

# Oxidative instability of ionomers in hydroxide-exchange-membrane electrolyzers

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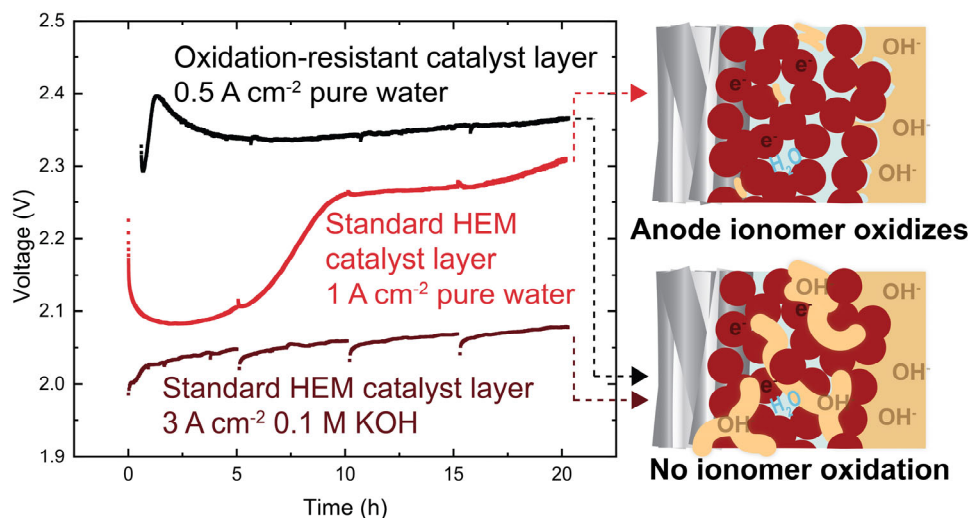
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## Abstract

Hydroxide exchange membrane (HEM) electrolyzers can produce green H<sub>2</sub> with only earth-abundant catalysts and electrolyte-free (nominally pure) water feed, significantly decreasing system cost and complexity. However, HEM technology suffers from short lifetimes, attributed in part to poor stability of anion-exchange polymers used in the membrane and catalyst layers. Here, we use electrochemical analysis and ex-situ characterization techniques to study anion exchange polymer degradation in electrolyzers. Using multiple ionomers, catalyst layer additives, and electrolyte feed, we show anode ionomer oxidation is the dominant degradation mechanism for all HEM-based electrolyzers tested. We show improved device stability using oxidation-resistant catalyst layer binders and offer new design strategies for advanced ionomer and catalyst layer development.

## TOC graphic



Ionomer oxidation is the dominant degradation pathway for pure-water HEM electrolyzers and may be mitigated by new catalyst layer design strategies.

## Introduction

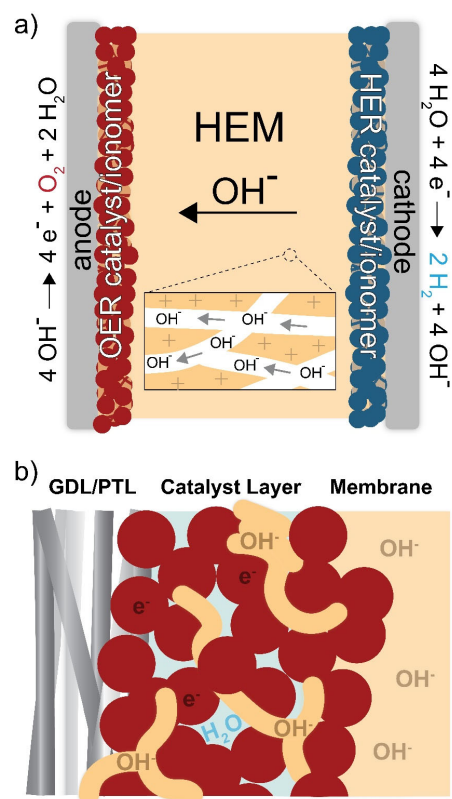
H<sub>2</sub> production has seen substantial investment as political and environmental factors drive a demand for increased renewable energy use.<sup>1-3</sup> Renewable energy technology typically yields electrical power, which can then be stored or converted to energy carriers such as renewable/green H<sub>2</sub>, which brings many benefits, including longer-duration and increased scale of energy storage compared to batteries.<sup>4</sup> Green H<sub>2</sub> also enables the otherwise-difficult decarbonization of manufacturing and industry sectors like chemical, metal, and fertilizer production.<sup>5</sup>

Of the various H<sub>2</sub> production technologies, low-temperature membrane electrolysis is attractive for its ability to operate using electrolyte-free water (as opposed to KOH electrolytes which complicates balance-of-plant components) and produce high-purity (>99.9%) H<sub>2</sub>. Proton-exchange-membrane (PEM) electrolysis is an established technology at megawatt scale<sup>6</sup> with gigawatt pilot projects deployed.<sup>7-9</sup> PEM electrolyzers use perfluorinated sulfonic acid polymers,

like Nafion, a cation-exchange ionomer with high  $H^+$  conductivity.<sup>10, 11</sup> PEM electrolytes achieve ~80% voltage efficiency at  $1 A cm^{-2}$  or higher<sup>12</sup> and steady-state degradation rates below  $20 \mu V h^{-1}$ .<sup>13</sup> However, the locally acidic environment necessitates the use of expensive precious-metal catalysts, in particular Ir, which limit device scale-up and deployment.<sup>14</sup> Substantial catalyst loading reductions are needed for PEM to achieve  $H_2$  cost targets.<sup>2</sup>

Hydroxide-exchange-membrane (HEM) electrolyzers are a developing technology with the potential to address the limitations of PEM electrolyzers (Fig. 1). They operate using an anion-selective membrane, which creates a locally alkaline environment enabling the use of inexpensive, earth-abundant catalyst and cell materials. However, the mobility of  $OH^-$  is half that of  $H^+$ , and therefore anion-exchange polymers must have twice the charge-carrying capacity of PEM polymers to achieve comparable conductivity. These transport limitations combined with the poor stability of anion-exchange polymers has prevented HEM electrolyzers from reaching maturity and commercial penetration.<sup>15</sup>

In addition to the ionomer (ion-exchange polymer) playing an essential role as the membrane, it is also used in the catalyst layer (Fig. 1b). The catalyst layer is deposited on the membrane or electrode porous-transport layer (PTL) using an ink. The ink is comprised of the catalyst, solvent, and dissolved ionomer that acts as a catalyst binder and enables ion transport to the active catalyst surface.<sup>16</sup> When the ink is deposited, the solvent evaporates and creates a porous layer of ionomer, catalyst, and void space for liquid/gas transport to/from the catalyst. The interactions between materials in this region directly impact device performance and durability,<sup>17-19</sup> as the impedance of electric, ionic, and reactant/product transport to/from the reaction zone reduces performance.<sup>20</sup>



**Figure 1.** Ion transport and reactivity in HEM electrolyzers. Schematics of a) electrolyzer cell and b) anode catalyst layer. OH<sup>-</sup> anions conduct through the ionomer, and electrons conduct through the catalyst. OER occurs at the ionomer/catalyst interface.

Anion-exchange ionomers have historically limited the performance and durability of HEM electrolyzer devices.<sup>15, 20-24</sup> Common cation-exchange ionomers are perfluorinated-sulfonic-acid-(PFSA)-type materials with high chemical stability.<sup>25</sup> Most anion-exchange ionomers are hydrocarbons (e.g. polybenzimidazoles, polyethers, polyphenylenes, etc.) which are more susceptible to chemical degradation by nucleophilic OH<sup>-</sup> in the strong alkaline conditions. While substantial polymer development in the past decade has improved electrolyte-free HEM electrolyzer performance,<sup>26-32</sup> further improvements are needed. Most efforts at improving the stability of HEM polymers have focused on alkaline chemical stability, including adding protecting groups near electrophilic sites,<sup>33-35</sup> partial fluorination,<sup>36</sup> and tuning side-chain length<sup>37</sup>

or cation identity.<sup>38, 39</sup> Ex-situ chemical stability, however, is not necessarily reflective of device conditions nor indicative of how a polymer will perform in a membrane-electrode assembly (MEA), in particular during operation with electrolyte-free (nominally pure) water feed. In the MEA, the polymer may degrade by other chemical and electrochemical means besides OH<sup>-</sup> attack. At the anode the ionomer is held at a strongly oxidizing potential and exposed to possible oxidizing species/intermediates produced during the oxygen-evolution reaction (OER). The oxidative and radical stability of anion exchange polymers has been investigated to various extents,<sup>40-44</sup> but few studies are conducted under device-relevant operating configurations and conditions.

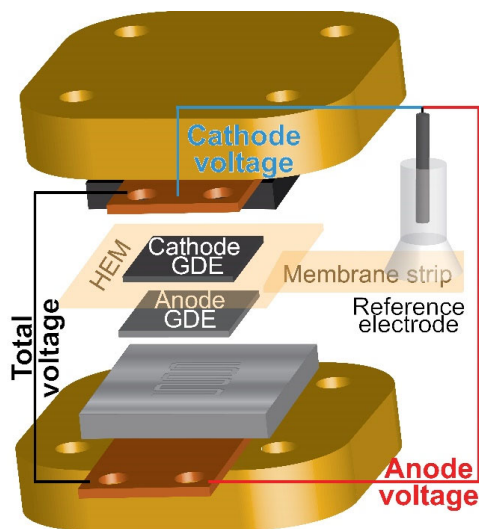
Here we report a comprehensive ionomer failure analysis of HEM electrolyzer MEAs operating with electrolyte-free water and uncover common oxidative processes that must be solved for commercialization. Using integrated reference electrodes and impedance analysis on the full MEA electrolyzer, post-mortem surface analysis, and cross-sectional electron-microscopy and chemical imaging, we find ionomer oxidation as a dominant degradation mechanism across all ionomer chemistries studied in locally alkaline conditions, even those with all sp<sup>3</sup> carbon and PFSA. We further investigate the effect of various additives and alternative feed modes on the extent of oxidation, showing pure-water operation degrading > 0.5 mV/h over 100 h using an oxidatively stable anode-catalyst layer. Lastly, we introduce catalyst-layer design strategies for next generation HEM electrolyzer devices.

## **Results and Discussion**

### *Degradation of TP-85 anion exchange ionomer*

HEM electrolyzers with an active area of 1 cm<sup>2</sup> were prepared and assembled as described in the methods section and elsewhere (Fig. S11a).<sup>19, 27</sup> IrO<sub>x</sub> on platinized Ti and Pt black on Toray

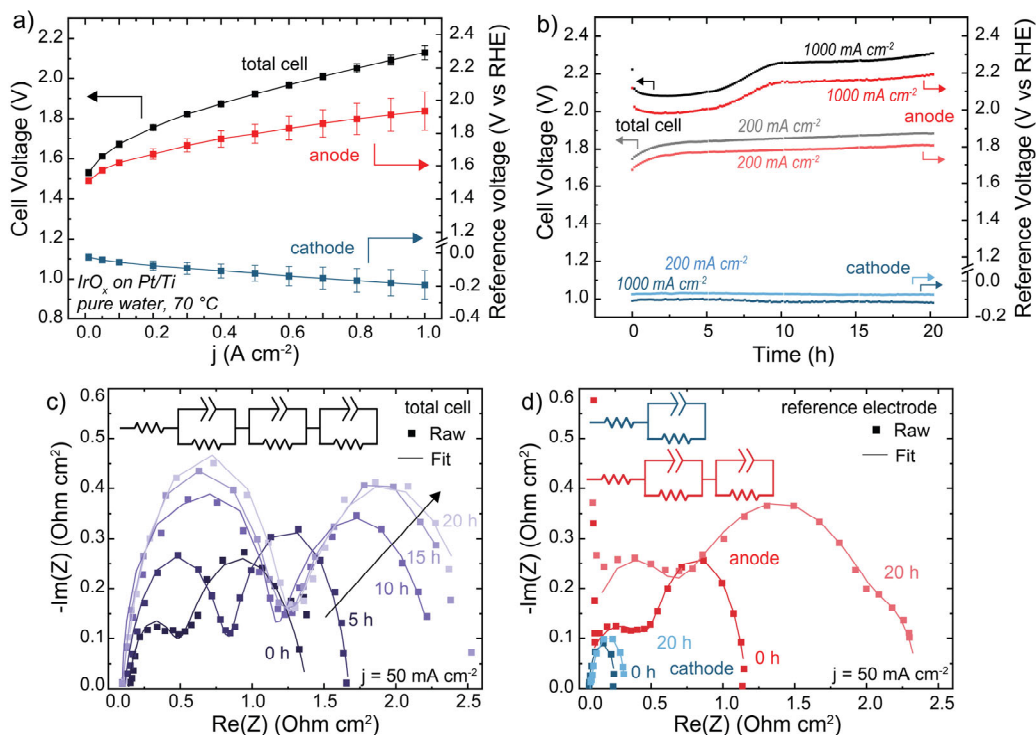
carbon-paper were used as the anode and cathode porous-transport electrodes (PTEs) respectively. Both electrodes were prepared with PiperION-A5 ionomer dispersions and devices were assembled with a 40-um-thick PiperION TP-85 membrane. For this study, the membrane and cathode remained constant for all experiments and only the anode PTE, including anode ionomer, was varied.



**Figure 2.** Schematic of the reference electrode integrated in the electrolyzer MEA and hardware. A reference electrode is placed on a strip of membrane attached to the HEM in the MEA. The voltage is measured from the cathode end plate or anode end plate versus the reference. Precision gasketing and a high conductivity HEM and reference strip are used to minimize mis-alignment reference-potential errors.<sup>45, 46</sup>

Understanding electrolyzer device degradation during operation is challenging and usually limited to information gained from two-electrode studies. To better understand the contribution of individual components to the total cell voltage, a reference electrode was integrated into the MEA.<sup>47</sup> A strip of membrane is attached to the edge of the membrane in the MEA and extended outside the cell hardware, where a reference electrode is attached to the membrane strip and used to measure the anode and cathode components to the total cell voltage (Fig. 2). A high conductivity

HEM and reference strip are used to minimize reference electrode potential errors from non-symmetric current distributions.<sup>45, 46</sup>



**Figure 3.** Performance and stability of a HEM electrolyzer. Cells were operated with an  $\text{IrO}_x/\text{TP-85}$  catalyst layer on Pt/Ti anode, TP-85 membrane, and Pt-black/TP-85 cathode. a) Polarization curve showing anode and cathode contribution to total cell voltage. Reported data is the average of three polarization curves and the error bars are one standard deviation. b) Cell durability at  $200 \text{ mA cm}^{-2}$  (gray total cell, light red anode and light blue cathode) and  $1 \text{ A cm}^{-2}$  (black total cell, dark red anode and dark blue cathode). c) Nyquist plots of total cell impedance collected at  $50 \text{ mA cm}^{-2}$  as a function of time during the  $1 \text{ A cm}^{-2}$  test. d) Nyquist plots of the anode and cathode impedance measured at  $50 \text{ mA cm}^{-2}$  before and after 20 h operation at  $1 \text{ A cm}^{-2}$ . Nyquist plots were fit to the inset equivalent circuit. Degradation is primarily evident in the anode impedance.

HEM electrolyzers were operated with electrolyte-free (nominally pure) water. The initial performance was  $2.1 \text{ V}$  at  $1 \text{ A cm}^{-2}$  (Fig. 3a). The polarization curve is recorded following a  $\sim 20$  min break-in period, during which some degradation may occur contributing to the high voltage

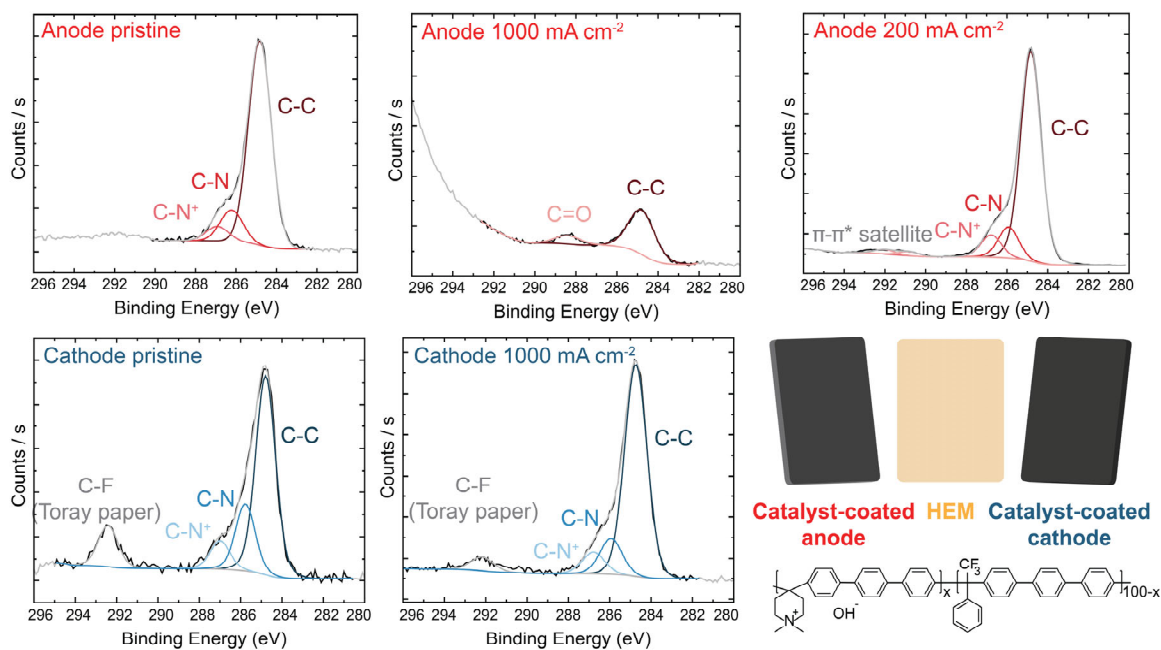
performance relative to PEM benchmark systems. During operation at  $1 \text{ A cm}^{-2}$ , the total cell voltage decreases for a short period before rapidly degrading at  $22 \text{ mV/h}$  from  $1 - 10 \text{ h}$  then stabilizing to  $4 \text{ mV/h}$  from  $10 - 20 \text{ h}$  (Fig. 3b). The reference electrode reveals this voltage degradation occurs at the anode. The cathode degradation was constant throughout the run at  $\sim 1 \text{ mV/h}$ , which may be due to non-optimal water management that could be solved with better ionomer and cathode electrode design, but is not the focus of this work.

The Nyquist plot of the full cell shows two semi-circles (Fig. 3c). During operation, the low frequency resistances of both semicircles increase with time. If these two processes were assumed to be the anode and cathode, this would suggest an increase in both OER and HER charge-transfer resistance. However, the anode and cathode Nyquist plots using the reference electrode show two semicircles for the anode, and one at the cathode (Fig. 3d). The second *RC* component at the anode may be due to a variety of processes, including ionomer oxidation reactions, a slow corrosion or dissolution mechanism, or water-dissociation reactions from OER occurring in lower pH regions in the catalyst layer. Impedance analysis of electrochemical devices is complicated<sup>48</sup> and more work is needed to assign mechanisms to each semicircle at the (degrading) anode. Previous measurements found OER faradaic efficiency of  $\sim 98 \%$  for the same MEA system.<sup>27</sup> After operation at  $1 \text{ A cm}^{-2}$ , both charge-transfer resistances at the anode increased significantly while the cathode increased only slightly, consistent with the conclusion that cell degradation is an anodic process. Simulated Nyquist data using values obtained from the reference electrode measurements agree with the raw total-cell impedance collected without the integrated reference electrode (Fig. S13).

When the operating current is lowered to  $200 \text{ mA cm}^{-2}$  the total-cell voltage-degradation rate decreases to  $7 \text{ mV/h}$  from  $0 - 10 \text{ h}$ , and  $3 \text{ mV/h}$  from  $10 - 20 \text{ h}$  (Fig. 3a). This voltage degradation



is at the anode; the average cathode degradation rate was  $50 \mu\text{V/h}$ . Interestingly, at  $200 \text{ mA cm}^{-2}$  the initial large decrease in voltage was not observed. A decrease in voltage can still indicate cell degradation, for example membrane thinning which decreases cell resistance, and is not necessarily cell performance improving.<sup>15</sup> The ionomer loading in the PTE is 20 wt% relative to catalyst mass, which was chosen to ensure sufficient ionomer sample signal for XPS and resolution for SEM cross-section analysis (discussed later). A high ionomer loading can contribute additional  $iR$  or mass-transport losses to the cell voltage. This initial voltage decrease is not observed when the ionomer content is decreased to 10 wt% (Fig. S14), and thus we interpret the initial voltage decrease at  $1 \text{ A cm}^{-2}$  as various coupled catalyst layer reorganization and degradation processes, which initially decreases catalyst-layer resistance and appears as an improvement in cell voltage.

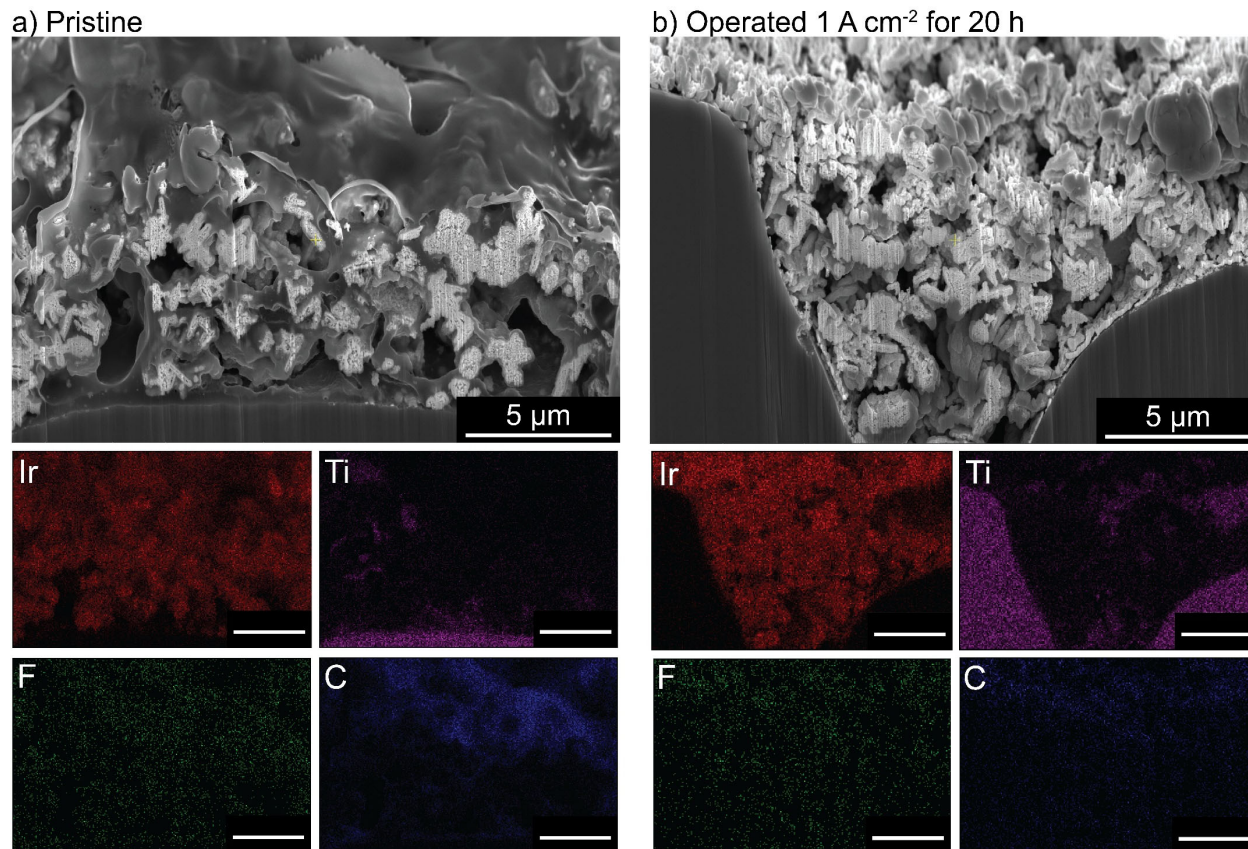


**Figure 4.** XPS analysis of  $\text{IrO}_x/\text{TP-85}$  anode and  $\text{Pt-black}/\text{TP-85}$  cathode. C 1s spectra of a) anode and b) cathode PTE. Inset shows the chemical structure of the TP-85 ionomer. Ionomer degradation is only observed on the anode PTE operating at high current.

X-ray photoelectron spectroscopy (XPS) analysis of the PTE surface was conducted to understand the anode-degradation mechanism (Fig. 4). The pristine anode PTE shows the expected spectra for the undamaged ionomer. No Ir XPS peak is observed (Fig. S15), as the PTE surface is sprayed with a top layer of ionomer and XPS only penetrates a few nm into the surface of the material. After operating at  $1 \text{ A cm}^{-2}$  for 20 h, the C 1s spectra from the cathode catalyst layer remains unchanged, while the anode C 1s spectra shows a new higher-binding-energy peak between 288 and 289 eV, consistent with carbonyl and/or ester group formation,<sup>19, 27, 41, 49</sup> and a loss of C-N content. This is accompanied by a loss of N 1s and F 1s peaks (Fig. S16), demonstrating both polymer backbone and cation groups have degraded and dissolved, at least from the surface layer analyzed. The surface of the anode PTE operated at  $200 \text{ mA cm}^{-2}$  for 20 h shows no obvious signal from ionomer oxidation, consistent with the more stable operating voltage and slower oxidation kinetics at lower anode potentials.

We note that XPS signal from carbonate or bicarbonate may also appear in the binding-energy range where oxidized carbon species were found. All electrodes are quenched in 3 M NaCl before drying and thus any carbonate from operation should be exchanged to  $\text{Cl}^-$  before analysis. We have previously shown this procedure is sufficient to exchange carbonate to chloride after testing of ionomer films in supporting carbonate electrolyte.<sup>41</sup> To confirm this assumption here, an MEA was prepared, and pure water was flowed through the device at  $70 \text{ }^\circ\text{C}$  without applied current. The PTE was ion exchanged and dried following the same procedure as the operated samples. XPS analysis shows only pristine polymer with no higher-binding-energy carbon peak (Fig. S17), indicating complete exchange of any absorbed carbonate. Therefore, growth of the high-binding-energy peak in the C region, combined with a loss of N and F signal, demonstrates severe ionomer oxidation in the anode catalyst layer. This oxidation is likely leading to reduced ionic transport to

the catalyst, decreased electrochemical active area due to detachment of catalyst particles, and thus the increase in the anode charge-transfer resistance measured by impedance.



**Figure 5** Cross-sectional imaging and EDX of an IrO<sub>x</sub>/TP-85 anode PTE a) before and b) after 20 h operation at 1 A cm<sup>-2</sup>. All scale bars are 5 μm. No ionomer is observed in the catalyst layer after operation.

PTEs were then cross-sectioned using a plasma-focused-ion-beam (PFIB) and imaged with a SEM. The pristine PTE has ionomer uniformly dispersed throughout the catalyst layer (Fig. 5a). After operation, no ionomer is observed, and only large aggregates of IrO<sub>x</sub> remain (Fig. 5b). The cross section of the control MEA with only water flow shows no ionomer degradation or loss from the catalyst layer (Fig. S18). The observed ionomer loss is thus a coupled

chemical/electrochemical/mechanical process, and not purely detachment due to poor catalyst layer adhesion.

For HEM electrolyzers multiple degradation mitigation strategies have been pursued. These generally fall into three categories; improved ionomer design, introducing stable catalyst layer additives, and operation with supporting electrolyte – each of which is explored and discussed in the next section.

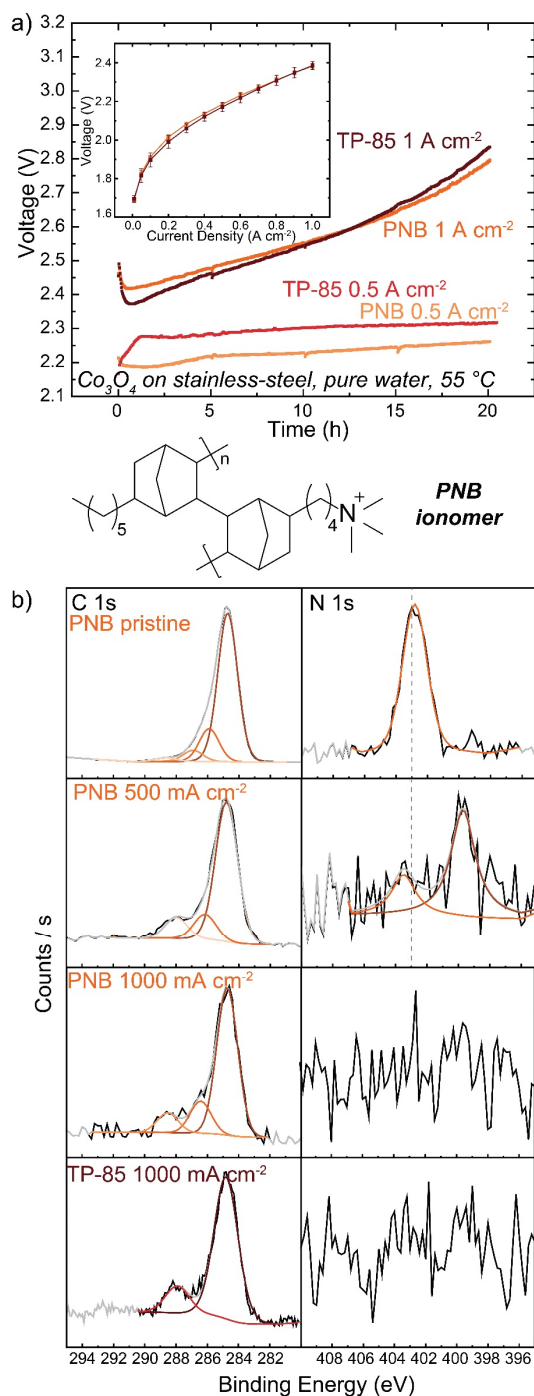
#### *All-sp<sup>3</sup> Norbornene-backbone ionomers*

Many polymer design strategies have been pursued to improve alkaline ionomer durability. The polynorbornene (PNB) backbone is of particular interest. The aromatic regions of HEM backbones are likely weak sites for oxidation,<sup>40, 41, 44</sup> therefore a fully sp<sup>3</sup>-hybridized backbone should be more resistant to oxidative damage. These and related polymers have shown promising performance and durability in HEM fuel cells<sup>50, 51</sup> and electrolyzers.<sup>52-54</sup>

Anode PTEs were prepared using Co<sub>3</sub>O<sub>4</sub> catalyst and the PNB ionomer on a woven stainless-steel substrate. MEAs were prepared with the same TP-85 membrane and Pt-black/TP-85 cathode PTE as previously. The PNB ionomers show nearly identical polarization performance as the equivalent TP-85 electrode (Fig. 6a inset). When operating at 500 mA cm<sup>-2</sup> the PNB ionomer appears more stable, with a more-linear voltage degradation as opposed to the rapid onset and stabilization behavior observed for the TP-85 (Fig. 6a, light red and light orange). However, substantial oxidation is still observed by XPS in conjugation with a loss of ammonium cation and growth of uncharged nitrogen species (Fig. 6b). At 1 A cm<sup>-2</sup>, both electrodes show similar voltage degradation (Fig. 6a, dark red and dark orange) and structural oxidation by XPS (Fig. 6b). The extent of oxidation appears less compared to the IrO<sub>x</sub> OER catalysts, which we have found

previously to be due to the lower electrical conductivity of  $\text{Co}_3\text{O}_4$  that limits the reaction zone to near the PTL and thus less is observed on the top (opposite side) of the deconstructed post-mortem catalyst layer.<sup>27</sup> Different catalysts are also expected to differently interact chemically/electrostatically with ionomer which may lead to different adsorption and oxidation behavior. In any case, the results here show the PNB ionomer oxidation is comparable to the TP-85 under the same operating conditions, despite having all single bonds.

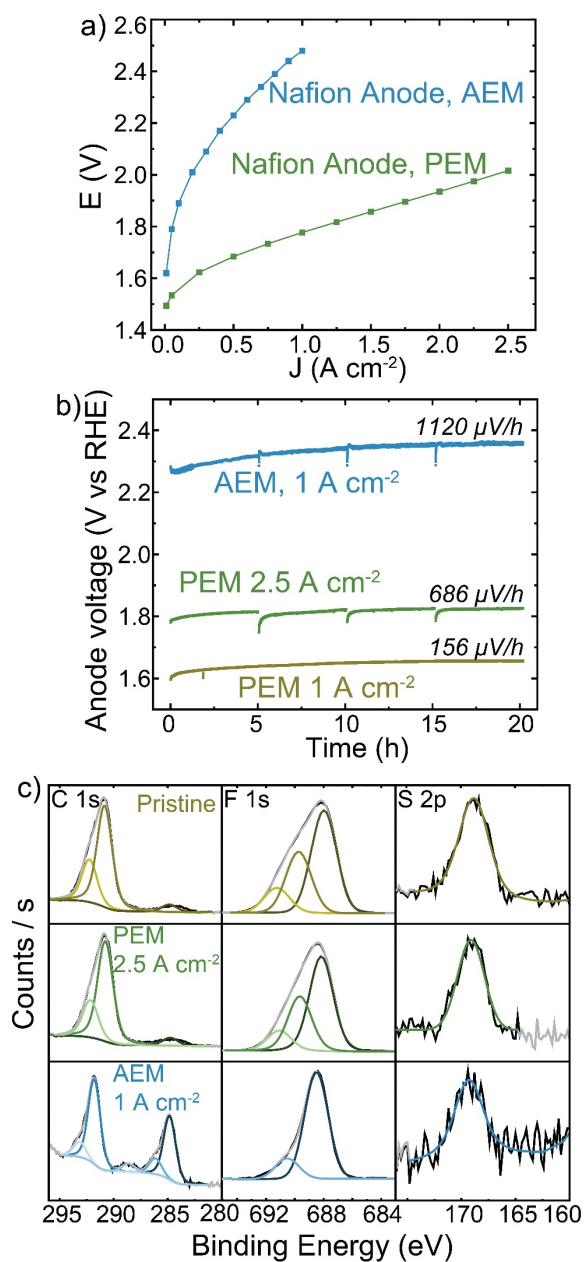
Other reports of PNB-based ionomers have shown stable voltage performance up to  $1 \text{ A cm}^{-2}$  during electrolyte-free water-electrolysis operation.<sup>52-54</sup> Other polymer characteristics can impact the extent of oxidation independent of polymer structure. Here, the ion-exchange capacity of the ionomer was tuned to result in the same voltage polarization performance as the TP-85 system, but the two polymers possess different water uptake and  $\text{OH}^-$  conductivity properties (Table S1). Ionomer water uptake can affect device stability, and a low water uptake material at the anode was shown to improve stability despite the performance losses from low ionic conductivity.<sup>53</sup> Water uptake will also affect how chemical  $\text{OH}^-$  and radical oxygen species access and interact with the ionomer, and thus ionomers with lower water uptake may not degrade as rapidly. The most-stable electrodes appear to be prepared with ground ionomer resin particles as opposed to the conventional dissolved/dispersed ionomer solution in ink as used here. Such electrodes often include PTFE additives. This observation presents an interesting question as to the effect of catalyst layer geometry and morphology on ionomer degradation and the role of non-ion-conducting additives as stabilizers in the catalyst layer.



**Figure 6.** PNB ionomer performance and durability. Cells were operated with a  $\text{Co}_3\text{O}_4$ /PNB or  $\text{Co}_3\text{O}_4$ /TP-85 catalyst on stainless-steel anode, TP-85 membrane, and Pt-black/TP-85 cathode. a) Cell durability at 500 mA cm<sup>-2</sup> (light red TP-85 and light orange PNB) and 1 A cm<sup>-2</sup> (dark red TP-85 and dark orange PNB). Inset shows polarization performance (dark red TP-85 and dark orange PNB). b) XPS comparison of pristine and operated anode PTEs. Both systems show similar voltage degradation and anode ionomer oxidation, despite differences in ionomer chemistry.

### *Degradation in electrodes with stabilizing additives*

Despite Nafion being a cation-conducting polymer, some HEM studies have pursued it as a binder to improve system lifetimes (because PEM electrolyzers show far superior stability). A Nafion anode PTE was prepared with IrO<sub>x</sub> catalyst on platinized Ti and operated with a TP-85 membrane and Pt-black/TP-85 cathode PTE. The performance and durability were compared to a conventional PEM baseline with a Nafion membrane and Pt-black/Nafion cathode. The PEM electrolyzer reached 2 V at 2.5 A cm<sup>-2</sup> (Fig. 7a). The PEM cells were operated at 1 A cm<sup>-2</sup> and 2.5 A cm<sup>-2</sup> to compare equivalent current and voltage conditions to the performance of the TP-85 HEM and ionomer system. Both PEM systems showed degradation rates below 1 mV/h (Fig. 7b). There was some initial voltage degradation, which is common for the startup of PEM systems as cell break-in/conditioning is longer, often many hours, during which ion transport channels are established. Further, most PEM electrolyzers use catalyst-coated membranes, while the PEM devices prepared here were catalyst-coated PTEs for direct comparison to the HEM electrolyzers. The initial degradation may be attributed to interfacial optimization between the catalyst layer and membrane. The degradation rate stabilizes to near-expected PEM rates. The degradation rate of the Nafion PTE operated with a HEM was an order of magnitude larger than that of the PEM at the equivalent operating current. XPS analysis of the surface of the PEM-operated Nafion anodes shows no obvious oxidation of the pristine material (Fig. 7c, yellow and green). However, the surface of the HEM-operated Nafion shows the growth of C-C and oxidized carbon species, a decrease in the higher C-F contribution, and a loss of higher binding energy F, consistent with a loss of CF<sub>3</sub> content in the polymer. The sulfonate group is still resolvable, but with higher signal noise level than the PEM system. This suggests a side chain scission or loss mechanism, which is believed to be a dominant degradation pathway for Nafion polymer.<sup>25, 55</sup>



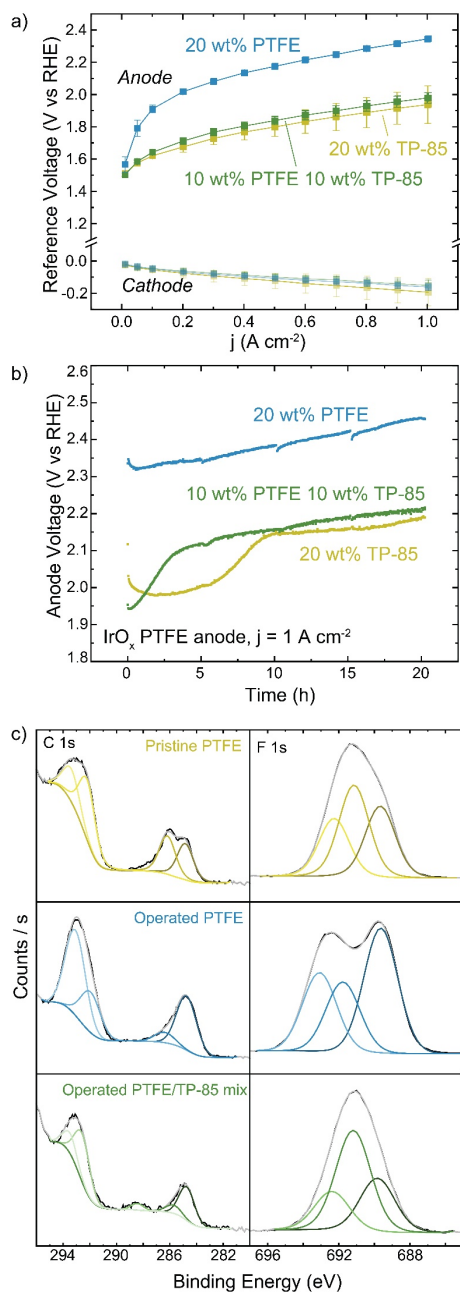
**Figure 7.** Nafion PTE operation in different membrane-pH environments. All cells were operated with a Nafion/IrO<sub>x</sub> catalyst on Pt/Ti anode, TP-85 or Nafion membrane, and Pt-black/TP-85 or Pt-black/Nafion cathode (matching the membrane). a) polarization comparison of Nafion PTE operating in a PEM MEA (green) and HEM MEA (blue). b) Nafion anode durability when operating in a PEM MEA at  $1 \text{ A cm}^{-2}$  (yellow) and  $2.5 \text{ A cm}^{-2}$  (green) and HEM MEA at  $1 \text{ A cm}^{-2}$  (blue). c) XPS of Nafion PTEs before operation (yellow), after operation with a PEM MEA at  $2.5 \text{ A cm}^{-2}$  (green) and after operation with a HEM MEA at  $1 \text{ A cm}^{-2}$  (blue). Degradation at the Nafion anode PTE is only observed when operating with a HEM.



When operated with a HEM, the Nafion anode could create a bipolar interface between the anode and membrane, with proton transport through the anode and hydroxide transport from the cathode through the HEM recombining to form water at the anode/membrane interface. However, studies using mixed cation-ionomer/alkaline-membrane devices suggest the membrane pH environment will dictate the pH at the electrode/membrane interface more than ion transport in the ionomer of the catalyst layer.<sup>56, 57</sup> The XPS degradation studies here support the existence of a high pH environment at the catalyst layer/HEM interface. SEM cross-section analysis did not yield conclusive results regarding bulk catalyst-layer degradation, as the Nafion content was only 5% and no significant difference in ionomer environment is observed between the pristine Nafion PTE and the electrode operated with a HEM (Fig. S19).

Nafion is known to be stable across a wide pH range and as a membrane is chemically stable in many acid and alkaline electrochemical device applications. However, as a binder in a HEM catalyst layer it experiences high-surface-area contact with the strongly oxidizing anode catalyst and is exposed to a high concentration of radical oxygen species from intermediates. Combined with the high-pH environment, even Nafion suffers thus oxidative damage.

One mechanistic explanation for this broad instability is that the ionomer near the catalyst is polarized in the strong double-layer electric field, leading to increased susceptibility to nucleophilic attack by  $\text{OH}^-$ , whereas in acidic systems no equivalent strong nucleophile exists. Alkaline oxidative environments are common in organic cleaning solutions used in semiconductor processing, for example RCA2.<sup>58</sup>



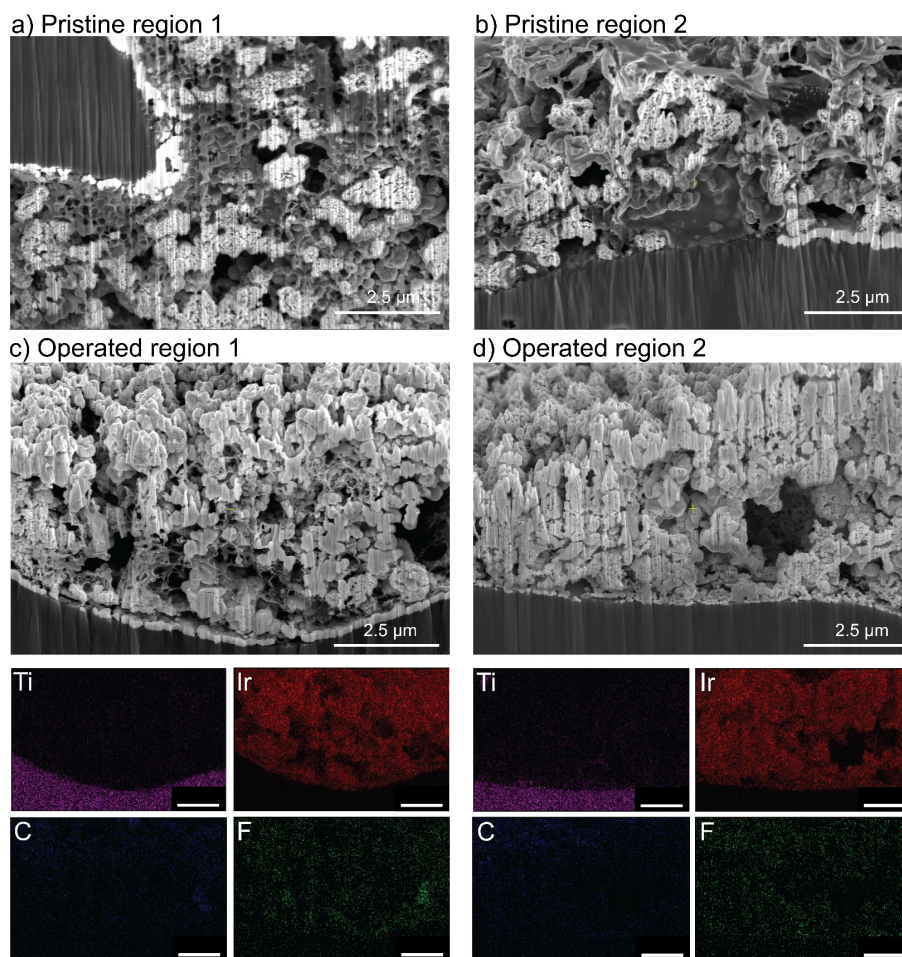
**Figure 8.** Effect of PTFE on electrolyzer performance. Cells were operated with an  $\text{IrO}_x$  catalyst on Pt/Ti anode with the indicated ionomer and/or binder, TP-85 membrane, and Pt-black/TP-85 cathode. a) polarization curves of the anode and cathode potentials. Data shown is the average of three replicate measurements and error bars are one standard deviation. b) anode voltage during durability testing at  $1 \text{ A cm}^{-2}$  and c) XPS of the pristine PTFE anode (yellow), operated PTFE anode (blue), and operated mixed PTFE/TP-85 anode (green). No oxidation is observed for the PTFE-only system.

PTFE is also used as a non-conductive stabilizing additive. Anode electrodes were prepared with  $\text{IrO}_x$  catalyst on platinized Ti and either TP-85, PTFE, or a 50:50 wt% mixture of the two in the catalyst ink. The mass of total binder and ionomer relative to catalyst in the ink was kept constant for all electrodes. The reference electrode technique was used to determine changes to the cathode and anode as components of the total-cell voltage. Interestingly, the replacement of half the mass of ionomer with PTFE did not affect cell performance (Fig. 8a). When only PTFE is present in the anode catalyst layer the voltage performance is very poor, as there is little-to-no ionic conductivity in the anode catalyst layer and thus only OER catalyst in direct contact with the HEM is active. The voltage-degradation profiles are quite different for the three electrodes (Fig. 8b). Both electrodes containing TP-85 ionomer show a rapid degradation onset before stabilizing. The degradation profile of the electrode that contains a PTFE/TP-85 mixture matches that of the electrode operated with 10% TP-85 (the equivalent mass of just TP-85 in the electrode) and reaches a steady-state degradation rate of 5.4 mV/h for the last 10 h, comparable to the TP-85 system. The rapid degradation onset is not observed for the PTFE-only system. The steady-state degradation rate is 7 mV/h over the entire run.

XPS of the mixed-polymer PTE shows C-F contribution from the PTFE and oxidized carbon (Fig. 8). XPS of the PTFE-only system shows no oxidized carbon by XPS (Fig. 8c). Interestingly, the operated PTFE shows a change in F 1s region. This suggests a defluorination degradation mechanism, however, this is not consistent with the lack of changes in the C-F content in the C 1s region. The change in the F 1s region is thus attributed to a polymer/sample inhomogeneity or sample-charging artifact.

Cross-sectioning of the pristine mixed PTFE/TP-85 electrode shows the distribution of binder was not homogenous through the catalyst layer (Fig. 9). The polymers are indistinguishable by

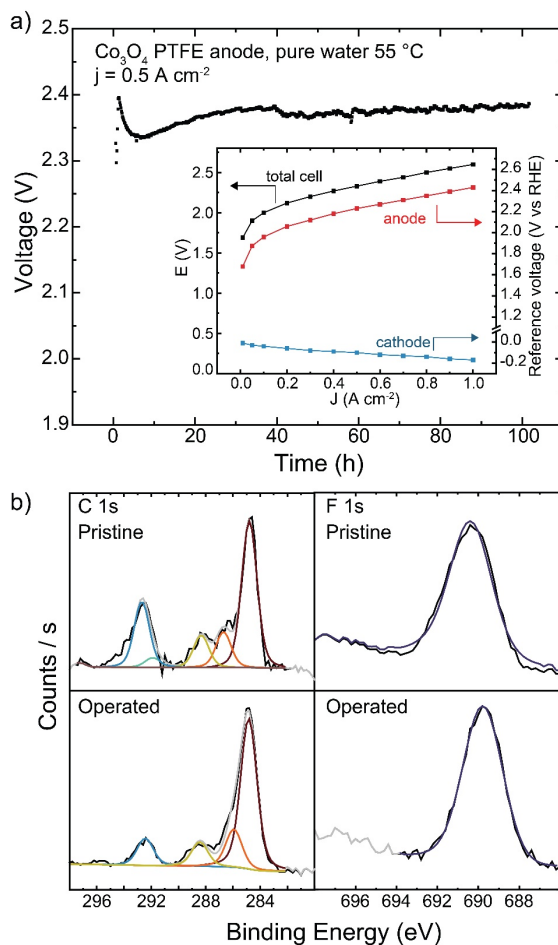
EDX, as they only contain C and F content, but they show distinctly different texture/morphology. Some regions show the binder has a smooth texture, the same as what is observed for the TP-85-only catalyst layers and is thus assigned to the TP-85 ionomer (Fig. 9b). Other regions show a porous binder environment (Fig. 9a), which is assigned as PTFE binder. After operation, the mixed PTFE/TP-85 electrode shows regions of the porous-textured binder (Fig. 9c) and large catalyst aggregations with no binder (Fig. 9d), which were likely regions where TP-85 has degraded and been flushed from the system.



**Figure 9.** Cross-sectional analysis of IrO<sub>x</sub>/mixed binder anode PTE. SEM images of different regions of the pristine catalyst layer (a and b) and SEM with EDX maps of two operated regions (c and d). Only PTFE binder is observed in the catalyst layer after operation.

Despite different degrees of oxidative damage, all systems show similar voltage degradation from 10 - 20 h. All three electrolyzers were operated with a TP-85 membrane that is susceptible to oxidation at the anode PTE surface. The similar steady-state degradation rate after 10 h may be due to catalyst oxidizing the membrane surface, increasing ionic resistance between membrane and catalyst layer. The PTFE-only system shows a slightly higher steady-state degradation rate, which is likely due to catalyst detachment or non-uniformities in the catalyst layer. PTFE contains no ionic components and does not interact strongly in the ink solution with the solvent or catalyst, creating a poor catalyst dispersion. The quality of the ink and catalyst layer deposited can impact device performance independent of the properties of the individual components.<sup>19</sup> Further, PTFE on its own is a poor catalyst binder, and the catalyst was observed to detach from the electrode during MEA preparation. SEM imaging shows the distribution of PTFE in the pristine catalyst layer was also non-uniform with large agglomerates of PTFE. The PTFE electrode charged too rapidly under the electron beam to obtain usable images (but a video is available as Sup. Video 1). The PTFE catalyst layer after operation shows large areas of the bare exposed Ti support and no large PTFE agglomerates, suggesting some PTFE washed away during operation.

As PTFE is the only polymer to show no oxidative damage during electrolyte-free operation in the current study, longer-duration testing was conducted. When operating with  $\text{Co}_3\text{O}_4$  catalyst at  $500 \text{ mA cm}^{-2}$ , the cell operated for 100 h with a degradation rate of 0.3 mV/h (Fig. 10a). No changes to polymer structure were observed by XPS after operation (Fig. 10b). While cell voltage was high for commercial applications, advanced electrode designs that use stable binders or additives, but maintain ionic conductivity in the catalyst layer, may be a viable solution for pure-water HEM operation.



**Figure 10.** Long-term operation of a PTFE-containing anode. a) HEM electrolyzer operation with a  $\text{Co}_3\text{O}_4/\text{PTFE}$ -coated stainless-steel anode PTFE, TP-85 membrane, and Pt-black TP-85 cathode for 100 h. Inset shows cathode and anode contributions to total cell voltage. b) XPS of the anode catalyst layer before and after 100 h operation.

### *Effect of supporting hydroxide electrolyte*

HEM electrolyzers have improved performance and stability when operating in KOH electrolyte.<sup>52, 59</sup> A  $\text{Co}_3\text{O}_4$  TP-85 anode on a Ni-alloy substrate (to prevent corrosion in KOH on the PTFE) was operated in 0.1 M KOH and also in electrolyte-free water (Fig. 11). When fed with KOH, the catalyst layer is saturated with electrolyte and all catalyst sites are exposed to  $\text{OH}^-$ , as opposed to pure water where only catalyst sites in contact with the ionomer are active. The addition of electrolyte is expected to increase catalyst electrochemically active surface area, increase ionic

conductivity of the catalyst layer, and decrease transport losses. This is reflected in the polarization data, as improvements in 0.1 M KOH are observed in the kinetic, ohmic, and mass-transport regions of the polarization curve (Fig. 11a). The cells were then operated at  $1 \text{ A cm}^{-2}$  for 20 h (Fig. 11b), and a smaller degradation rate  $< 1 \text{ mV/h}$  was found, compared to the rapid degradation of the pure water cell at  $17 \text{ mV/h}$ . A third cell was then operated with 0.1 M KOH at  $3 \text{ A cm}^{-2}$  so the starting operating voltage was  $\sim 2 \text{ V}$  where ionomer oxidation is known to occur in the electrolyte-free water system. The voltage was also more stable at a higher operating current, with a cell degradation of  $2.4 \text{ mV/h}$ . The anodes operated in 0.1 M KOH also show no obvious evidence of oxidized carbon, even after operating at voltages comparable to the electrolyte-free-water devices (Fig. 11c). Only the electrolyte-free cell shows a growth of oxidized carbon in conjunction with a loss of N and F signal.

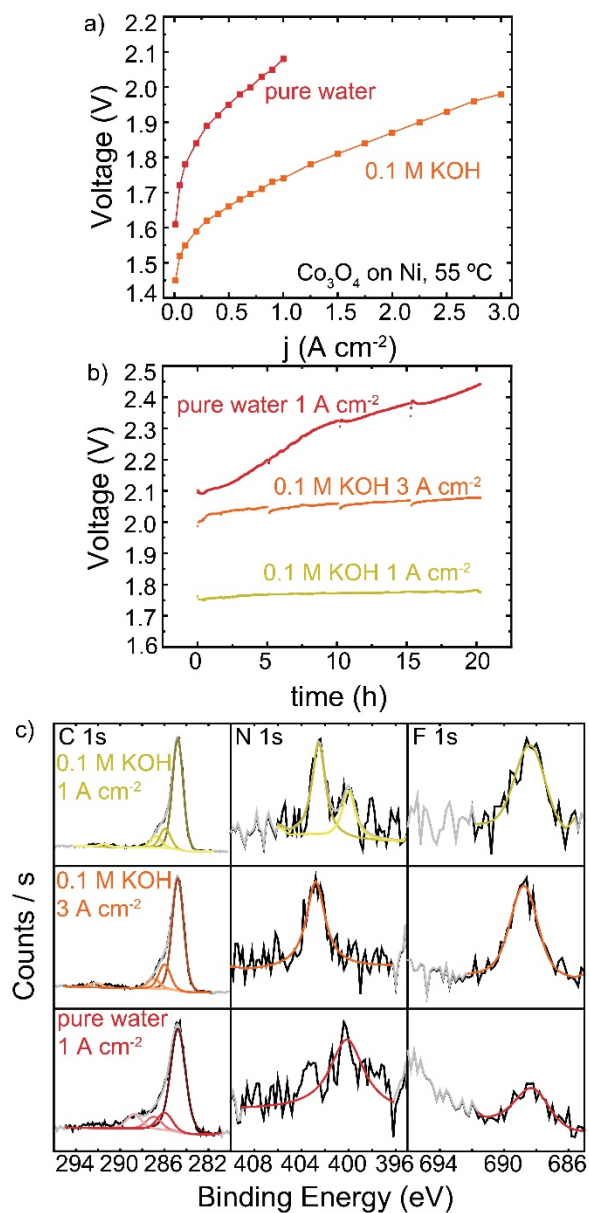
In electrolyte-free water, the weakest, most-easily oxidized polymer sites degrade first. This leads to an increase in cell voltage, which may induce a larger driving force at the remaining catalyst/ionomer interface for oxidation, driving cascading degradation until substantial ionomer is oxidized. In KOH, the degradation of ionically conductive polymer is compensated by the presence of supporting  $\text{OH}^-$ . Local oxidation may lead to some catalyst detachment and loss of binder but does not appear to dramatically increase cell voltage and therefore does not increase the driving potential for oxidation.

The potential distribution and structure of the electrical double layer at the catalyst surface may be quite different in electrolyte-free water versus in supporting electrolyte. In alkaline conditions, metal-oxide surfaces are likely negatively charged (due to deprotonation) leading to absorption of cationic or polymer backbone groups from the ionomer, as has been invoked earlier for other reasons.<sup>35, 38, 60-65</sup> Without supporting electrolytes, ionomer therefore must play a

fundamental role in the formation of the double layer requiring it to be in close vicinity to the polarized catalyst. The presence of mobile, soluble ions in supporting electrolyte likely leads to displacement of ionomer from direct involvement in the double layer, and this may be responsible for substantially reducing the degradation rate compared to pure water. Alternative strategies to exclude ionomer from the double-layer region therefore might be expected to also reduce oxidation rates.

While these results show operation in supporting electrolyte suppresses ionomer oxidation improving cell stability, the durability testing here was relatively short. The ionomer and membrane may continue degrading at longer operating time, particularly over months or years, leading to slow catalyst detachment or membrane thinning as is observed on a shorter time-scales in the pure water tests.





**Figure 11.** HEM electrolyzer operation in 0.1 M KOH versus pure-water feed. All cells were operated with a  $\text{Co}_3\text{O}_4$ /TP-85-coated Ni PTE, TP-85 membrane, and Pt-black/TP-85 cathode. a) polarization curves of electrolyte-free water (red), and 0.1 M KOH (orange) water feed, b) durability of electrolyte-free water (red) and 0.1 M KOH (yellow) feed at 1  $\text{A cm}^{-2}$  and 0.1 M KOH at 3  $\text{A cm}^{-2}$  (orange; for operation at a comparable starting voltage to the electrolyte-free water system). Even under high voltages/currents, the presence of 0.1 M KOH dramatically suppresses oxidation, perhaps due to differences in double-layer structure.

## Conclusion

We compared HEM electrolyzer operation with chemically varied ionomers, catalyst layer additives, and feed modes to understand the extent of ionomer oxidation and its impact on cell performance. Anode ionomer oxidation is the dominant degradation mechanism for all HEM-based devices operating in nominally pure water. All hydrocarbon-based anion-exchange ionomers oxidize rapidly, losing both backbone and cationic side-chain groups. Nafion oxidizes in a HEM electrolyzer but not PEM electrolyzer, indicating the high rate of degradation can be in part attributed to the combination of the strongly oxidizing environment and high pH. No oxidative damage was observed when using PTFE, showing the promise of stable additives in improving HEM electrolyzer operation.

This work illustrates the significant challenge facing pure-water HEM electrolysis, as no organic ion-conducting material was found to be stable under electrolyte-free operating conditions. While PTFE showed stable operation, the high ion-transport resistance in the catalyst layer results in low voltage efficiencies and is therefore not a promising route to commercialization on its own. For nominally-pure-water operation, next-generation HEM cells must look beyond solely ionomer innovations to advanced catalyst layers. Improved catalyst-layer interfacial design should minimize ionomer contact, and therefore degradation, but maintain OH<sup>-</sup> conductivity. These could enable competitive performance and lifetimes for commercialized pure-water HEM electrolyzer devices at dramatically lower materials costs than current membrane technologies.

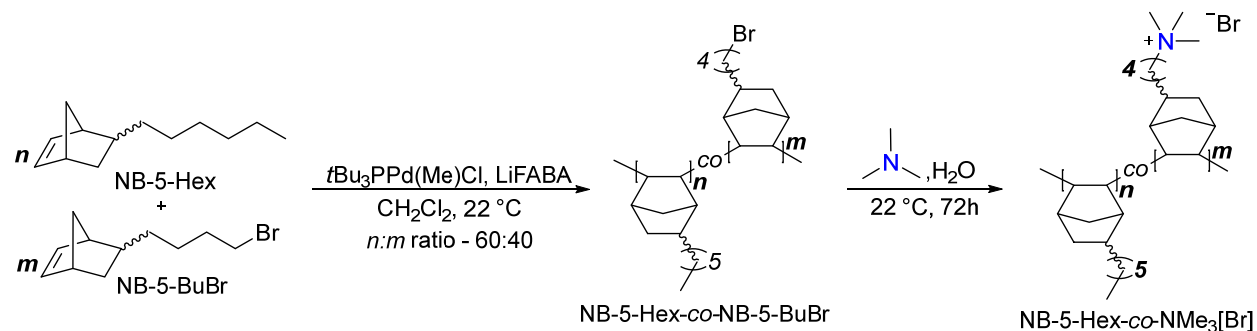
## Materials and Methods

*Polynorbornene ionomer synthesis.*

*Materials.* All chemicals were purchased from commercially available sources and were used as received. Tri-tert-butylphosphine palladium (II) methyl chloride was synthesized with modifications to an existing literature procedure.<sup>66</sup> 5-hexylbicyclo[2.2.1]hept-2-ene (NB-5-Hex) and 5-(4-bromobutyl)bicyclo[2.2.1]hept-2-ene (NB-5-BuBr) were prepared according to prior work.<sup>67</sup> All polymerizations were performed in anhydrous, degassed CH<sub>2</sub>Cl<sub>2</sub> under N<sub>2</sub>. Initiation of the Pd catalyst to form the active complex was accomplished using tetrakis(pentafluorophenyl)boron lithium ethyl etherate.

*NMR Analysis.* All NMR spectra were recorded on a 500 MHz Bruker Avance 3 Spectrometer or a 500 MHz Bruker Neo Spectrometer with Prodigy Cryoprobe. The <sup>1</sup>H NMR spectra were referenced to residual CHCl<sub>3</sub> (7.26 ppm).

*Gel-Permeation Chromatography (GPC).* Measurements were performed on a Waters Instrument equipped with a 2690 autosampler, a Waters 2414 refractive index (RI) detector, and two SDV columns (Porosity 1000 and 100000 Å; Polymer Standard Services). The eluent tetrahydrofuran (THF) was doped with 10 mM lithium bis(trifluoromethanesulfonyl)imide (flow rate of 1 mL/min, 40 °C). A nine-point calibration based on polystyrene standards (Polystyrene, ReadyCal Kit, Polymer Standard Services) was applied for determination of molecular weight.



**Scheme 1.** General synthesis of 60:40 NB-5-Hex-co-NMe<sub>3</sub> HEM

*Statistical copolymerization procedure for 60:40 NB-5-Hex-co-NB-5-BuBr copolymer.* In a N<sub>2</sub> glovebox, tetrakis(pentafluorophenyl)boron lithium ethyl etherate (0.0264 mmol), tri-tert-butylphosphine palladium (II) methyl chloride (0.0264 mmol), and dry CH<sub>2</sub>Cl<sub>2</sub> (6.6 mL) were added to an oven-dried Schlenk flask equipped with a stir bar. 5-n-hexyl-2-norbornene (7.92 mmol) and 5-(4-bromobutyl)-2-norbornene (5.28 mmol) were added to a separate vessel and dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (59.1 mL). Both solutions were brought to a benchtop stir plate, and the Pd catalyst reaction mixture was stirred for 15 min at 22 °C to ensure formation of the active cationic Pd catalyst. The solution of 5-*n*-hexyl-2-norbornene and 5-(4-bromobutyl)-2-norbornene in CH<sub>2</sub>Cl<sub>2</sub> was then injected into the activated catalyst solution. The polymerization reaction was stirred, and a 0.05 mL aliquot was removed at various timepoints for crude analysis by <sup>1</sup>H NMR spectroscopy to ensure complete consumption of the two monomers (disappearance of the vinyl protons). Polymers were precipitated into a large excess of methanol, which yielded an off-white stringy polymer that was filtered and dried *in vacuo* for 17 h at 22 °C (2.51 g, 96% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ ppm: 3.4 (br s, 2H), 2.6 – 0.96 (br, all other protons except for hexyl norbornene -CH<sub>3</sub>), 0.88 (br s, 4.5 H) (Fig. S2).

*Functional group incorporation.* Incorporation of NB-5-BuBr in the NB-5-Hex-co-NB-5-BuBr copolymers was determined as in our prior report.<sup>67</sup> The ratios of the -CH<sub>2</sub>Br signal from the bromobutyl chain and the -CH<sub>3</sub> signal from the hexyl chain were compared to determine the relative ratio of the two monomers. The integration for the methylene signal was set to two (corresponding to one repeat unit of BrBuNB) and the value for the hexyl signal was divided by three to determine the relative ratio of hNB units. A sample calculation is shown in Figure S2. In

the  $^1\text{H}$  NMR spectrum for the 60:40 copolymer, a 2:4.5 ratio should be observed for the  $-\text{CH}_2\text{Br}$  signal on the NB-5-BuBr the terminal methyl group from the hexyl chain of the NB-5-Hex, so the reported assignments for the terminal methyl group are set to 4.5.

*Solution casting of 60:40 NB-5-Hex-co-NB-5-BuBr copolymers.* 150 mg of polymer was dissolved in 3 mL of  $\text{CHCl}_3$ . Upon complete dissolution, the solution was filtered through a 0.22  $\mu\text{m}$  syringe filter onto a stainless-steel dish (diameter – 5 cm). The  $\text{CHCl}_3$  evaporated over an hour to afford a clear freestanding film, which was removed from the dish by immersion in deionized water. The polymer was then dried *in vacuo* to remove water and any other residual solvents.

*Synthesis of 60:40 NB-5-Hex-co-NMe<sub>3</sub> Polymer.* The dried NB-5-Hex-co-NB-5-BuBr polymer film was immersed in an aqueous solution of 25% (w/v) trimethylamine for 48 h at room temperature. The solution was then replaced with fresh aqueous trimethylamine and the films were immersed for an additional 24 h. The films were removed and immersed in 3  $\times$  100 mL portions of deionized water for 1 h each. The films were then dried *in vacuo* to afford the trimethylammonium-functionalized polymers. Accurate  $^1\text{H}$  integrals were difficult to obtain due to overlapping solvent and signal broadness. Spectral data:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ : $\text{CD}_3\text{OD}$  1:1)  $\delta$  ppm: 3.0 (br s, 9H,  $\text{NMe}_3$   $-\text{CH}_3$ ), 2.5 – 0.76 (br, all other protons except for hexyl norbornene  $-\text{CH}_3$ ), 0.56 (br s, 6H) (Fig. S2).

*Catalyst dispersions.* Materials were prepared as previously reported.<sup>19, 27</sup> Pt-black (high surface area, Fuel Cell Store) was used as the cathode catalyst for all studies.  $\text{IrO}_x$  (core-shell Ir/ $\text{IrO}_x$ , Fuel Cell Store) or  $\text{Co}_3\text{O}_4$  (99.5%, 30-50nm, US Nano) nanoparticles were used as the anode catalyst.

For HEM devices, cathode and anode ink solutions were prepared identically. For every 100 mg of catalyst, 0.5 g of 18.2 M $\Omega$ ·cm H<sub>2</sub>O was added, followed by 1.7 g of 2-propanol. The PiperION-A5 ionomer suspension (TP-85, 5% w/w, Versogen) was added (200 mg) to yield the final 10 wt. % ( $w_{\text{ionomer}}/w_{\text{catalyst}}$ ) ink. For PEM studies, inks were prepared similarly but with 100 mg of D520 Nafion dispersion (alcohol-based 1000 EW at 5 wt%, Fuel Cell Store) as the ionomer to yield the final 5 wt. % ( $w_{\text{ionomer}}/w_{\text{catalyst}}$ ) ink. Inks were then bath-sonicated (Branson 1510R-MTH) with 5 °C water recirculating to maintain a room temperature bath. Inks were sonicated for a minimum of 1 h (Pt and Co<sub>3</sub>O<sub>4</sub>) or 2 h (IrO<sub>x</sub>) until fully dispersed.

*Electrode preparation.* Toray carbon paper (090, Fuel Cell Store) was used as the cathode electrode material for all studies. The anode was either a stainless-steel mesh filter material (25AL3, Bekaert), platinized Ti (Nel Hydrogen), or Ni-alloy (Hastelloy X, UNS 06002, Technetics Inc.). In all cases the support was taped to a hot plate set to 80 °C and catalyst inks were air-brush coated onto the substrate (Testors, Aztek A2203, part of the Amazing Airbrush kit). A catalyst loading between 3 and 3.5 mg·cm<sup>-2</sup> was used to ensure a sufficiently thick catalyst layer for cross-sectional analysis. Loading was determined by mass difference. A thin layer (~5 wt. %  $w_{\text{ionomer}}/w_{\text{catalyst}}$ ) of ionomer suspension was sprayed on top of the catalyst layer.

*Membrane conditioning.* PiperION TP-85 (40  $\mu$ m, Versogen) membranes were conditioned according to manufacturer instructions. The membranes were soaked in 0.5 M KOH for 48 h, replacing the solution with fresh KOH after 24 h. Membranes were stored in 0.5 M KOH solution when not in use. For PEM experiments, Nafion (212, Fuel Cell Store) was hydrated in 18.2 M $\Omega$ ·cm water and stored in water when not in use.

*MEA assembly.* MEAs were assembled in an adapted PEM fuel-cell hardware (Fuel Cell Technologies, 5 cm<sup>2</sup> hardware) with stainless-steel (pure water feed) or Ni (KOH feed) anode flow fields and a graphite cathode flow field. Gasket material (0.005” and 0.002” PET/PETE clear film, McMaster-Carr) was laser cut to an active area of 1 cm<sup>2</sup>. Sintered platinized Ti frits (Baoji Yinggao Metal Materials Co., Ltd.) were used as spacers between the flow fields and PTEs to maintain uniform compression across the MEA (Fig. S9a). The conditioned membrane was submerged in a beaker of 18.2 M $\Omega$ ·cm water then rinsed with 18.2 M $\Omega$ ·cm water for 10 s before assembly. Materials were assembled in the stack and tightened to 5.6 N·m.

*Assembly with an integrated reference electrode.* For some experiments, the cells were operated with an integrated reference electrode. Cells with an integrated reference electrode were constructed as previously reported.<sup>47</sup> An extended description of the reference-electrode technique is included in the supporting information (Fig. S3-12). Upon assembly, a strip of membrane is laid next to the anode porous transport electrode (PTE) and extended outside the cell hardware. The HEM is laid on top of the PTE and overlaps with the strip. The cathode PTE is placed on top, and the cell is assembled as usual. After assembly, a O-ring joint to straight-glass adapter is clamped to the membrane strip and filled with 0.1 M KOH (Fig. S12). A reference electrode (Hg/HgO, CH Instruments Inc.) is inserted in solution and the glassware is sealed with parafilm. The strip is kept hydrated with an intravenous bag dripping 18.2 M $\Omega$ ·cm water on the strip every 7 min (Fig. S12).

*Electrolyzer operation.* A water supply reservoir was filled with 18.2 M $\Omega$ ·cm water. This water is nominally pure (but not necessarily 18.2 M $\Omega$ ·cm), and is referred to as “electrolyte-free” water feed in this context. Water was flowed to either the anode or both cathode and anode at 125 mL·min<sup>-1</sup>. The anode water flow was recirculated in the system, while the cathode water was flowed into a chemical hood, degassed in a plastic jug, then recirculated back into the water tank. Cell temperature was monitored with a thermocouple inserted into the cell hardware. Cells were conditioned by stepping the current from 100 mA·cm<sup>-2</sup> to 1 A·cm<sup>-2</sup>, holding for 60 s at each step up to 700 mA cm<sup>-2</sup>, then 90 s from 800 mA cm<sup>-2</sup> to 1 A cm<sup>-2</sup>. The cell was then held at 1 V to test for pinholes or other short-circuit pathways in the cell (the steady state electrolysis current decays to zero at < 1.23 V, while shunt currents persist). When operating with KOH this step was bypassed, as ions can be transported across the membrane below 1.23 V when operating with supporting electrolyte. The cell was brought back to 1 A·cm<sup>-2</sup> for 2 min to stabilize. The potential was then recorded, and the current was decreased in 100 mA·cm<sup>-2</sup> steps measuring the potential for 10 s at each step to collect the polarization (*J-V*) curve. When operating with the reference electrode, water flow to the cathode was closed and the cell was held at 100 mA·cm<sup>-2</sup> for 1 min to accumulate H<sub>2</sub> on the Pt catalyst. The cell OCV was then measured for 1 min and the reference electrode voltage versus the cathode (now poised at RHE) was used to calibrate the reference voltage for each run. The cell was held at constant current for stability testing. Galvanostatic electrochemical impedance spectroscopy (GEIS) was collected at 50 mA cm<sup>-2</sup> and 500 mA cm<sup>-2</sup> after collecting the *J-V* curve every 5 h of the stability run.

*Post-operation sample preservation.* After operation, cells were disassembled according to standard methods.<sup>68</sup> MEAs were quenched in 3 M NaCl solution overnight to exchange OH<sup>-</sup> for



Cl<sup>-</sup> ions. The MEA components were then submerged in a beaker of 18.2 MΩ·cm water and rinsed vigorously for 30 s before air drying at room temperature overnight.

*XPS analysis.* Catalyst layers were analyzed with X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250 (ThermoScientific) using an Al K $\alpha$  monochromated (20 eV pass energy, 500  $\mu$ m spot size) source. The samples were charge-neutralized using an in-lens electron source. The stage was electrically floated to reduce sample charging. Spectra were analyzed using ThermoScientific Avantage 4.88 software. The C 1s signal at 284.8 eV was used to calibrate the binding energy scale.

*SEM cross-sectioning and imaging.* PTEs were cross-sectioned and imaged using a plasma focused-ion-beam (PFIB) scanning-electron microscope (SEM) (Helios Hydra Multi-Ion Species Plasma FIB, Thermo Fischer). The ion beam was operated at a 30 kV accelerating voltage. The beam was focused at 0.1 nA, as the current was sufficiently low to not damage the polymer in the catalyst layer. Current was then increased to 1 or 2.5  $\mu$ A without imaging and a section of PTE was blind cut. The edge was then polished at 15 nA, again without active imaging to not damage the catalyst layer. Electron imaging and energy dispersive spectroscopy (EDS) was collected at a 10 kV accelerating voltage and 0.8 or 1.6 nA electron beam current.

### **Author Contributions**

G.A.L. and S.W.B. designed the study, analyzed the data, and wrote the manuscript. G. A. L. collected and analyzed all electrolyzer, SEM, and XPS data, with electrolyzer support from W. L. T. and SEM support from V. B. The PNB ionomer system was designed by J. C. G. and K. J. T.

N., with synthesis and characterization conducted by J. C. G.

## Acknowledgements

This work was supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Fuel Cell Technologies Office (FCTO) under award DE-EE0008841 and by De Nora Tech, LLC. J. C. G. acknowledges support from the Center for Alkaline-Based Energy Solutions (CABES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES) under Award DE-SC0019445. G. A. L. acknowledges additional support from the University of Oregon through the John Keana Graduate Fellowship. We acknowledge the use of shared instrumentation in the Center for Advanced Materials Characterization in Oregon (CAMCOR). The authors are grateful to Nel Hydrogen for providing the platinumized PTL material, Dr. Stephen Golledge for XPS analysis guidance, L. Chen for assistance with the integrated reference electrode experiments, the Yan lab for their advice regarding KOH electrolyzer testing, and Cy Fujimoto and Nick D'Antona for insightful discussion.

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