁻²) to accelerate the degradation to be able to study the degradation of the separator. The electrodes in this case were prepared using Nafion as the binder to avoid binder degradation in the electrodes (which occurred on a much smaller time-scale, as discussed, and which could convolute the separator degradation experiment results) and to permit us to focus only on AEM separator degradation. We used 0.1 M sodium bicarbonate instead of ultrapure water (as the electrolysis solution) to allow ionic conduction in the GDEs and to minimize osmotic losses within the electrode. The experiment were performed using the same set-up described earlier at 50°C, keeping the electrolyzer cell at 1 A.cm⁻² for 48 hours or until mechanical failure of the MEA. Postmortem analysis of the MEA showed a thinning of the membrane during operation as well as the formation of the same degradation peaks at 1.2 ppm and 0.9 ppm (peaks A1 and A2), (see 1H NMR spectrum in figure S7). We also found the same peak (A1) when we performed the 2D HMOC experiment (Figure S8). These results were adequate to confirm AEM backbone degradation in accordance with the mechanism discussed previously.

Careful examination of the data in Figures 4 and 5 confirmed larger degradation peaks (A1 and A2) for the binder in the cathode than for the same binder at the anode. To investigate whether the AEM separator preferentially degraded proximal to a particular electrode, we performed another experiment using same conditions described in previous paragraph, wherein we placed two separate (and equivalent) membranes between the GDEs while assembling the MEA. We used Nafion bound electrodes and 0.1 M sodium bicarbonate as electrolysis solution as described in the previous experiment, and for the same reasons. We ran the electrolyzer at 1 Acm⁻² for 20 hours. Postmortem analysis of the MEA revealed extreme thinning of the membrane proximal to the anode (the membrane was also heavily cracked and exceptionally brittle) and no changes in the membrane proximal to the cathode (1H NMR of the latter membrane did not show any differences when compared with the pristine AEM, as shown in Figure S10). The 1H NMR spectrum of the membrane recovered from the anode side yielded the same degradation peaks at 1.2 ppm and 0.9 ppm discussed before, confirming it underwent backbone degradation (see Figure S9 in the ESI). Because of membrane thinning, the sample recovered was very small and so it was not possible to perform 2D HMOC NMR spectroscopy on this sample. The membrane in the cathode side (Figure S10) did not show any appreciable signs of degradation (no thinning and no changes in the NMR spectra when compared with pristine polymer).

Based on these findings, we confirmed that the degradation of the polymer backbone was triggered by the presence of positive charges close to the aromatic backbone (the same polymers without these charged sites are extremely stable in alkaline solutions). Currently, we are working on the synthesis of AEMs with long alkyl chains separating the cationic groups from the polymer backbone to minimize these electronic effects and engender improved stability in alkaline media. We believe this strategy can be effectively employed to prepare more stable AEMs for water electrolyzers. This idea is supported by the work of Tomoi,46 Hibbs,29 Pivovar,47 and Xu,48 that has shown that cation groups attached to long alkyl pedant groups (greater than n ≥ 3 carbons) substantially improve cation stability in alkaline media.

Experimental

Poly(p-phenylene oxide) was brominated via free radical bromination following the procedure described in detail in our previous work.42 n-Bromosuccinimide and azobisisobutyronitrile were used as brominating agent and free radical initiator, respectively. The resulting brominated polymer had 0.36 mol of Br in the benzyl position per polymer repeating unit, and 0.16 mol of Br in the aryl position (backbone) per polymer repeating unit. Br in the aryl position (backbone) increases the hydrophobicity of the backbone and allows high ion exchange capacities with relatively low water uptakes. Brominated PPO was reacted with the desired organic base in (either trimethylamine or 1-azabiclohexane, a.k.a quinclidine) to obtain the anion exchange membrane. Finally, the solutions were cast on glass plates on a leveled surface in an oven at 70°C to evaporate the solvent and obtain the thin film membranes. The membranes (in bromide form) were ion exchanged to the hydroxide form prior to use by immersion in 1 M KOH for 24 hours followed by rinsing with abundant DI water to remove excess hydroxide. More details of the synthesis can be found in the ESI (section 1).

NMR samples were prepared by dissolving 0.1 g of AEM material (in chloride form) in 1 mL of deuterated dimethylsulfoxide, to which 35 μL of tetramethylsilane (TMS) was added as internal standard (chemical shift = 0 ppm). Peak labels used in the 1H NMR spectra are shown in Figure 1. The assignment of the different protons present in the polymer to each NMR spectrum peak was done based on previous reported work.9,42

Samples of electrode binder for postmortem NMR spectroscopy analysis were prepared using the following procedure. First, the AEM binder in the GDE was exchanged to chloride form by immersion in 1M sodium chloride overnight (this ionic form was more stable and more soluble in common solvents). Then, the binder was dissolved by sonication of the electrode in a mixture of isopropanol/water (1:1 weight) for 2 hours. We evaluated the solubility of AEM membrane in several solvents and established that the AEM had good solubility in the isopropanol/water mixture. The catalyst present in suspension was removed by centrifugation (at 14,000 rpm for 15 minutes), the solvent evaporated in an oven at 70°C, and the precipitate (AEM electrode binder) dissolved in 1 mL deuterated dimethylsulfoxide. Finally, the solution was transferred to a NMR tube and 35 μL of tetramethylsilane (TMS) was added as an internal standard.

The following NMR spectroscopy experiments were performed on a Bruker Avance 360 MHz NMR spectrometer to identify any possible degradation products formed during the operation of the alkaline membrane water electrolyzer, and to identify degradation mechanisms: 1) 1H NMR spectra (collected at 360 MHz); 2) 13C NMR spectra (collected at 90 MHz – proton decoupled); and 3) 1H-13C heteronuclear multiple-quantum correlation spectroscopy (HMOC). The parameters used in the experiments are listed in table S1. Only the 1H NMR spectra are shown in the manuscript. All other relevant spectra are included under ESI (Figures S1-S10). Further details of the methodology can be found in our previous papers.8,42

The electrolyzer membrane electrode assemblies (MEAs) were prepared by sandwiching an AEM between two gas diffusion elec-
todes (GDEs), each with an active area of 25 cm$^2$. Neither heating nor mechanical pressing was employed during this process. Details regarding the preparation and testing of the MEAs are provided under Section 4 of the ESI. Platinum black (Sigma Aldrich, 10 m$^2$ g$^{-1}$) was used as the hydrogen evolution (cathode) electrocatalyst, while iridium oxide (Sigma Aldrich, 20 m$^2$ g$^{-1}$) was used as oxygen evolution (anode) electrocatalyst. These catalysts are benchmark materials and were chosen here to ensure that the focus could be placed on investigating AEM degradation. A catalyst loading of 2.5 mg cm$^{-2}$ was used at both electrodes. The same AEM material was used (in solutionized form) as the electrode binder, with a loading of 30 wt%.

The electrolysis experiments were performed with ultrapure water at 50 °C. The ultrapure water was fed to the anode side and recirculated to the storage tank at a flow rate of 400 mL min$^{-1}$. The water was stored at 50 °C with continuous bubbling of nitrogen to remove dissolved carbon dioxide. To minimize carbon dioxide uptake by the membrane, the entire set-up was assembled and placed in an inflatable polyethylene glove box (AtmosBag glove bag, Sigma Aldrich). The carbon dioxide within this bag was removed before starting each experiment by purging the bag with nitrogen for approximately 1 hour (100 mL min$^{-1}$). Polarization curves were obtained by stepping the current density and holding for 2 minutes at each current density to assure pseudo-stationary conditions. Data acquisition was stopped when the cell voltage exceeded 2.5 V. Section 4 of the ESI details the procedures used for water electrolysis testing and GDE preparation.

Conclusions

We investigated the performance and degradation of poly(2,6-dimethyl 1,4-phenylene)oxide (PPO) based AEMs during the electrolysis of ultrapure water at 50 °C using electrochemical testing and 1-D and 2-D NMR spectroscopy. The PPO AEMs were derivatized with two different bases, namely trimethylamine (TMA) and quaternary ammonium (ABCO) cations. The PPO AEMs underwent chemical degradation during operation in an alkaline membrane water electrolyzer. The cell voltage was 1.15 A/cm$^2$ for BrPPO-ABCO$^+$ and BrPPO-TMA$^+$ increased by 0.4 V and 0.2 V respectively after 5 hours of operation at 0.1 A/cm$^2$. Postmortem analysis of the membrane and AEM binder recovered from the electrodes using 1D and 2D NMR spectroscopy revealed degradation via backbone hydrolysis triggered by the presence of charged cation groups (fixed quaternary ammonium). The degradation occurred preferentially in the vicinity of the anode. Experiments performed by placing two equivalent membranes in the MEA proximal to each electrode suggested that the degradation occurred preferentially at the anode. We did not observe degradation of quaternary ammonium groups over this timeframe, corroborating degradation of the membrane separator and the electrode binder.

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