Achieving High-Performance and 2000 h Stability in Anion Exchange Membrane Fuel Cells by Manipulating Ionomer Properties and Electrode Optimization

Noor Ul Hassan, Mrinmay Mandal, Garrett Huang, Horie Adabi Firouzjaie, Paul A. Kohl, and William E. Mustain*

1. Introduction

Over the past few decades, fuel cells have emerged as a potential high-efficiency, clean energy source for a wide range of applications. Proton exchange membrane fuel cells (PEMFCs) have received significant attention due to their high energy density and well-established materials (e.g., Pt-based catalysts and Nafion membranes and ionomers).[1,2] However, PEMFCs are commercially challenged due to the high cost of these materials and component manufacturing costs, which are driven by the fact that PEMFCs require specialized component materials due to the highly acidic operating environment. To alleviate these costs, anion exchange membrane fuel cells (AEMFCs) have recently emerged as an alternative to PEMFCs. The higher pH operating environment offers several advantages such as lower material and manufacturing costs. For example, AEMFCs can use platinum group metal (PGM) free cathodes, have more facile oxygen reduction kinetics,[3,4] and may enable a wider range of fuels (e.g., methanol, hydrazine).

However, early AEMFC developments suffered from very low overall performance and durability.[5,6] From a durability perspective, cells were mostly believed to be limited by chemical degradation of the anion exchange membrane (AEM) and ionomer at high pH. Because of this, there has been a significant amount of investment targeting the design and manufacturing of stable AEMs and ionomers. As a result, several AEMs have been shown to be stable both at elevated temperature (≥80 °C) and pH for hundreds or even thousands of hours during ex situ testing.[7–11]

Another issue that has started to be addressed in the AEMFC literature is water management. Water is formed at the AEMFC hydrogen anode and consumed at the oxygen cathode. As water is produced at the anode, it must be removed to avoid flooding—either through the anode gas stream or, preferably, through the AEM to the cathode (via backdiffusion) where it is needed to react.[12] If too little water is supplied to the cathode, it can dry out; if more water arrives to the cathode than can be reacted, it is also possible for the cathode to flood. Therefore, there is a need for both the anode and cathode catalyst layers to be able to passively transport water. The ability of the ionomer in the catalyst layer to facilitate such ion transport is related to the overall hydrophilicity of the monomers used in the polymer membranes and ionomer. One example where ionomer water uptake has been limiting is the well-known ethylene-tetrafluoroethylene copolymer (ETFE) based powder ionomer.[13] Though the ion exchange capacity (IEC) of that material is modest (only 1.24 meq g⁻¹),
recent work has found that its water uptake was very large, and the high water content of the AEMFC anode resulted in excessive electrode swelling,[14] which blocked the catalyst sites and hindered gas transport, resulting in lower cell performance in fully humidified cells.[15] One of the ways that the amount of water in the electrodes can be reduced and avoid swelling is to lower the relative humidity of the feed gases during AEMFC operation and rely on convective evaporation to remove excess anode water.[16,17] Another method to mitigate electrode swelling is to reconfigure the electrode composition and architecture. For example, Yang et al.[18] showed that ionomer content plays a significant role in activation, ohmic and mass transport losses within the cell. Later, Omasta et al.[19] optimized the ionomer:carbon:catalyst ratio of an AEMFC anode catalyst layer, finding that having increased void space in the catalyst layer can improve performance and operational stability, likely by being able to accommodate swelling. Recently, Truong et al.[20] and Peng et al.[21] have shown that adding a hydrophobic agent (PTFE) into the catalyst layers can improve both performance and stability.

Another method that can be used to control the water transport properties of the electrodes is to modify the anion exchange ionomers in the catalyst layer. For example, Sun et al.[22] prepared pendant quaternary ammonium-based ionomers and demonstrated low Ohmic and charge transfer resistances resulting from balanced conductivity-hydrophobicity and dimensional stability. Unlu et al.[23] devised an ionomer impregnation method and achieved higher performance by balancing the ionomer distribution within the catalyst layer. Zhou et al.[23] demonstrated significantly reduced ionomer water uptake by employing hydrophobic octafluoro-biphenyl groups in the backbone and prepared a series of partially fluorinated copoly(arylene ether) alkaline ionomers followed by amination with trimethylamine.

Other studies have provided insight into how AEMFC ionomers might be designed somewhat differently than the AEM itself. For instance, Ahlfield et al.[24] pointed out that when operating as an AEM, the polymer needs to act as a low gas permeability separator while facilitating bulk ion transport. As an ionomer, higher gas solubility is preferred, and transport occurs at short lengths, not through the bulk. This suggests that the ionomers in the catalyst layer may require different properties than the polymers for AEMs, even if they come from the same chemical family. Also, Li et al.[25] suggested that the use of ionomers with high IEC or high water uptake properties may lead to limited gas transport to the catalyst due to unwanted cation-hydroxide-water co-adsorption. Moreover, such ionomers can facilitate swelling and anode flooding as discussed above. It is also likely that the AEMFC cathode, where water is consumed, would benefit from higher water retention in the catalyst layer. Therefore, ionomers with differing IEC and/or water uptake than the AEM might be expected to lead to higher performance. It is also likely that the optimum ionomers for the anode and cathode are not the same.

Studies of varied ionomer properties, such as the ones discussed above, are possible with a number of polymer chemistries. However, an effective approach might be to fine-tune the properties of already high-performing materials. One family of materials that has shown excellent performance in AEMFCs and is highly tunable is poly(norbornene) tetrablock copolymers. Recently, Mandal et al., reported highly conductive cross-linked poly(norbornene) membranes (198 mS cm\(^{-1}\)) that showed no significant ionic conductivity loss over 1000 h in 1 m KOH at 80 °C.[25] Huang et al., used similar materials in AEMFCs, enabling very high peak power density to be achieved (3.4 W cm\(^{-2}\)) under H\(_2\)/O\(_2\) reacting gases,[26] which was recently improved to 3.5 W cm\(^{-2}\) by using thinner membranes.[27]

In this study, three poly(norbornene) tetrablock copolymer ionomers with different IEC, molecular weight, dispersity, and water uptake were synthesized and fully characterized for their physical and electrochemical properties. The ionomers were integrated into operating AEMFCs with symmetric (same ionomer in both catalyst layers) and asymmetric (different ionomers in the anode and cathode catalyst layers) electrode configurations. After finding an appropriate balance of water uptake properties for the anode and cathode ionomers, additional electrode engineering was performed to increase their hydrophobicity. These final, highest performing, electrodes were operated at various conditions, including long-term testing (2000 h) with excellent results. Overall, this work highlights the balance between ionic conductivity, hydrophobicity and morphology (molecular weight) of ionomers which are essential for high-performance and long-term stability in AEMFCs.

## 2. Results and Discussion

### 2.1. Ionomer Properties

Table 1 shows the characteristic properties of the three ionomers investigated in this study. Of the synthesized ionomers, GT78 had the highest IEC (3.74 meq g\(^{-1}\)) because of the highest mole fraction of quaternary ammonium group (i.e., 78 mol%). GT32 had the lowest IEC of 1.88 meq g\(^{-1}\), whereas the IEC of GT64 (3.37 meq g\(^{-1}\)) lies in between GT78 and GT32. The molecular weights (\(M_n\)) of the three ionomers, GT78, GT64, and GT32, were 103.6, 50.96, and 114.9 kg mol\(^{-1}\), respectively. The \(M_n\) of GT32 and GT78 were nearly twice that of GT64. Higher molecular weights enable greater chain entanglement and the formation of more efficient channels to transport hydroxide and water. This is clearly shown when comparing the hydroxide mobility (the quotient of the hydroxyl ionic conductivity, \(\sigma\), and the IEC) of GT64 and GT32. For GT32, \(\sigma/\text{IEC} (80 \, ^\circ\text{C})\) was 65.2, whereas for GT64, \(\sigma/\text{IEC} (80 \, ^\circ\text{C})\) was 54.2.[27,28] The water uptake (WU) of the GT32, GT64, and GT78 polymers was measured by first casting a film as described in the Experimental section. The WU for the GT78, GT64, and GT32 ionomers at room temperature were 163%, 90%, and 63%, respectively. The increasing trend in WU of a polymer with IEC is due to a higher concentration of ion pairs and their hydration.[27,29,30] Also, increased IEC typically translates to a polymer with increased hydrophilicity. Hence, it is expected that in an operating cell, the higher IEC ionomers will take-up more water and swell to a greater extent while the lower IEC ionomer (relatively more hydrophobic character) will uptake less water and may even allow the electrodes to more effectively reject water. Both extremes could create flooding or dry out conditions if
improperly implemented, which would have a negative effect on cell performance.

### 2.2. Single Cell Performance

AEMFC performance with the GTXX ionomers was compared by collecting polarization and power density curves with H₂/O₂ feed gases entering the cell at a volumetric flow rate of 1 L min⁻¹. As discussed in the Experimental section, prior to recording any data, the dew point of the anode and cathode reacting gases was optimized and the cell temperature was set at 80 °C. In the discussion below, the dew points are displayed in an anode/cathode format, i.e., 71/73 °C would refer to a dew point of 71 °C at the anode and 73 °C at the cathode. Figure 1 compares the polarization and power curves for AEMFCs with a symmetric ionomer configuration, meaning that one of the GT32, GT64, or GT78 ionomers was used both in the anode and cathode. When GT32 was used as the ionomer in both electrodes (blue curves), the optimized reacting gas dew points were 79/80 °C. The same procedure was used to find the optimized dew points for cells employing GT64 (green curves) and GT78 (red curves) ionomers at both electrodes, which were 76/78 and 74/77 °C, respectively. The trend in the dew points follows an inverse relationship to the IEC and WU, where the lowest WU ionomers require the highest dew point for operation. The high dew point values for cells symmetrically employing the GT32 ionomers operate with a narrow balance between hydration and dry out. In terms of the peak power density and current density at 0.2V, there was not a clear trend with the ionomer WU, however, the mass transfer limited current density was higher with GT78 most likely due to its higher WU and resulting water transport. The GT32 electrodes and GT78 electrodes showed very similar peak power density, 2.2 W cm⁻². Cells with GT64 ionomer in both electrodes showed low performance relative to the other two (1.6 W cm⁻²) and an early transition to mass transport limited behavior.

With GT32 ionomer in both electrodes, the sudden transition of the cell at 5 A cm⁻² to transport limited behavior suggests that near 5 A cm⁻² there is either excess water in the anode or a deficiency of water in the cathode. During the experiment, the average cell high-frequency resistance (HFR) with GT32 ionomer in both electrodes was higher (6.2 mΩcm², areal-specific resistance, ASR = 31 mΩ cm²) than the electrodes with GT64 (5.6 mΩcm, ASR = 28 mΩ cm²) and GT78 (5.4 mΩcm or ASR 27 mΩ cm²) ionomers, despite the fact that the dew points were the highest for GT32. High dew points suppress convective evaporation, and hence typically keep the membrane well-hydrated. The higher HFR suggests that there is likely a deficiency in liquid water in the cathode, due to the low water uptake of the polymer there. For the electrodes with GT78 in both electrodes, the polymer has the highest water uptake and the lowest optimized dew points. This likely allows the cell to balance the generation and transport of the water fairly well, though the performance-limiting process here is most likely water removal and anode flooding. This explains the gradual decay in the cell voltage at higher current density instead of the sudden mass transport observed drop in current with GT32.

Finally, the cells using GT64 ionomer in both electrodes did not perform well. One explanation for this could be directly linked to the WU of GT64, which fell between GT32 and GT78. Another possible contributor to the observed performance is the hydroxide mobility (σ/IEC), which is also an indicator for water transport rate. GT64 had the lowest σ/IEC, which suggests that the rate that water can be taken up by the polymer is the lowest. It also requires the dew points of the reacting gases to be higher than GT78, suppressing convective evaporation. Another possible explanation for the lower performance of the cells comprised of GT64 ionomer is due to its low M_w compared to GT32 and GT78. Fujimoto et al. linked mechanical properties with polymer molecular weight and showed that less than 20% change in polymer molecular weight can lead to a 300% change in mechanical elongation under certain conditions. In this case, the low M_w of GT64 ionomer could have made it more sensitive to mechanical elongation and brittle fracture as it swelled upon exposure to liquid water. The poor mechanical strength of the polymer may disrupt the electrochemical polymer/catalyst interface and triple phase boundary.

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**Table 1. Characteristic properties of the GTXX ionomers investigated in this study.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>M_w [kg mol⁻¹]</th>
<th>Disperity [D]</th>
<th>IEC [meq g⁻¹]</th>
<th>Water uptake [%]</th>
<th>Ionic ASR [Ohm cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GT32</td>
<td>114.9</td>
<td>1.42</td>
<td>1.88</td>
<td>63</td>
<td>0.08</td>
</tr>
<tr>
<td>GT64</td>
<td>50.96</td>
<td>2.02</td>
<td>3.37</td>
<td>90</td>
<td>0.05</td>
</tr>
<tr>
<td>GT78</td>
<td>103.6</td>
<td>1.30</td>
<td>3.74</td>
<td>163</td>
<td>0.06</td>
</tr>
</tbody>
</table>

- Block copolymers using bromobutyl norbornene (BBNB) as the halogenated block; b) Measured by gel permeation chromatography at RT in THF relative to polystyrene standards; c) IEC (Ion Exchange Capacity) was determined by ¹H NMR; d) From ref. [28]; e) From ref. [27].
Hence, GT64 may represent an undesirable combination of properties for AEMFC electrodes, despite performing very well as an AEM. Based on these results, GT32 and GT78 were down-selected for further investigation.

Because the anode and cathode in the AEMFC operate very differently—the latter produces water and the former consumes it—it is possible that their ionomer requirements are different. In other words, one electrode may benefit from increased water uptake, either providing a buffer for water at the anode or holding in reacting water at the cathode. The effect of ionomer hydrophobicity/hydrophilicity on cell performance was investigated by making asymmetric electrodes with different ionomers in each electrode. Figure 2a shows polarization curves and power curves for the asymmetric deployment of the GT32 and GT78 ionomers. In one embodiment, GT32 was used in the anode electrode and GT78 was used in the cathode. In the other embodiment, GT78 was used in the anode electrode and GT32 was used in the cathode. For the former (blue color), the optimized dew points were 79/80 °C. In the latter case, the optimized dew points were much lower, 70/75 °C. From a performance perspective, the better configuration was GT78 at the anode and GT32 at the cathode. The peak power density was only slightly higher than the data in Figure 1, 2.3 W cm$^{-2}$, though the achievable current at 0.2 V was much higher (8.2 vs 7.4 A cm$^{-2}$).

The combination of GT32 at the anode and GT78 at the cathode suffered from ohmic losses and mass transport losses, which can be seen by observing the broad peak of the power density curve, transitioning to sudden and severe mass transport limitations. This is supported by looking at the average HFR recorded during testing. The average HFR with the GT32/GT78 in the anode/cathode was around 5.6 mΩm (ASR = 28 mΩ cm$^2$) compared to 5.1 mΩm (ASR = 25.5 mΩ cm$^2$) for GT78/GT32. This is despite the fact that the optimized dew points for the GT32/GT78 configuration were much higher than the GT78/GT32 configuration. The fact that GT78 on the anode side and GT32 on the cathode side, with lower optimized reacting gas dew points, leads to higher performance suggests that the higher water uptake and IEC of GT78 helps the anode electrode discharge water more quickly to the membrane (for backdiffusion to the cathode) and to the anode gas. At the cathode, the main difference between having GT32 and GT78 ionomer (Figure 2b) is that there is slight increase in the cell performance at higher current densities, > 4A cm$^{-2}$. However, the overall shape of both polarization curves suggests that there is an underlying mass transport issue limiting both cells that could be remedied. One possible explanation for such behavior is low water content at the cathode—where the GT78 ionomer distributes the water too quickly, moving it from the AEM through the cathode to the GDL and flowfield instead of retaining it to either react or keep the cathode hydrated. If this were true, the high current density cell performance would be improved by adding backpressure to the cathode side of the cell. Adding backpressure would suppress convective evaporation, essentially allowing additional water to be retained by the cathode ionomer. The application and significance of backpressure in AEMFCs has been studied by several researchers.\[12,32,33\] In this case, the result of adding backpressure to the cathode side was a clear increase in performance. Not only was the high current density performance increased (Figure 2b), but the kinetics were also slightly enhanced as well. This resulted in an increase in the peak power density to 2.7 W cm$^{-2}$ with optimized reacting gas dew points of 68/73 °C. The lower reacting gas dewpoints with the backpressurization were lower than the case without backpressure, likely to balance the amount of water taken up by the polymer and limit swelling. In contrast, application of back pressure on the anode side had a negative effect due to flooding, supporting the conclusion above that evaporation at the anode is critical. Moreover, application of back pressure was not effective when added to either of the electrodes when the anode/cathode ionomer configuration was GT32/GT78.

Based on the results in Figure 2, it appears that the anode prefers more conductive and hydrophilic ionomers than the cathode to increase performance as long as electrode flooding does not occur. This might explain why our results—where the

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**Figure 2.** Behavior of asymmetric deployment of the GTXX ionomers. a) Polarization and power curves at optimized dew points comparing the asymmetric deployment of GT32 and GT78 ionomers in Type 1 GDEs, no backpressure; b) polarization and power curves at optimized dew points comparing Type 1 GDEs, GT78 ionomer both sides, GT78/GT32 configuration without and with 200 kPa backpressure applied to the cathode side only. For all experiments, the cell with temperature was 80 °C, H$_2$/O$_2$ flow rates were 1 L min$^{-1}$, and AEM was GT64-15.
anode prefers the high IEC ionomer and the cathode prefers the low IEC ionomer—differ from Leonard and coworkers.[31] As evidenced by the lower mass transport limiting current in their study and lower cell performance at higher humidity conditions, their hexyltrimethyl ammonium-functionalized poly(phenylene) AEM and poly(fluorene) ionomer likely have lower water transport properties than the poly(norbornene) materials in this work. This led to the observation that their anode preferred the low IEC ionomer and cathode preferred the high IEC ionomer.

In addition to the preferred asymmetric electrode configuration for high IEC and higher water transport materials, the data above also showed that the application of back pressure was effective in terms of enhancing performance by allowing for additional water into the cathode. Therefore, to allow for high water content while imbibing the electrodes with an increased ability to reject excessive liquid water, Type 2 gas diffusion electrodes (GDEs) were investigated where PTFE was incorporated into both catalyst layers. At the cathode, it is also possible that adding PTFE in the electrode makes it even more hydrophobic than the AEM, effectively holding water at the AEM/cathode interface where water is needed for the reaction, without having extensive water throughout the catalyst layer which may lead to flooding. In all Type 2 GDE configurations, the peak power and current density increased compared to the results in Figure 2 without the added hydrophobic agent. The results for all of the Type 2 electrodes are shown in Figures S1 and S2 (Supporting Information) and the best combination is presented and discussed below.

Of particular note is the performance of the cells that were constructed with Type 2 GT78 ionomer GDEs at the anode and Type 2 GT32 ionomer GDEs at the cathode, Figure 3. In this configuration, the cell peak power density and maximum achievable current density were the highest of any investigated configuration. A peak power density of around 3.2 W cm⁻² was obtained with H₂/O₂ while a peak power density of around 1.75 W cm⁻² was recorded with H₂/Air (CO₂-free) reactivity gases. As can be seen from the H₂/Air polarization curve, mass transport issues become noticeable at higher current density, but not in H₂/O₂ cells, which suggests that the mass transport-limiting process in these high performing cells is oxygen, not water, transport. These two facts (water transport from the anode to the cathode and oxygen is the limiting reagent in air-cathode cells) implies that the critical active cathode area is at the cathode/membrane interface. Operating on H₂/O₂, it is noteworthy that these cells could operate at currents exceeding 9.0 A cm⁻² at 0.2 V.

2.3. Long-Term Durability

It has been well-documented that the durability of prior AEMFCs has been mostly poor,[5,34,35] and durability has remained one of the critical issues limiting the expansion of AEMFC deployment and commercial consideration. To some extent, the previous poor durability is troubling because many modern membranes and ionomers have shown acceptable ex situ stability for several hundred hours. This suggests that operational stability may be a function of more than chemical stability, and that other variables exacerbate the stability problem, such as the balance and transport of water. Because water likely plays an important role in the operational stability, and the results above show that the physical properties of the ionomer play an important role in AEMFC operation, the ionomer properties might also influence AEMFC durability.

Figure 4 shows the results of a 2000 h durability test for an AEMFC operating at 600 mA cm⁻² with Type 2 electrodes with the GT78 ionomer at the anode and the GT32 ionomer at the cathode. For this cell, the reacting gas flow rates were both 0.3 L min⁻¹ and no backpressure was applied. The initial anode/cathode reacting gas dew points were 72/74 °C, though the dew points were slightly adjusted occasionally to ensure that the cell had adequate humidification. The results presented here show the lowest reported voltage decay rate for any AEMFC reported to date: only 15 μV h⁻¹. Additionally, the HFR only increased by around 3.6 mΩ (ASR increase of 18 mΩ cm⁻²). It is noted that an increase in ASR of 18 mΩ cm⁻² corresponds to a 11 mV increase in resistive loss over the life of the cell compared to the 15 μV h⁻¹ for 2000 h, which is a total loss of 30 mV over the 2000 h period. Hence, a significant fraction of the voltage loss during the experiment was caused by the slow increase in the ASR. This was further confirmed by the negligible change in the polarization curves over the 2000 h test (Figure S4, Supporting Information, collected in the region of operational interest). It should be noted that the durability experiment was performed at conditions different from those for the polarization experiments. This may account for the lower performance for the polarization curves in Figure S4 (Supporting Information) compared to the polarization curve in Figure 3. First, a lower flow rate was used (0.3 vs 1.0 L min⁻¹). Second, the operating temperature was slightly lower (75 vs 80 °C). Third, the relative humidities of both the anode and cathode reacting gases were higher. All of these changes were made to increase the amount of liquid water present in the cell and increase the
3. Conclusions

In this work, three tetrablock poly(norbornene) copolymers—GT32, GT64, and GT78—were synthesized and incorporated into the anode and cathode of operating AEMFCs. These ionomers demonstrated excellent dimensional stability without significantly sacrificing the ionic conductivity. IEC, water uptake, and molecular weight were evaluated for each polymer and tied to AEMFC performance and durability. It was demonstrated that a combination of hydrophilic (GT78) ionomer in the anode electrode and more hydrophobic (GT32) ionomer in the cathode electrode resulted in the best behavior. This was demonstrated that a combination of hydrophilic (GT78) ionomer in the anode electrode and more hydrophobic (GT32) ionomer in the cathode electrode resulted in the best behavior. This was demonstrated that a combination of hydrophilic (GT78) ionomer in the anode electrode and more hydrophobic (GT32) ionomer in the cathode electrode resulted in the best behavior. This was demonstrated that a combination of hydrophilic (GT78) ionomer in the anode electrode and more hydrophobic (GT32) ionomer in the cathode electrode resulted in the best behavior.

The improvements here were enabled by a combination of high performing AEMs, new ionomers and electrode engineering to create highly effective GDEs—and the results presented here can be used by the field as a guide and benchmark for future work.

4. Experimental Section

**Tetrablock Copolymer Ionomer Preparation:** Three tetrablock copolymers, denoted as GTXX, were synthesized following a previously reported procedure using bromobutyl norbornene (BBNB) and bromopropyl norbornene (BPBN).[7,28] In a typical procedure, the catalyst solution was prepared by dissolving (η3-allyl)Pd(PPh3)Cl and Li[FABA] in a mixture of α,α,α,α-tetrachlorotoluene (TFT) and toluene. The monomer, butyl norbornene (BuNB), and toluene were mixed together to make a 5 wt% solution of the monomer. Next, the catalyst solution was injected under vigorous stirring. After the polymerization was complete, the second monomer, BNB/BPNB, in toluene was added to the reaction mixture and allowed to polymerize. The tetrablock copolymers were synthesized by sequential addition of the two monomers. The polymers were precipitated in methanol and the solid polymers were collected after filtration. In their designation GTXX, the XX is the percentage of the monomers that were halogenated. Hence, GT32, GT64, and GT78 describe polymers that contain 32, 64, and 78 mol% BNB, respectively. In essence, the number designation is an indicator of the ion exchange capacity, which impacts other variables such as hydrophilicity and water uptake.

After synthesis, the polymers 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 GT32, GT64, and GT78 were determined by gel permeation chromatography (GPC) (Shimadzu) equipped with an LC-20 AD HPLC pump and a refractive index detector (RID-20A, 120 V). GPC measurements were performed in tetrahydrofuran (THF) with an eluent flow rate of 1.0 mL min⁻¹ at 30 °C and calibrated against a polystyrene standard.

**Measurement of Ionomer Properties:** The IEC of the precursor polymers was determined by 1H NMR. The detailed procedure for calculating IEC by this method has already been reported.[24] Mohr’s titration method was used to measure the IEC of the membranes after cross-linking and quaternization to confirm the accuracy of the NMR results.[20,27] In a typical procedure, the polymer 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 deionized (DI) water, and dried in vacuum for >24 h. The dry film weight was recorded. Next, the membranes were immersed in a fixed volume of 0.05 M NaNO3 for 24 h. Finally, the released Cl⁻ was titrated with an aqueous AgNO₃ solution using K₂Cr₂O₇ (10 wt%) as the indicator. Measurements were performed in triplicate to ensure repeatability. The IEC was calculated using Equation (1)

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

where \(C_{\text{AgNO}_3}\) is the concentration of AgNO₃ (0.05 mol L⁻¹), \(V_{\text{AgNO}_3}\) is the volume of AgNO₃ (mL) solution needed for titration, and \(M_g\) (g) is the weight of the dried sample.

To determine the WU, the dry mass (\(M_d\)) of the film was measured by drying the films in a vacuum oven.[21,28] Next, the films were immersed in 18.2 MΩ DI water for 24 h. After removing the film from the DI water, the excess surface water was wiped from the surface and the wet mass (\(M_w\)) was measured. For both \(M_d\) and \(M_w\) measurements were made on multiple films and an average value is reported here. Then, the water uptake was calculated using Equation (2)

\[
\text{WU} = \frac{M_w - M_d}{M_d}\times 100\%
\]
It is pertinent to mention that water uptake measurements for GT64 and GT78 were made after adding 5% cross-linker (N,N′,N′-tetramethyl-1,6-hexanediamine) while for GT32, no cross-linker was added. The cross-linker was added to avoid gel formation due to more hydrophilic properties of the GT64 and GT78 ionomers and reliable water uptake measurements were not possible without adding the cross-linker. Then, the percent swelling for each ionomer was calculated by Equation (3), where \( V_4 \) is dry volume of the membrane and \( V_3 \) is the volume of the fully hydrated membrane after removing excess surface water. The volumes were calculated by measuring and multiplying the film length, width, and thickness in both the dry and hydrated states.

\[
\text{Swelling (\%) } = \frac{V_3 - V_4}{V_4} \times 100
\]

(3)

Ionic area specific resistance (ASR) was calculated using Equation (4)

\[
\text{ASR} \left( \Omega \cdot \text{cm}^2 \right) = \frac{L}{\sigma}
\]

(4)

where \( L \) is the film thickness in cm and \( \sigma \) is the ionic conductivity in S cm\(^{-1}\) (at 80 °C). The in-plane hydroxide conductivity of the membrane samples was measured by four probe electrochemical impedance spectroscopy (EIS) using a PAR 2273 potentiostat/galvanostat (Princeton Applied Research) for frequencies from 1 Hz to 2 MHz.

Finally, the storage modulus of the GT64-15 AEM was measured by dynamic mechanical analysis (DMA) using a TA Instruments Q800 under a 1 Hz single-frequency strain mode in air at 30 °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%.40

Electrode Fabrication Using GTXX Ionomers: GDEs were fabricated using a previously developed method26,27 where a catalyst ink was made from the GTXX ionomers, DI H\(_2\)O/isopropanol alcohol solvent, and Pt-based electrocatalysts. 40% Pt/C (Alfa Aesar HiSPEC 4000, Pt nominally 40 wt%, supported on Vulcan XC-72R carbon) was used for the anode and cathode GDEs (without any hot pressing) and the cell was torqued to 45 in. lb. 6 mil (150 μm thick) PTFE sheets were used as the gasket material at both the anode and cathode.

AEMFC Testing: All of the operating AEMFCs in this work were controlled using a Scribner 850e fuel cell test station. At cell startup, \( N_2 \) was flowed through the anode and cathode at 0.4 L min\(^{-1}\) and 100% relative humidity until a cell temperature of 60 °C was reached. Then, the \( N_2 \) feeds were switched to pure H\(_2\) and O\(_2\) and a constant voltage of 0.5 V was applied to initiate the cell break-in procedure. After a stable current density was established, the dew points of the anode and cathode reacting gases were systematically optimized as previously described. After 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 backpressurization was also set. After the cell equilibrated at the desired conditions for around 30 min, a polarization curve was collected by slowly sweeping the voltage from the open circuit voltage to 0.1 V at a 10 mVs\(^{-1}\) scan rate. The top-performing electrode configuration was further subjected to the DOE long-term AEMFC durability protocol where the cell was held at a constant current density of 600 mA cm\(^{-2}\) for 2000 h. During this long-term test, the cell temperature was set at 75 °C while the dew points of the reacting gases were initially set to 72 °C at the anode and 74 °C at the cathode. The dew points were adjusted occasionally (±1 °C) to ensure adequate membrane hydration. Also, the cell HFR was monitored (at a frequency of 7 kHz) by the fuel cell test station throughout the test.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.
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