High ionic conductivity membranes can be used to minimize ohmic losses in electrochemical devices such as fuel cells, flow batteries, and electrolyzers. Alkaline conditions are attractive because of the facile electrochemical reaction kinetics at high pH for oxygen reduction and water oxidation. Device operation at high pH allows for the use of non-premium metal catalysts, simpler design for the balance of plant, and reduced fuel crossover. However, it is imperative that the AEMs are thin, have long-term alkaline stability, and high hydroxide ion conductivity. There have been issues in the past with AEMs showing low ionic conductivity, poor stability at high pH, and high water uptake (leading to dimensional changes); however, these issues are being systematically addressed.

The formation of multi-block copolymers (BCP) is a means to achieve phase segregation within polymers in order to create high-mobility ion conduction channels within the hydrophilic phase of the polymer membrane. Previously, we have reported AEMs consisting of poly(norbornene) BCPs with record high hydroxide conductivity, 198 mS/cm, and very high peak power density in a hydrogen/oxygen fuel cell, 3.4 W/cm² at 80°C. In addition, the poly(norbornene) polymer, as well as the membranes made from the polymer, were shown to have excellent thermal and mechanical properties. The Sx2 substitution and Hoffmann elimination degradation routes were suppressed by tethering the quaternary ammonium headgroup to the all-hydrocarbon poly(norbornene) backbone via a long alkyl hydrocarbon chain. Trimethyl quaternary ammonium cation head-groups have been shown to be stable cations in AEMs, and their low molecular weight enables high ion exchange capacity (IEC). Water management is a key factor in achieving high AEMFC performance. The AEM plays a key role in balancing the water content and distribution during device operation. It has been shown that a significant majority of the reacting water at the AEMFC cathode is provided by back-diffusion of water produced at the AEMFC anode. This suggests that high AEM water permeability is beneficial in AEMFCs. However, excessive AEM water uptake can flood the ion conducting channels within the polymer and lead to membrane softening and mechanical failure. Thus, high water permeability without high water solubility appears to be a critical feature for AEMFCs. Waters of hydration are necessary for hydroxide ion conduction; however, excessive unbound (i.e. free) water leads to low hydroxide mobility and membrane distortion. Hence, it is necessary to balance the amount of free and bound water inside the membranes to yield the maximum hydroxide mobility and water transport. Cross-linking is an effective way to reduce water uptake and swelling. However, AEMs with high cross-linking density can become too rigid, leading to poor ion mobility, mechanical properties and water diffusivity. Water management is important in AEMFC performance. When CO₂-containing air is fed to an operating AEMFC, the hydroxide anions produced by the reduction of oxygen at the positive electrode react with carbon dioxide to produce carbonated anions with lower mobility than hydroxide (i.e. carbonate or bicarbonate), increasing ohmic-related losses. Additionally, these carbonated anions can rapidly populate the AEM and AEMFC anode, leading to significant thermodynamic and kinetic-related losses. It has been stated that the adverse effects of membrane carbonation could be minimized by using AEMs with very high ionic conductivity so that the decrease in mobility upon carbonation can be mitigated and cell decarbonation during operation through the so-called “self-purging” mechanism can occur more rapidly. Hence, AEMs with very high conductivity are most desirable. In this study, the synthesis of chemically stable AEMs with record high conductivity, 212 mS/cm at 80°C, and their implementation into AEMFCs are described. This new AEM enables record performance in a hydrogen/oxygen AEMFC with a peak power density of 3.5 W/cm² and maximum current density of 9.7 A/cm² at 0.15 V at 80°C when
water transport from the anode to cathode is controlled. Light cross-linking was used to control the WU at high IEC in this polymer, 3.88 meq/g. It is shown that thin, reinforced, high-conductivity membranes with excellent water transport are critical components in producing high-power AEMFCs. A comparison of AEMFC membrane thickness supports the hypothesis that water transport from anode to cathode is a critical factor in the achievable current and power density.

**Experimental**

**Materials.**—The monomers, butyl norbornene (BuNB), bromobutyl norbornene (BBNB) and bromopropyl norbornene (BPNB), were supplied by Promerus, LLC (Brecksville, OH). Prior to polymerization, the monomers were purified by distillation over sodium and degassed in three freeze-pump-thaw cycles. The procedures were carried out under a dry argon atmosphere in a glove box with the rigorous exclusion of moisture and air. The catalyst ([allyl]palladium(triisopropylphosphine)chloride, (n^3-allyl)Pd(Pr,P,PCI)] was prepared following a previously published procedure.40 Lithium tetrakis(pentafluorophenyl)-borate·(2.5Et 2O) (Li[FABA]) was purchased from Boulder Scientific Co. and used as-received. 

**Tetrablock copolymer synthesis and characterization.**—The tetrablock copolymers, GT82, GT78, and GT64 (polymers containing 82 mol%, 78 mol%, and 64 mol% of the halogenated monomer, respectively) were synthesized following a previously reported procedure using bromobutyl norbornene (BBNB) and bromopropyl norbornene (BPNB).21,23 The polymer samples were analyzed by 1H NMR using a Bruker Avance 400 MHz NMR instrument using CDCl3 as the solvent. The number average molecular weight (Mn) and dispersity (D) of GT82, GT78, and GT64 were determined by gel permeation chromatography (GPC) (Shimadzu) equipped with an LC-20 AD HPLC pump and a refractive index detector (RID-20 A, 120 V). GPC measurements were performed in THF with the eluent flow rate of 1.0 mL/min at 30°C and calibrated against a polystyrene standard.

**Film and membrane casting.**—In this paper, the non-reinforced materials formed into sheets for testing will be referred to as ‘films’ and the reinforced polymer materials will be referred to as ‘membranes’. The precursor tetrablock copolymers were dissolved in chloroform (2 to 3 wt%) and cast into freestanding films for conductivity tests. The cross-linking agent, TMHDA, was added to the solution in different molar ratios (5 to 20 mol%) with respect to the moles of halogenated monomer in the polymer (determined by 1H NMR). After stirring for 10 min at room temperature, the solution was filtered through a 0.45 μm poly(tetrafluoroethylene) (PTFE) membrane syringe filter and poured into a 4 cm diameter aluminum dish. The aluminum dish was placed in a preheated oven at 60°C and dried for 24 h. The colorless, transparent, flexible and freestanding films were cut into 1 cm × 1 cm × 0.2 cm. The hydrated precursor polymer in toluene, forming a 10 wt% solution, was added to the solution in different molar ratios (5 to 20 mol%) with respect to the moles of halogenated monomer in the polymer (determined by 1H NMR). After stirring for 30 min at room temperature until homogenous and translucent, the solution was filtered through a 0.45 μm PTFE membrane syringe filter. The precursor polymer solution was applied to a thin, microporous PTFE support membrane for reinforcement. The membranes, nominally 10 μm thick, were formed by drying at room temperature. The membranes were quaternized with 50 wt% aqueous trimethylamine solution for 48 h at room temperature to convert the bromobutyl/bromopropyl moieties to quaternary ammonium head-groups. The quaternized membranes were ion-exchanged from bromide ions to hydroxide ions by immersion in 1 M NaOH solution under nitrogen for 24 h.

**Hydroxide conductivity.**—The hydroxide conductivity of the films was measured using four-point probe electrochemical impedance spectroscopy (1 Hz to 1 MHz) with a PAR 2273 potentiostat. The films were cut into 1 × 4 cm strips and tested in HPLC-grade water under a nitrogen purge to minimize carbonation. The films were allowed to equilibrate for 30 min prior to each measurement. The in-plane ionic conductivity was calculated using Equation 1.

\[
\sigma = \frac{L}{W \cdot R}
\]  

In Eq. 1, \(\sigma\) is the ionic conductivity, \(L\) is the length between sensing electrodes, \(W\) and \(t\) are the width and thickness of the films, respectively, and \(R\) is the measured resistance. The CO\(_3^{2-}\) conductivity was measured after storing the films (initially in hydroxide form) in saturated aqueous K\(_2\)CO\(_3\) for 24 h. The long-term (>1000 h) alkaline stability was determined by periodically measuring the ionic conductivity after soaking the films in hydroxide-form in aqueous 1 M NaOH at 80°C in a Teflon-lined Parr reactor. Prior to each measurement, the films were taken out of solution and thoroughly washed with DI water. After each measurement, the films were stored in the reactors with fresh NaOH solution. After equilibration, each data point was measured in triplicate and the average value is reported here. The deviation in the measurement of each data point was <0.5%. Long-term chemical stability was probed by FT-IR analysis at the same state as the conductivity was measured using a Nicolet 6700 FT-IR spectrometer.

\[\text{I}EC, \text{WU, hydration number (λ), number of freezable (N}_{\text{free}}\) and non-freezable water (N}_{\text{bound}}\) molecules.\]—The ion-exchange capacity (IEC) of the precursor polymers were determined by 1H NMR. Mohr’s titration method was used to measure the IEC of the films after cross-linking and quaternization to confirm the accuracy of the NMR results.41 In a typical procedure, the material in Br\(^-\) form was converted to Cl\(^-\) form by soaking in 0.1 M NaCl solution for 24 h. The film was removed from the NaCl solution, thoroughly washed with DI water and dried in vacuum for >2 h. The dry film weight was recorded. Next, the films were immersed in a fixed volume of 0.05 M NaNO\(_3\) for 24 h. Finally, the released Cl\(^-\) was titrated with 0.05M AgNO\(_3\) using K\(_2\)CrO\(_4\) (10 wt%) as the indicator. Measurements were performed in triplicate to ensure repeatability. The IEC was calculated using Equation 2.

\[\text{IEC} = \frac{V_{\text{AgNO}_3} \times C_{\text{AgNO}_3}}{M_d} \]  

In Eq. 2, \(V_{\text{AgNO}_3}\) (mL) is the volume of AgNO\(_3\) solution, \(C_{\text{AgNO}_3}\) (0.05 mol L\(^{-1}\)) is the concentration of AgNO\(_3\) solution, and \(M_d\) (g) is the weight of the dried sample. The water uptake was calculated using Equation 3.

\[\text{WU} (\%) = \frac{M_u - M_d}{M_d} \times 100\]  

In Eq. 3, \(M_u\) is the dry mass of the film and \(M_d\) is the wet mass of the film after dabbing off excess surface water with a dry towel. The mass of the films was measured at room temperature in OH\(^-\) form. The hydration number (\(\lambda\)) or the number of water molecules per ionic group, was calculated using Equation 4.

\[\lambda = \frac{1000 \times \text{WU\%}}{\text{IEC} \times 18}\]
The number of freezable water \( (N_{\text{free}}) \) and bound water (or non-freezable water) \( (N_{\text{bound}}) \) was determined by differential scanning calorimetry (DSC). DSC measurements were carried out on a Discovery DSC with an autosampler (TA Instruments). The samples were fully hydrated by soaking in deionized water for one week. After excess water on the surface was removed, a 5 to 10 mg sample was quickly cut and sealed in an aluminum DSC pan. The sample was first cooled to −70°C at 5°C/min and then heated to 30°C at 5°C/min under \( N_2 \) (20 mL/min). The quantity of freezable and non-freezable water was determined by Equations 5 to 7.\(^{42−44}\)

\[
N_{\text{free}} = \frac{M_{\text{free}}}{M_{\text{tot}}} \times \lambda \quad [5]
\]

\[
M_{\text{free}} = \frac{H_{\text{ice}}}{(M_W - M_d) / M_w} \quad [6]
\]

\[
M_w = \frac{H_{\text{ice}}}{\Delta C_p \Delta T_f} \quad [7]
\]

\( \Delta C_p \) is the difference between the specific heat capacity of liquid water and ice. \( \Delta T_f \) is the freezing point depression.

**Thermal and mechanical stability.** —The thermal stability of the dried film in bromide ion form was studied using thermogravimetric analysis (TGA) on a TA Instruments Q50 analyzer. The temperature was ramped at 10°C/min up to 800°C in a nitrogen atmosphere. The storage modulus of the reinforced composite membranes was measured by dynamic mechanical analysis (DMA) using a TA Instruments Q800 under a 1 Hz single-frequency strain mode in air at 25°C. A fully hydrated, rectangular sample was loaded into the DMA with tension clamps after removing surface water. Experiential parameters for the DMA were set to 0.1% strain and a preload force of 0.01 N with a force track of 125%.

**Fuel cell testing.** —Catalyst inks were made from an ETFE-g-poly(VBTMAC) powder ionomer\(^{15}\) and Pt-based electrocatalysts. 40% Pt/C (Alfa Aesar HiSPEC 4000, Pt nominally 40 wt%, supported on Vulcan XC-72R carbon) was used at the cathode and 60% Pt-Ru/C (Alfa Aesar HiSPEC 10000, Pt nominally 40 wt%, and Ru, nominally 20 wt%, supported on Vulcan XC-72R carbon) was used as the anode. The details for ink formulation and fabrication of gas diffusion electrodes (GDEs) have been previously reported.\(^{30,31}\) AEMFCs with 5 cm\(^2\) active area were assembled by placing the anode and cathode GDEs on opposite sides of the AEM in Scribner fuel cell hardware with a single channel serpentine flow field. Fuel cell experiments were controlled using a Scribner 850e fuel cell test station.

At cell startup, \( N_2 \) at 100% relative humidity was flowed through the anode and cathode until a cell temperature of 60°C was reached. Then, the \( N_2 \) flows were switched to UHP H\(_2\) and O\(_2\) and a constant voltage of 0.5 V was applied to allow the cell to break-in. After a stable current density was established, the dew points of the anode and cathode reacting gases were optimized. The cell temperature was gradually increased to 80°C in 5°C increments, with the anode/cathode dew points being simultaneously optimized with the cell temperature to avoid membrane dry out. After the cell temperature reached 80°C, the degree of back-pressurization was also set. After the cell equilibrated at the desired conditions, a polarization curve was collected by slowly sweeping the voltage from open circuit to 0.1 V at 10 mV/s scan rate. Cell performance was also investigated with CO\(_2\)-free air fed to the cathode. In this case, the H\(_2\)/O\(_2\) cell testing, the cathode gas was switched to air and the system was allowed to equilibrate at the same reacting gas dew points and back pressurization for 10 min. Then, the reacting gas dew points and back pressurization were again optimized using the same procedure as above before the polarization curve was collected.

Constant current density stability tests were performed for ca. 100 hours at 600 mA/cm\(^2\). These cells were broken-in using the same procedure described above. UHP H\(_2\) was fed to the anode and CO\(_2\)-free air was fed to the cathode in lieu of UHP O\(_2\). The dew points of the reacting gases were adjusted periodically during durability testing to ensure adequate membrane hydration. Also, the cell high frequency resistance (HFR) was monitored (at a frequency of 7 kHz) by the fuel cell test station throughout the test.

**Results and Discussion**

**Synthesis and characterization of poly(norbornene) tetrablock copolymer.** —The tetrablock copolymers were synthesized using a hydrophilic monomer, either BPNB or BBNB, and a hydrophobic monomer, BuNB. The polymers were synthesized following a previous reported procedure.\(^{21,23}\) The number average molecular weights (\( M_n \)) and dispersity (\( D \)) of the tetrablock copolymers were determined by GPC. The \( M_n \) and \( D \) of the tetrablock copolymers were 57.7 kDa and 1.41, respectively, for GT82; 50.96 kDa and 2.02, respectively, for GT64, and 103.6 kDa and 1.3, respectively, for GT78. Previously, the successful formation of tetrablock copolymers by the sequential addition of individual monomer moieties over time was demonstrated.\(^{21,23}\) GPC traces of the two polymers are shown in Figure 1. The precursor block copolymers with a range of IECs (3.37–3.88 meq/g) were cross-linked with TMHDA at different molar concentration (5 to 20 mol%) with respect to the moles of brominated sites in the tetrablock polymer, Scheme 1. A previous study showed that the conductivity was lower if the cross-linker concentration was <5 mol%.\(^{25}\) Also, membranes and films without cross-linking are unsuitable for fuel cell testing due to their gel-like character and excess WU after soaking in TMA. A summary of film properties as the IEC and degree of crosslinking were changed is provided in Table I. The mole percent of the cross-linker with respect to the available cross-linking sites is indicated by the sample name. For example, GT82-5 has 82% of the monomers in the polymer functionalized with the quaternary ammonium cation and 5 mol% added cross-linker with respect to the original moles of bromobutyl sites.
Scheme 1. Synthesis of cross-linked AEMs using BBNB and BPNB as the halogenated block.

The IEC of the precursor polymers was evaluated by $^1$H NMR, and an example for GT82 is shown in Figure 2. The IEC values obtained by $^1$H NMR were spot-checked by titration, as described in the Experimental Section. From Figure 2, the combined mol% and wt% of hydrophobic and halogenated block were calculated. The mass of TMHDA was included in the calculation of the final IEC values, which ranged from 3.25 to 3.84 meq/g. In addition, the IEC values were also measured by titration. The IEC values measured by NMR and titration matched well as shown in Table I. In order to confirm that the brominated head-groups were fully quaternized, the films were analyzed by

Table I. Properties of cross-linked poly(butyl norbornene-b-bromobutyl norbornene-b-butyl norbornene-b-bromobutyl norbornene) and poly(butyl norbornene-b-bromopropyl norbornene-b-butyl norbornene-b-bromopropyl norbornene) films in hydroxide form.

<table>
<thead>
<tr>
<th>Block Copolymer</th>
<th>Cross-linker</th>
<th>Conductivity (mS/cm)</th>
<th>25°C</th>
<th>80°C</th>
<th>IEC (meq/g)</th>
<th>IEC (meq/g)</th>
<th>σ/IEC</th>
<th>Ionic ASR</th>
<th>Water</th>
<th>Hydration</th>
</tr>
</thead>
<tbody>
<tr>
<td>GT82-5a</td>
<td>5</td>
<td>109</td>
<td>212</td>
<td>3.84</td>
<td>3.76</td>
<td>55.2</td>
<td>0.04</td>
<td>122</td>
<td>17.6</td>
<td>7.59</td>
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<tr>
<td>GT82-10a</td>
<td>10</td>
<td>90</td>
<td>193</td>
<td>3.80</td>
<td>3.71</td>
<td>50.8</td>
<td>0.05</td>
<td>87</td>
<td>12.7</td>
<td>1.04</td>
</tr>
<tr>
<td>GT82-15a</td>
<td>15</td>
<td>67</td>
<td>147</td>
<td>3.76</td>
<td>3.70</td>
<td>39.1</td>
<td>0.06</td>
<td>67</td>
<td>9.90</td>
<td>1.41</td>
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<tr>
<td>GT82-20a</td>
<td>20</td>
<td>55</td>
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<td>3.72</td>
<td>3.69</td>
<td>34.4</td>
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<td>61</td>
<td>9.11</td>
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<td>96</td>
<td>162</td>
<td>3.70</td>
<td>3.61</td>
<td>43.8</td>
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<td>163</td>
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<tr>
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<td>181</td>
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<td>GT64-10</td>
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<td>3.24</td>
<td>48.9</td>
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<tr>
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<td>3.26</td>
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<td>3.16</td>
<td>36.7</td>
<td>0.07</td>
<td>43</td>
<td>7.35</td>
<td>0.09</td>
</tr>
</tbody>
</table>

*Block copolymers using bromobutyl norbornene (BBNB) as the halogenated block.
*OH$^-$ conductivity was measured by four-probe conductivity cell.
*IEC was determined by $^1$H NMR.
*IEC was determined by titration.
*Ionic conductivity at 80°C/IEC.
*Water uptake was measured at room temperature. GT82-5 can be explained as the polymer with 82 mol% of the halogenated monomer and the polymer is cross-linked with 5 mol% of TMHDA.
FT-IR in precursor polymer form after cross-linking, and after cross-linking and quaternization. The disappearance of the alkyl bromide peak at 646 cm$^{-1}$ and the appearance of quaternary ammonium peaks at 908 cm$^{-1}$, 968 cm$^{-1}$, and 1481 cm$^{-1}$ show complete quaternization, within the sensitivity of the FTIR, Figure 3. In addition, the successful incorporation of TMHDA after cross-linking was also indicated by the appearance of a new quaternary ammonium peak at 1481 cm$^{-1}$ in the IR spectra, Figure 3.

**Hydroxide conductivity ($\sigma$) and ionic area specific resistance (ASR).**—As discussed in the Introduction, AEMs with high hydroxide conductivity are desired for electrochemical devices. The hydroxide conductivity was measured at four temperatures between 25°C and 80°C. As shown in Figure 4 (left), the conductivity increased with temperature. The slope of ln($\sigma$) vs. $1/T$ was used to calculate an effective activation energy ($E_a$) using the Arrhenius Equation, Figure 4 (right). The calculated activation energy, 10.8 to 13.6 kJ/mol, is comparable to previously reported AEMs and Nafion-117 materials. It was previously reported that a maximum conductivity was obtained at a particular TMHDA concentration. At 80°C, the GT82 conductivity decreased from 212 to 128 mS/cm with an increase in TMHDA concentration from 5 mol% to 20 mol% due to an insufficient amount of bound and free water for hydration and ion conduction inside the film. For GT64, the conductivity was 181 and 119 mS/cm at 80°C at 5 mol% and 20 mol% TMHDA, respectively. The conductivity of GT78 at 5 mol% and 15 mol% TMHDA was 162 and 138 mS/cm, respectively, at 80°C. The lower conductivity at 5 mol% TMHDA for GT78 in comparison to GT64 (162 vs. 181 mS/cm at 80°C) shows the importance of proper water management inside the films. GT78-5 had 12.7 free waters per ion pair (a relatively high value), whereas GT64-5 had 3.2 free waters per ion pair (more optimized). The excess free water in GT78-5 led to lower mobility (43.8 S g/cm eq) compared to GT64-5 (54.2 S g/cm eq).

The ionic area specific resistance (ASR) is an important membrane metric for electrochemical devices. The ASR can be calculated by multiplying the film resistance by the measurement area. Ex-situ ASR values for each of the films are shown in Table I. It was observed that the ASR values were able to meet the US Department of Energy AEM target of ≤0.04 ohm cm$^2$.
Figure 4. Plot of ionic conductivity of cross-linked AEMs at different temperature (left), Arrhenius plot of ln(σ) vs inverse temperature (right).

The effect of carbonation on anion conductivity, Equations 8 and 9, was also investigated.

\[
\text{OH}^- + \text{CO}_2 \leftrightarrow \text{HCO}_3^- \quad [8]
\]

\[
\text{OH}^- + \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \quad [9]
\]

GT64-5 and GT64-10 were selected for study of the carbonate conductivity because they have a good balance of conductivity and water uptake. The comparison of OH⁻ and CO₃²⁻ conductivity for GT64-5 and GT64-10 with temperature is shown in Figure 5 (left). The OH⁻ conductivity for GT64-5 was 84 mS/cm and 181 mS/cm at 25°C and 80°C, respectively. In the CO₃²⁻ form, the conductivity of GT64-5 was 18 mS/cm and 54 mS/cm at 25°C and 80°C, respectively. For GT64-10, the conductivity before and after carbonation was 74 mS/cm vs. 15 mS/cm at 25°C, and 162 mS/cm vs. 47 mS/cm at 80°C. The ratio of the OH⁻ to CO₃²⁻ mobility was 4.7 (GT64-5) and 4.9 (GT64-10) at 25°C. This is in agreement with a previous reported mobility ratio of 5.26 That is, carbonate has only about 20% to 22% of the mobility of hydroxide at 25°C. At 80°C, the mobility ratio decreased to 3.4 and 3.7 for GT64-5 and GT64-10, respectively. Hence, the adverse effect of carbonation on anion mobility becomes comparatively less significant at fuel cell-relevant temperatures. It is noted AEMFC carbonation has other negative effects on fuel cell performance, such as lowering the pH at the negative electrode, inducing kinetic losses at the anode, and buildup of CO₂ in the hydrogen fuel if it is recirculated.12,39

The activation energy (E_a) for OH⁻ and CO₃²⁻ transport was calculated from the ln(σ) vs 1/T for GT64-5 and GT64-10, Figure 5 (right). The E_a values were 12.3 kJ/mol (OH⁻) and 17.6 kJ/mol (CO₃²⁻) for GT64-5, and 12.6 kJ/mol (OH⁻) vs. 18.4 kJ/mol (CO₃²⁻) for GT64-10.

**Water Uptake (WU).** The conductivity of a film is closely related to its water uptake per ion because the water is needed for ion hydration and transport.49 The WU of the films was measured at room temperature and the results are shown in Table I. The WU of the film decreased with TMHDA concentration. For GT82-5, the WU was 122% and the AEM showed a conductivity of 212 mS/cm at 80°C. The films with the highest TMHDA concentration, GT82-20, had only 61% WU and a much lower conductivity, 128 mS/cm at 80°C. Clearly, both WU and...
conductivity decrease with cross-link density, as expected. A similar trend was observed for GT64. However, interestingly, GT78-5 had the highest WU, 163%, which is likely due to its high molecular weight, $M_w = 103.6$ kDa, resulting in larger channels that can accumulate excess free water; however, this led GT78-5 to have the lowest measured conductivity for a film with 5% TMHDA. Figure 6 (left) shows the variation of WU and IEC with TMHDA concentration for GT82. As shown in Figure 6 (left), WU decreased significantly with TMHDA concentration, although the IEC dropped marginally. Hence, it is clear that light cross-linking is an effective strategy to mitigate WU without sacrificing IEC. The WU can also be viewed in terms of hydration number ($\lambda$), which is a measure of the number of water molecules per ion pair (i.e. anion-cation pair) was calculated from $\lambda = N_{\text{bound}} / \text{IEC}$, were related to the amount of $N_{\text{bound}}$ and $N_{\text{free}}$ waters in the film. For GT82-5, the conductivity and mobility were 212 mS/cm and 55 (S g$^{-1}$)/(eq cm), respectively, at 80°C. Both $\sigma$ and $\lambda$/IEC decrease with TMHDA concentration, although the IEC changed marginally (3.72 to 3.84 meq/g), $\lambda$, and conductivity changed dramatically.

The number of bound or non-freezable ($N_{\text{bound}}$) water and unbound or freezeable ($N_{\text{free}}$) water molecules per ion pair (i.e. anion-cation pair) was calculated from $\lambda$ using DSC measurements. It is shown in Table I that increasing the TMHDA concentration decreased both $N_{\text{bound}}$ and $N_{\text{free}}$. For example, GT82-20 had the lowest $N_{\text{bound}}$ and $N_{\text{free}}$ waters, 0 and 9, respectively. For GT82-5, the $N_{\text{bound}}$ and $N_{\text{free}}$ were 7.6 and 10, respectively. The ionic conductivity ($\sigma$) and mobility, as measured by $\sigma$/IEC, were related to the amount of $N_{\text{bound}}$ and $N_{\text{free}}$ waters in the film. For GT82-5, the conductivity and mobility were 212 mS/cm and 55 (S g$^{-1}$)/(eq cm), respectively, at 80°C. Both $\sigma$ and $\lambda$/IEC decrease to 128 mS/cm and 34 (S g$^{-1}$)/(eq cm), respectively, for GT82-20 due to insufficient $N_{\text{bound}}$ and $N_{\text{free}}$ waters inside the film. As shown in Table I for GT64-5, $\sigma$ and $\lambda$/IEC decrease with TMHDA concentration. For GT78-5, the $N_{\text{bound}}$ and $N_{\text{free}}$ were 11 and 12.7, respectively. The higher value of $N_{\text{free}}$, 12.7, caused flooding of the ion conductive channels and the conductivity was lower than GT64-5 (181 vs. 162 mS/cm at 80°C).

At high TMHDA concentration, the film is more rigid and it is difficult for water molecules to populate the film. The lack of sufficient free and bound water inside the film causes the conductivity to decrease. The membrane with an optimum amount of bound and free water is expected to produce the most effective membrane in a fuel cell.

**Thermal, alkaline stability and mechanical properties.**—Thermogravimetric analysis (TGA) was used to measure the thermal stability of the films in Br$^-$ form. Four significant weight loss regions were observed. Figure 7. The weight loss in the first temperature step below 100°C corresponds to evaporation of water or organic solvents from the film. The weight loss resulting from the decomposition of the quaternary ammonium group was observed at ca. 275°C. The third step at 350°C was due to the decomposition of the alkyl side chains in the polymer. In the fourth step, polymer backbone degradation took place at $>400^\circ$C. The variation in IEC had no significant effect on the thermal stability. The results were in-line with the previously published norbornene polymers.

The durability and lifespan of alkaline electrochemical devices depends on the chemical stability of the AEMs. The films were aged in 1 M NaOH for more than 1000 h and the conductivity was measured at regular intervals. Each data point was measured in triplicate and there was $<0.5\%$ deviation in the individual measurements. The loss in hydroxide ion conductivity was plotted as a function of aging time. As shown in Figure 8 (left), the AEMs had $<1.5\%$ loss in ionic conductivity over 1000 h. This is in agreement with previously published results.

The alkaline stability was further confirmed by monitoring the structural change before and after the alkaline treatment using FT-IR spectroscopy. Figure 8 (right) shows the appearance/disappearance of new/old peaks in the IR spectrum. The unchanged C-N stretching frequencies at 911, 971, and 1483 cm$^{-1}$ indicates that the head-group moiety was intact after alkaline aging.

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The elastic modulus of the GT-64 and GT-82 polymer films (without reinforcement) was compared to the modulus of the reinforced GT-64 membranes, which was previously reported.\textsuperscript{24} The modulus of the membranes increases with cross-linking. PTFE reinforcement of the polymer significantly increases the elastic modulus. For example, the GT82 films with 10 mol\% or 15 mol\% crosslinking had an elastic modulus of 45 to 50 MPa. GT64 with similar crosslinker had about half the value of GT82; however, the results are not directly comparable because of the different molecular weight of the polymers.

\textbf{Fuel cell performance.---}GT82-15 was selected for detailed analysis in an alkaline fuel cell because of its high conductivity and balanced WU. The GT82-15 membrane was loaded into a 5 cm\(^2\) single cell AEMFC with identical electrodes to those published previously.\textsuperscript{24} In these electrodes, a small amount of PTFE is added to both the anode and cathode electrodes in order to help with water management. This allows the results obtained in this study to be directly compared to the literature state-of-the-art. Polarization curves were collected with both H\(_2\)/O\(_2\) and H\(_2\)/air (CO\(_2\)-free) feed gases entering the cell at a volumetric flowrate of 1 L/min, and the results are shown in Figure 9. Positively, the GT82-15 based AEMFC was able to achieve a power density of 3.5 W/cm\(^2\) and a maximum current density of 9.7 A/cm\(^2\) at 80°C, making this cell the highest-performing AEMFC reported to-date.\textsuperscript{24,55} The high performance was due to a combination of factors: (i) very high ionic conductivity (i.e. low internal resistance loss) and (ii) very high water transport through the AEM from the hydrogen anode to the oxygen cathode during operation. A critical current-limiting factor in AEMFC's is the rate of water transport from the water-producing negative electrode to the water-consuming positive electrode.\textsuperscript{32}

In order to show the influence of anode-cathode water transport on the achievable current density and peak power more definitively, two variables were changed in the next batch of fuel cell tests. First, the electrode composition was changed to be identical to a previous study\textsuperscript{50} where no PTFE was added to the catalyst layers. This is important because in these tests, the electrode itself does little to remove water from the anode. This places an even greater burden on the membrane to transport water from the anode to the cathode. This change in the electrodes is expected to reduce the overall achievable current and power, but the purpose of this experiment is to show the importance of water transport through the membrane, not just achieving the highest power density. Second, the membrane and membrane thickness was varied; GT78-15 membranes with thicknesses of 10 \(\mu\)m, 20 \(\mu\)m and 30 \(\mu\)m were used. Testing different thicknesses is important because the diffusional flux of water from the hydrogen anode to the oxygen cathode is inversely proportional to thickness. The cells were operated under various conditions and their performance and operating HFR were measured in order to understand the water transport behavior during operation. Figure 10 shows the results of AEMFC tests with GT78-15 AEMs with different thicknesses. The cell with the 10 \(\mu\)m membrane has a lower peak power density and achievable current than the cell in Figure 9, due to the experimental conditions noted above. However, the performance was still very high, and higher than other cells with identical electrodes.\textsuperscript{30} The optimized dew points for the cell with the 10 \(\mu\)m AEM were 75°C and 77°C at the anode and cathode, respectively. The peak power density was 1.95 W/cm\(^2\) and the cell was able to support a current density of 6.3 A/cm\(^2\) at 0.1 V. Also, the average HFR during operation was 5.8 m\(\Omega\), which corresponds to an ASR of 0.029 \(\Omega\) cm\(^2\), which is somewhat lower than the ex-situ value for this AEM reported in Table I. The in-situ ASR of this membrane is also the lowest of any AEM reported to date in an operating AEMFC.

**Figure 8.** Alkaline stability analysis of cross-linked AEMs in 1 M NaOH solution at 80°C. OH\(^-\) conductivity loss over time (left). Structural characterization using FT-IR spectroscopy (right).

**Figure 9.** Current-voltage (filled) and current-power density (empty) curves for AEMFCs with a 10 \(\mu\)m GT82-15 AEM, operating with H\(_2\)/O\(_2\) (blue) and H\(_2\)/air (red) feeds at 1 L/min. The cell temperature was 80°C. The anode/cathode dew points for the cells operating with O\(_2\) and air (CO\(_2\)-free) at the cathode were 66°C/75°C and 70°C/78°C, respectively. The Anode: 0.70 mgPtRu/cm\(^2\); 0.05 MPa backpressure. Cathode: 0.60 mgPt/cm\(^2\); 0.1 MPa backpressure.
Figure 10. Current-voltage (filled) and current-power density (empty) curves for AEMFCs assembled with GT78-15 AEMs with three thicknesses: 10 μm, 20 μm and 30 μm. All cells were operated with H2/O2 reacting gases at 80°C with no back pressurization. The anode and cathode catalyst loadings were 0.70 mg Pd/cm² and 0.60 mg Pt/cm², respectively. The AEMFCs operated with 10 μm (blue) and 20 μm (red) were operated at anode/cathode dew points of 75°C/77°C. AEMFCs assembled with the 30 μm AEM were operated at anode/cathode dew points of 75°C/77°C (cyan) and 70°C/72°C (purple).

As shown in Figure 10, as the thickness of the AEM increased, the achievable peak power density significantly decreased. However, the decrease in current and power density were not caused by an increase in the voltage drop across the thicker membrane because the ASR of the 20 μm GT78-15 AEM was slightly lower (5.6 mΩ) than the HFR of the 10 μm GT78-15 AEM (5.8 mΩ). Although the ASR is proportional to the membrane thickness, the membrane conductivity depends on the WU. During operation in a fuel cell, the hydration state of the membrane varies across the membrane as water is consumed at the cathode and produced at the anode. This means that λ in an operating cell will have a spatial dependence with a lower value at the oxygen cathode and a higher value at the hydrogen anode. Thus, in an operating cell, very thin membranes can have higher HFR because the local hydration state is less favorable. This local hydration gradient is likely more exaggerated in very thin membranes than thicker membranes. This is supported by the observation that during operation, the HFR for the 30 μm was 80% higher than the HFR for the 20 μm AEM (i.e. 50% higher thickness led to 80% higher HFR). The gradient in hydration number does call into question the validity of ex-situ hydroxide concentration within the membrane) in operating cells is non-uniform and is likely to be low at the oxygen cathode. No degradation in performance with time was observed, however, and the long-term durability of these AEMs will be the subject of a future study.

The values for the optimized dew points of the feed gases were different for the 10 μm and 20 μm thick membranes. Figure 10 showed the performance for all cells at the optimized dew points for the 10 μm AEM, 75°C and 77°C, respectively, for the anode and cathode. The optimized dew points for the 20 μm membrane were 70°C for the anode and 73°C for the cathode. The difference in the optimized dew points is important because the dew point helps to set the rate of water evaporation from the anode where water is produced. The water formed at the anode either evaporates into the anode reacting gas or diffuses across the membrane to the cathode. The lower the dew point of the incoming anode, the higher the rate of evaporation. If the rate of water removal from the anode is not fast enough, anode flooding occurs. Combined with the lower achievable power density and lower current density for the thicker membrane, the lower values for the optimum dew points show that the rate of water transport through the AEM is lower, resulting in lower water flux and current at the oxygen cathode. This is the first time that the AEM thickness and water transport rates have been linked, which is important for understanding the design and operation of AEMs and AEMFCs.

The distortion of the polarization and power curves (Fig. 10) at higher thicknesses and higher dew points also suggests that water dynamics are playing a significant role in device performance. In the 30 μm thick AEM, there is an initial polarization that reaches an apparent mass transport limit at ca. 1.5 A/cm². Then, there is an inflection point as the cell passes 2 A/cm² where this limitation appears to be somewhat alleviated. This can be explained by observing the rate of water consumption at the cathode at high current. Water consumption at the cathode dries out the electrode and lowers the local hydration number of the AEM, but a higher water flux from the anode through the membrane allows the cell to support a higher current density without anode-flooding. It should be noted that the distorted current-voltage shape can be avoided by increasing the amount of water removed from the cell by lowering the oxygen dew point. Also shown in Figure 10 are polarization and power curves for a cell with the 30 μm GT78-15 AEM operated at anode and cathode dew points of 70°C and 72°C, respectively. The cell performance at the reduced reacting gas dew points curves are denoted as “GT78-15 30 μm (RDP)”. As shown, the polarization curve has a more typical shape and a higher peak power density was achieved. Lowering the feed gas dew points in this cell does come at the expense of reduced performance in the kinetic region and higher HFR (ca. 14 mΩ) and ASR (0.07 Ω cm²) due to the relatively lower rate of water transport through the thicker AEM.

The dynamics between the cell performance at one static set of dew points and optimal dew points for each AEM thickness shows the dew point sensitivity of AEMFCs. In general, the thicker the AEM, the more sensitive the AEMFC performance was to the reacting gas dew points. With the thickest AEM tested here (30 μm), even the shape of the polarization curve changed when the reacting gas dew points were too high. In addition, the distorted shape was still prevalent when the anode and cathode dew points were each only 2°C higher that their optimized values. With thinner AEMs, the shapes of the polarization curves were less sensitive to the dew points, as was the achievable current and peak power density. For example, when the dew points for the 20 μm AEMs were increased by 2°C, the peak power density decreased by ca. 5% from its maximum value and the current density at 0.1 V was nearly identical. It was only when the dew points were increased by 6°C to 8°C that the peak power and achievable current density were significantly affected. For the cells operating with the 10 μm AEM, their performance was slightly more sensitive to the dew point values than the 20 μm membranes, but the shape of the polarization curve did not change as a result of altering the dew points. For these cells, if the dewpoints were either raised or lowered by 2°C, there was around a 10% drop in the peak power density, although the achievable current density at 0.1 V was similar.

Finally, in-situ stability is an important factor in all fuel cells. Constant-current, short term durability tests were performed with the GT82-15 membrane-based AEMFC, Figure 11 (identical configuration to the cell in Figure 9). Remarkably, at a constant current density of 600 mA/cm² under H2/air (CO₂-free), the cell voltage loss was negligible over 100 h. The cell voltage fluctuation at the 80 h point was due to a change in the feed dew points caused by automatic filling of cold water into the test station humidifier. The high frequency resistance (HFR) of the cell was nearly constant over the entire experiment. The extremely stable HFR suggests very little, if any, degradation of the GT82-15 membrane during testing, which is in good agreement with the ex-situ chemical stability tests for this AEM, discussed above. The most likely reason drop in the maximum current with air (about 3.5 A/cm²) compared to the maximum current density with pure oxygen (about 9.5 A/cm²)) is permeation of oxygen through the ionomer at the positive electrode.

Discussion

High ionic conductivity, rapid water transport, long-term alkaline stability and the ability to make thin, robust membranes are the key properties that are needed from AEMs in AEMFCs. The effect of car-
Conduction has an impact in fuel cell operation because the mobility of carbonate is significantly lower than hydroxide. Thus, membranes with very high hydroxide conductivities (e.g., >200 mS/cm at 80°C) are favored. The properties of several AEMs reported in the literature, and their comparison to this work are shown in Table II. Previously, Wang et al. synthesized radiation-grafted HDPE and LDPE AEMs with high hydroxide conductivity, 202 to 214 mS/cm at 80°C; however, there was 6.2 to 8% decrease in conductivity after 500 h ex-situ aging.\textsuperscript{55,56} Later, Zhu et al. developed cross-linked, comb-shaped PPO films with ionic conductivity of 200 mS/cm (80°C) that showed a 27% decrease in conductivity after 500 h aging.\textsuperscript{57} Recently, Zhu et al. reported an AEM able to achieve 201 mS/cm (80°C) and 15.8% loss in conductivity over 1000 h with poly(olefin)-based AEMs.\textsuperscript{58} Jannasch reported QPip-tethered PPO based AEMs with high ionic conductivity of 221 mS/cm at 80°C, but 15% degradation occurred after only 240 h.\textsuperscript{59} Recently, we have reported the synthesis of poly(norbornene) films by vinyl addition and ROMP.\textsuperscript{22,23} The films have high ionic conductivity, ca. 200 mS/cm (80°C), and no detectable loss in ionic conductivity in ex-situ aging at 80°C. The hydroxide conducting films synthesized in this study had little or no degradation (< 1.5% degradation over 1000 h at 80°C in 1 M NaOH) and record high ionic conductivity, 212 mS/cm at 80°C for a stable AEM. The simple backbone structure containing all sp\textsuperscript{3} hybridized carbons provides a hydrophobic backbone with minimal bond polarity (inhibiting hydroxide attack) and is a lower-cost alternative to AEMs with fluorinated backbones.\textsuperscript{14,25,29,60}

This study also shows that the critical AEM features responsible for the leap in fuel cell performance shown here are the mechanical properties (i.e., ability to fabricate ultra-thin membranes) and water transport (i.e., transporting water from the anode to the water-consuming cathode). Water removal from the anode is critical for preventing anode flooding and supplying water to the oxygen cathode. Humidification/dehumidification of the feed gases alone is not sufficient for achieving high current density because the inner portion of the electrodes (closest to the AEM) are the most active regions. Thus, high water flux from the anode to the cathode is the most effective means of mitigating anode flooding and supplying the water to the cathode. Ultra-thin membranes facilitate high flux rates for water and minimize the parasitic voltage drop across the membrane. Very light cross-linking in the AEMs used here provided enough control over WU so that very high IEC values could be used without mechanical distortion of the membranes.

Conclusions

A series of cross-linked poly(norbornene) membranes were synthesized for electrochemical devices, and were demonstrated in AEM-FCs. The precursor polymers were cross-linked with a hexyl spacer diamine (TMHDA) in different mol% with respect to the halogenated monomer in the polymer chain. The IECs after cross-linking were 3.25 to 3.84 meq/g. Light cross-linking was found to be effective in mitigating the effect of high IECs toward high water uptake and low mechanical stability. The 10.1 bound water molecules and 7.6 free water molecules were optimum for hydration and effective conduction of ions through the film (GT82-5) to produce maximum ionic conductivity. The record high ionic conductivity of 212 mS/cm at 80°C was achieved with only < 1.5% loss in ionic conductivity over 1000 h of aging in 1 M NaOH at 80°C. The films were stable up to 400°C.

### Table II. Properties (hydroxide ion conductivity, alkaline stability, water uptake etc.) of highly conducting (>190 mS/cm at 80°C) AEMs.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>OH\textsuperscript{−} Conductivity (mS/cm)\textsuperscript{b}</th>
<th>IEC (meq/g)\textsuperscript{c}</th>
<th>Water Uptake\textsuperscript{d} (%)</th>
<th>Alkaline stability\textsuperscript{f}</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross-linked membranes using VA poly(norbornene)</td>
<td>198</td>
<td>3.43</td>
<td>69</td>
<td>&lt;1.5% degradation after 1000 h</td>
<td>23</td>
</tr>
<tr>
<td>Cross-linked membranes using ROMP poly(norbornene)</td>
<td>195</td>
<td>4.51</td>
<td>115</td>
<td>Retained its initial conductivity after 792 h</td>
<td>22</td>
</tr>
<tr>
<td>Cross-linked membranes using VA poly(norbornene)\textsuperscript{d}</td>
<td>212</td>
<td>3.84 (3.76)</td>
<td>122</td>
<td>&lt;1.5% degradation after 1000 h</td>
<td>This work</td>
</tr>
<tr>
<td>HDPE-based radiation-grafted AEM</td>
<td>214\textsuperscript{e}</td>
<td>(2.44)</td>
<td>155</td>
<td>8% drop in ionic conductivity after 500 h</td>
<td>55</td>
</tr>
<tr>
<td>LDPE-based radiation-grafted AEM</td>
<td>202\textsuperscript{e}</td>
<td>(2.54)</td>
<td>149</td>
<td>6.2% drop in ionic conductivity after 500 h</td>
<td>56</td>
</tr>
<tr>
<td>Crossed-linked comb-shaped PPO membranes</td>
<td>200</td>
<td>2.63 (2.35)</td>
<td>144</td>
<td>27% decrease in conductivity for similar membrane after 500 h</td>
<td>57</td>
</tr>
<tr>
<td>Poly(olefin)-based AEMs</td>
<td>201</td>
<td>2.76 (2.41)</td>
<td>193</td>
<td>15.8% degradation after 1000 h</td>
<td>58</td>
</tr>
<tr>
<td>AEM Based on QPip-Tethered PPO</td>
<td>221</td>
<td>2.8 (2.6)</td>
<td>115</td>
<td>15% degradation after 240 h</td>
<td>59</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Block copolymers using bromobutyl norbornene (BBNB) as the halogenated block.

\textsuperscript{b}OH\textsuperscript{−} conductivity was measured at 80°C.

\textsuperscript{c}Measured at 100% relative humidity.

\textsuperscript{d}Theoretical IECs was determined by 1H NMR or feed ratio, numbers in the brackets indicate the IECs by titration.

\textsuperscript{e}Water uptake was measured at room temperature.

\textsuperscript{f}Stability assessment was performed at 80°C in 1 M NaOH or 1 M KOH.

\textsuperscript{g}Measurement was performed at 90°C. VA = vinyl addition; ROMP = ring-opening metathesis polymerization.
The $\text{H}_2/\text{O}_2$ fuel cell performance at 80°C showed a peak power density of 3.5 W/cm$^2$ and maximum current density of 9.7 A/cm$^2$. It was found that the mechanical properties and ability to form ultra-thin membranes is critical to obtaining high fuel cell performance.

**References**