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# Addressing the Challenge of Electrochemical Ionomer Oxidation in Future Anion Exchange Membrane Water Electrolyzers

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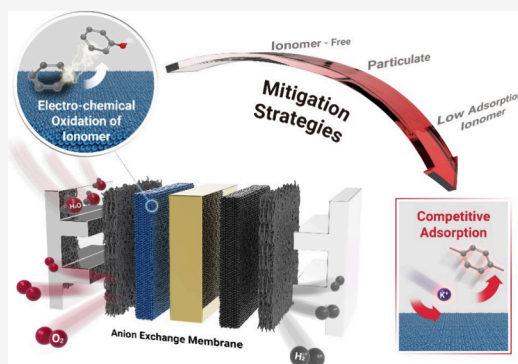


Article Recommendations



Supporting Information

**ABSTRACT:** Hydrogen production through anion-exchange membrane water electrolyzers (AEMWEs) offers cost advantages over proton-exchange membrane counterparts, mainly due to the good oxygen evolution reaction (OER) activity of platinum-group-metal-free catalysts in alkaline environments. However, the electrochemical oxidation of ionomers at the OER catalyst interface can decrease the local electrode pH, which limits AEMWE performance. Various strategies at the single-cell-level have been explored to address this issue. This work reviews the current understanding of electrochemical ionomer oxidation and strategies to mitigate it, providing our perspective on each approach. Our analysis highlights the competitive adsorption strategy as particularly promising for mitigating ionomer oxidation. This Perspective also outlines future directions for advancing high-performance alkaline AEMWEs and other energy devices using hydrocarbon ionomers.



Water electrolysis emerges as a key technology for sustainable hydrogen production, leveraging renewable and nuclear resources to offer a carbon-free solution. Low-temperature water electrolysis offer distinct advantages over high-temperature counterparts due to their ability to operate with short start–stop times and exhibit scalable flexibility, ranging from sub-kW to tens of MW. Proton exchange membrane water electrolyzers (PEMWEs) represent a mature technology capable of generating compressed hydrogen at a high production rate, achieving a heating value efficiency of at least 74% at 2 A cm<sup>-2</sup>.<sup>1</sup> However, PEMWEs rely on platinum-group metal (PGM) catalysts, such as iridium and platinum, along with expensive corrosion-resistant separator plates. These requirements pose significant challenges in reducing hydrogen production costs, particularly in large-scale systems.<sup>2</sup>

Anion-exchange membrane water electrolyzers (AEMWEs) present a promising alternative, mirroring the principles of PEMWEs but eschewing expensive materials in favor of PGM-free catalysts and more cost-effective separator plates.<sup>3</sup> However, the performance and durability of AEMWEs, which are fed with pure water, are notably inferior to their PEMWE counterparts.<sup>4,5</sup> The main cause of the poor performance of AEMWEs has been the subject of much recent work. Voltage breakdown analysis has revealed that one

reason for the low performance of AEMWEs is carbonation and the resulting high ohmic resistance.<sup>6</sup> However, the carbonation issue does not appear to be the primary reason for the inferior performance, as shown in the cells heavily carbonated by circulating dilute K<sub>2</sub>CO<sub>3</sub> solutions that exhibited higher performance than those fed with pure water.<sup>7,8</sup>

Another commonly stated reason is low local pH at the catalyst-ionomer interface with a pure water supply.<sup>9,10</sup> While the oxygen evolution reaction (OER) activity of catalysts increases with the local pH,<sup>11</sup> the high pH (≥14) driven by the high concentration of quaternary ammonium functional groups in the ionomer does not align with this hypothesis (Supporting Note 1). Furthermore, the pH effect alone cannot explain the shorter lifetime of pure water-fed AEMWEs<sup>12–15</sup> compared to the PEMWEs<sup>16,17</sup> and 1 M KOH-fed AEMWEs<sup>18–21</sup> that

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operate for several thousand hours without significant performance loss.

The disparity in materials within the membrane electrode assembly could be a critical factor contributing to the reduced performance of pure water-fed anion-exchange membrane water electrolyzers.

The disparity in materials within the membrane electrode assembly (MEA) could be a critical factor contributing to the reduced performance of pure water-fed AEMWEs. In an acidic PEMWE system, perfluorosulfonic acids (PFSAs) with a polytetrafluoroethylene backbone are standard, known for their minimal interaction with catalyst nanoparticles.<sup>22</sup> In contrast, AEMWE systems predominantly utilize hydrocarbon-based polymer electrolytes due to the challenges in stabilizing the junction point of the electron-withdrawing perfluoroalkyl chain and quaternized functional groups.<sup>23</sup> Conversely,

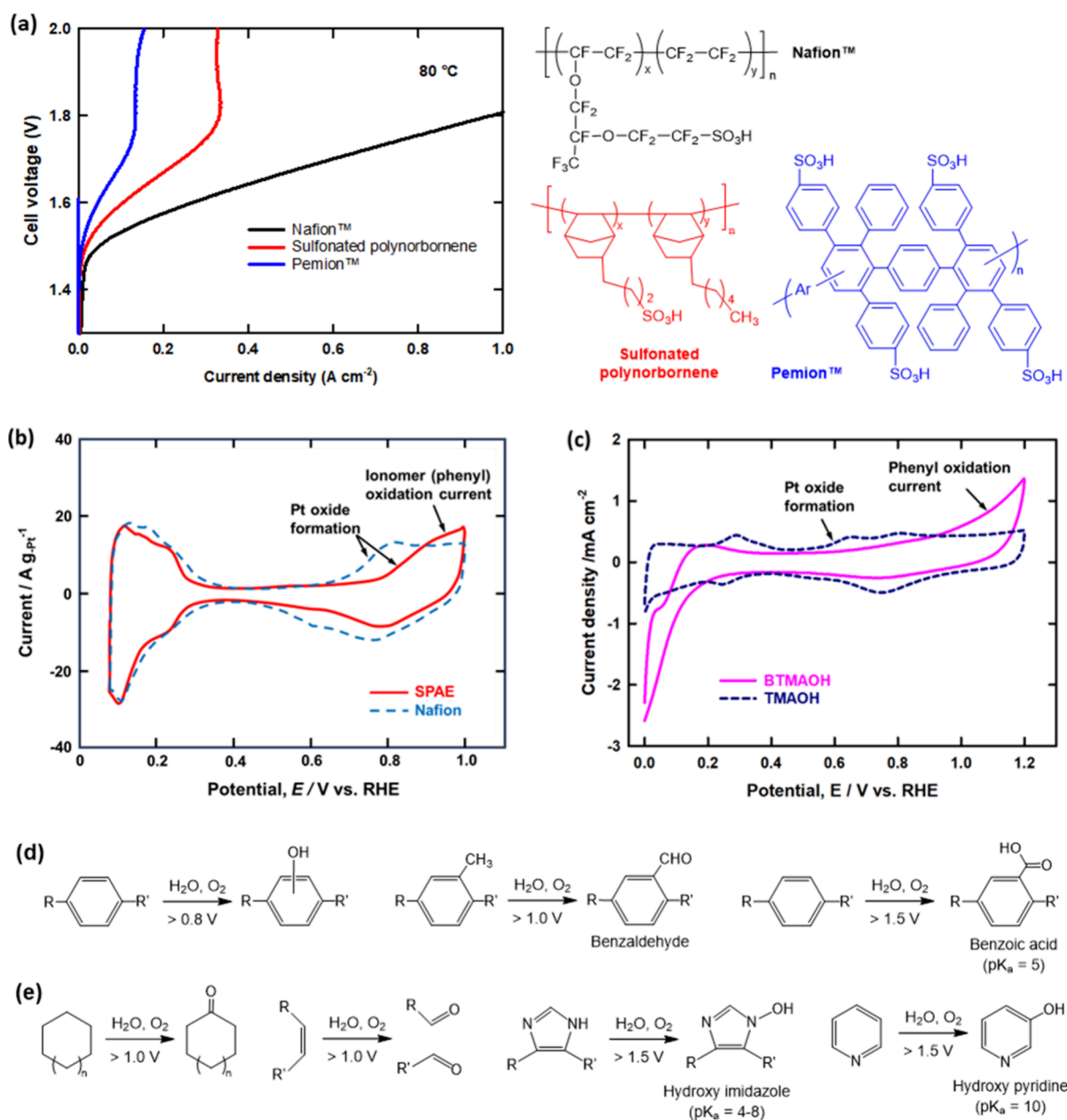


Figure 1. (a) Pure water-fed PEMWE performance comparison between PFSA ionomer and hydrocarbon-based ionomers. All cathodes were  $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$  with PFSA ionomer and the anode were loaded to  $0.4 \text{ mg}_{\text{IrO}_2} \text{ cm}^{-2}$  with the respective ionomer Pemion, sulfonated polynorbornene, or Nafion. The detailed polymer synthesis and testing method are described in Supporting Note 2. (b) CV comparison of PFSA Nafion-bonded and SPAE-bonded Pt/C catalyst. Reprinted in part with permission from ref 26. Copyright 2009 Elsevier. (c) CV comparison of Pt/C catalyst in 0.1 M tetramethylammonium hydroxide (TMAOH) and benzyltrimethylammonium hydroxide (BTMAOH) solution measured at  $25^\circ\text{C}$  and scan rate of  $20 \text{ mV s}^{-1}$  at 0 rpm. Adapted with permission from ref 27. Copyright 2007 American Chemical Society. (d) Electrochemical oxidation process of phenyl-containing compounds, and (e) electrochemical oxidation process of nonphenyl ionomer fragments.<sup>3,33–35</sup>

hydrocarbon ionomers easily adsorb onto catalyst surface and undergo oxidation at high electrochemical potentials, impacting the performance and durability of electrochemical devices.

This perspective article explores the electrochemical oxidation of hydrocarbon ionomers, assessing potential mitigation strategies while providing insights backed by single cell-level performance and durability data. Furthermore, we offer a forward-looking perspective on improving alkaline AEMWEs through these methods, laying the foundation for a more efficient and scalable AEMWE technology.

## ■ ELECTROCHEMICAL OXIDATION OF IONOMERS

Our initial investigation into the factors contributing to the subpar performance of pure water-fed AEMWEs focuses on the potential impact of the surface adsorption and electrochemical oxidation of hydrocarbon ionomers on OER catalysts. To substantiate this hypothesis, we examined whether hydrocarbon ionomer adsorption is also detrimental to PEMWE performance. This was achieved by comparing the PEMWE performance utilizing Nafion PFSA and more-adsorbing hydrocarbon ionomers at the anode (Figure 1a). Two hydrocarbon ionomers, Pemion and sulfonated polynorbornene, were chosen for the study. Pemion has a proton conductivity similar to Nafion (180 mS/cm) and sulfonated polynorbornene exhibits water uptake comparable to Nafion (34%) (Table S1). The electrolyzer, constructed with Nafion ionomer on both the cathode and anode, demonstrates robust performance with no noticeable mass transport limitations, achieving 1.0 A cm<sup>-2</sup> at 1.8 V. However, substituting solely the PFSA anode ionomer with the hydrocarbon-based ionomers impedes performance. This outcome underscores that the use of hydrocarbon ionomers can lead to substantial performance limitations in water electrolysis, irrespective of acidic or alkaline environments.

Detecting catalyst-ionomer interactions experimentally poses challenges, yet various analytical techniques have been employed.<sup>24,25</sup> The electrochemical oxidation of ionomers can be detected through electrochemical methods. In prior research, Watanabe et al. observed a significant reduction in the mass activity of a fuel cell MEA utilizing sulfonated poly(arylene ether) (SPAPE) compared to one employing Nafion PFSA ionomer.<sup>26</sup> The comparison of cyclic voltammograms (CVs) between the two MEAs revealed a shift in the onset potential of Pt oxide formation for the SPAPE cell toward a more positive value. Additionally, an increased current by electrochemical ionomer oxidation was observed beyond 0.8 V (Figure 1b). Similar CV behavior was noted under alkaline conditions (Figure 1c),<sup>27</sup> showing the depressed Pt oxide formation and emerging phenyl oxidative current beyond 0.8 V with the benzyltrimethylammonium hydroxide (BTMAOH) solution.

The immediate impact of electrochemical oxidation of hydrocarbon ionomer fragments is a change in local pH. Some oxidation products are acidic and neutralize quaternary ammonium groups, thereby reducing the local pH and resulting in lower oxygen evolution reaction activity of electrocatalysts.

The electrochemical oxidation of hydrocarbon structures is well-documented.<sup>28</sup> The most-studied ionomer fragment is the phenyl group, easily oxidized in the presence of PGM<sup>29</sup> and PGM-free<sup>30</sup> catalysts. Under the high anode potential of AEMWEs, various reactive oxygen-containing intermediates are likely formed on or near the OER catalyst, for example, hydroxide radicals, that can react with the phenyl groups to produce phenol at >0.8 V, benzaldehyde at >1.0 V, and benzoic acid at >1.5 V (Figure 1d).<sup>25,31</sup> The oxidizing potential can vary based on their substituents. The oxidized products can further oxidize to catechol, hydroquinone, and carbon dioxide or produce other electro-polymerized products. Electrochemical oxidation of cyclic alkanes and cyclic olefins such as norbornene occurs at ~1.0 V, producing cycloaliphatic ketones and aliphatic (di)carboxylic acids (Figure 1e).<sup>32</sup> Electrochemical oxidation of heterocycles, such as imidazole, indoles, or pyridine, occurs at relatively high (>1.5 V) and also varies based on the chemical environment.<sup>33,34</sup> Only unsaturated hydrocarbons (olefins) (oxidation potential: 1.9–2.8 V) and unactivated hydrocarbons (alkanes) (oxidation potential: > 2.7 V) might have sufficient electrochemical stability under the working voltage of AEMWEs.<sup>35</sup> The immediate impact of electrochemical oxidation of hydrocarbon ionomer fragments is a change in local pH. Some oxidation products, such as phenols (pK<sub>a</sub> = 10) and carboxylic acids (pK<sub>a</sub> = 4.9) are acidic and neutralize quaternary ammonium groups, thereby reducing the local pH and resulting in lower OER activity of electrocatalysts.<sup>36,37</sup> During extended-term operation, the reduction in the molecular weight of the ionomer causes catalyst particle loss and disintegration of electrodes.

## ■ FOUR STRATEGIES TO MITIGATE IONOMER OXIDATION

To counter the adverse effects of ionomer oxidation, several approaches have been explored in designing high-performance AEMWEs. This section discusses the four most successful strategies, outlining their pros and cons to provide guidance for future directions.

**Ionomer-Free Electrode.** This strategy involves eliminating ionomeric binders from electrodes and replacing them with liquid electrolytes, facilitating necessary hydroxide conduction. Incorporating ionomer-free OER catalysts can be achieved not only through free-standing catalyst form but also via advanced techniques like magnetron sputtering deposition<sup>38</sup> or *in situ* catalyst particle formation.<sup>39</sup> Conventional AEMs or non-quaternized ion-solvating membranes such as polybenzimidazole (PBI)<sup>40</sup> or poly(ethylene oxide)<sup>41</sup> can serve as separators.

The performance of ionomer-free AEMWEs heavily depends on the catalyst type and supporting electrolyte concentration. While self-supporting PGM-free catalysts can yield performance similar to zero-gap liquid alkaline electrolyzers employing a diaphragm membrane like Zirfon (Figure 2a), nanoparticle OER catalysts improve performance significantly (Figure 2b).

This approach addresses concerns related to unwanted ionomer adsorption and electrochemical oxidation. Demonstrations of high-performance using nanoparticle OER catalysts have been successful across various membrane types, surpassing the capabilities of traditional liquid alkaline systems. However, compared to conventional pure-water-fed AEMWEs, a drawback is the reliance on corrosive supporting electrolytes, which can lead to degradation of MEA components and increase system complexity. Decreasing the molar concentration of supporting electrolytes results in higher electrode

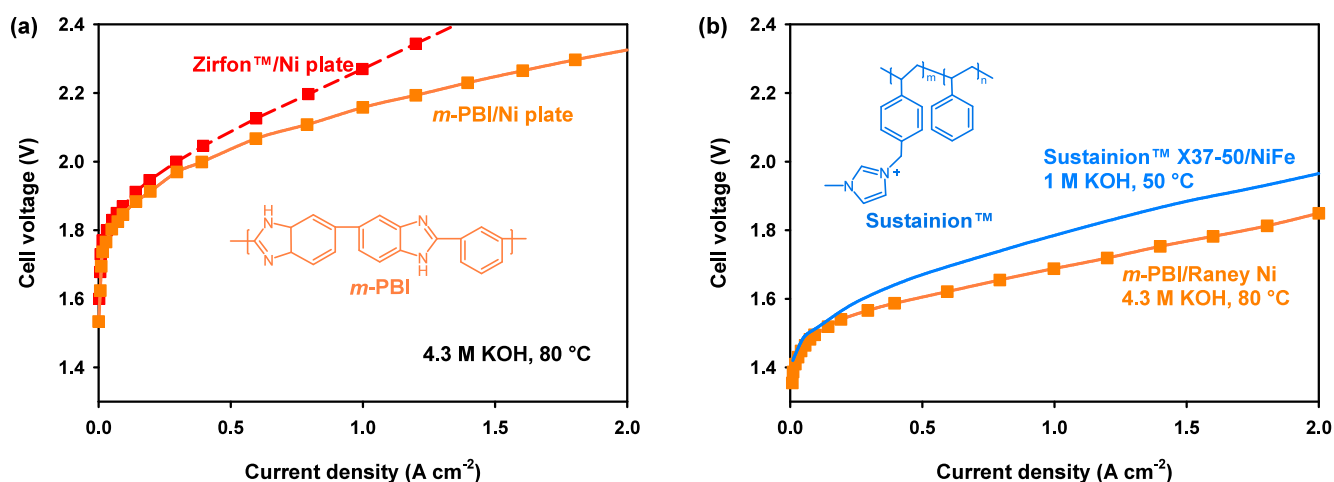


Figure 2. Performance of ionomer-free AEMWEs. (a) Comparison between Zirfon (thickness: 500  $\mu\text{m}$ ) and ion-solvating *m*-PBI membrane (thickness: 40  $\mu\text{m}$ ) with Ni-perforated plate OER catalyst. Adapted with permission from ref 40. Copyright 2019 Royal Society of Chemistry, CC-BY 3.0 (<https://creativecommons.org/licenses/by/3.0/>). (b) Performance with OER nanoparticle catalysts. MEA1 (light blue): membrane, quaternized (Sustainion X37-50, thickness: 50  $\mu\text{m}$ ); anode, NiFe; cathode, Pt/C (2  $\text{mg}_{\text{Pt}} \text{cm}^{-2}$ ); electrode preparation, modified-CCM with in situ catalyst synthesis; long-term test, degradation rate of 0.07  $\text{mV h}^{-1}$  after 200 h at 1  $\text{A cm}^{-2}$ . MEA2 (orange): membrane, poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole) (*m*-PBI, thickness: 40  $\mu\text{m}$ ); anode, Raney-type nickel; cathode, Raney-type nickel-molybdenum; electrode preparation, vacuum plasma spraying; long-term test, cell failed after  $\sim$ 130 h under current density cycling of 0.1  $\text{A cm}^{-2}$  for 16 h and 1  $\text{A cm}^{-2}$  for 8 h. Adapted with permission from ref 39. Copyright 2023 American Chemical Society. Adapted with permission from ref 40. Copyright 2019 Royal Society of Chemistry, CC-BY 3.0 (<https://creativecommons.org/licenses/by/3.0/>).

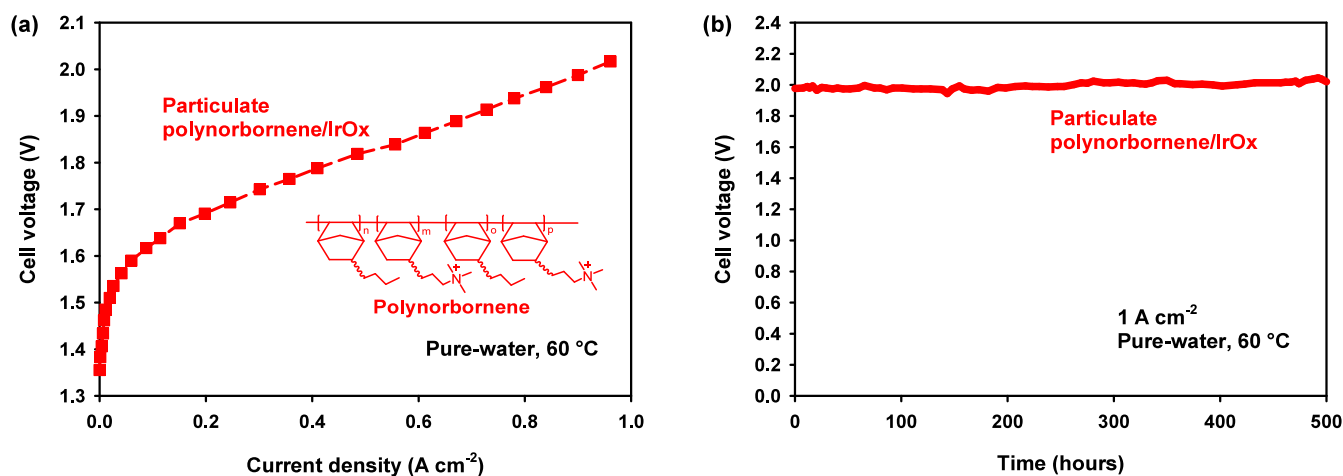


Figure 3. (a) Performance and (b) durability of particulate ionomer bonded AEMWEs under pure water feeding conditions: AEM, quaternized polynorbornene (thickness: 30  $\mu\text{m}$ ); anode, IrO<sub>x</sub>; cathode, PtNi. Reprinted with permission from ref 12. Copyright 2022 IOP Publishing Limited, CC-BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>).

overpotential,<sup>38</sup> making it challenging to achieve high performance for ionomer-free AEMWEs fed with pure water. The current technical challenge involves developing more-alkaline-stable membranes and advanced nanoparticle deposition that enable commercially viable performance and long-term electrolyzer operation (>10,000 h). Several recent papers reported sulfonation of ion-solvating PBI membranes enhances hydroxide conductivity by absorbing more KOH without a degradation penalty, offering new opportunities to develop high-performance AEMWEs.<sup>42,43</sup>

**Particulate Ionomeric Binders.** A unique strategy to minimize undesired ionomer-catalyst interactions is utilizing ionomers in particulate forms instead of traditional thin-film ionomer electrodes.<sup>44</sup> Typically, insoluble ionomers, such as quaternized ethylene tetrafluoroethylene (ETFE)<sup>45</sup> and polynorbornene,<sup>46</sup> have been employed in particulate iono-

meric binders. These ionomer systems possess phenyl-free polymer backbones, resulting in lower adsorption energy with OER catalysts.<sup>47</sup> In addition, the particulate form reduces contact with catalysts.

The loss of intimate interaction between the catalysts and ionomers can lead to new challenges particularly related to water transport and retention in the catalyst layer. Huang et al. have suggested that the heterogeneous electrode structure resulting from the use of particulate ionomers can lead to the formation of larger bubbles trapped inside the electrode, thereby impeding the mass transport of water.<sup>48</sup> There are several approaches that can manipulate water retention and transport within the electrodes. One possible method is to incorporate polytetrafluoroethylene (PTFE) coparticles to manipulate wettability and rapidly increase the generation of gas bubbles. Additionally, adding PTFE particles may provide

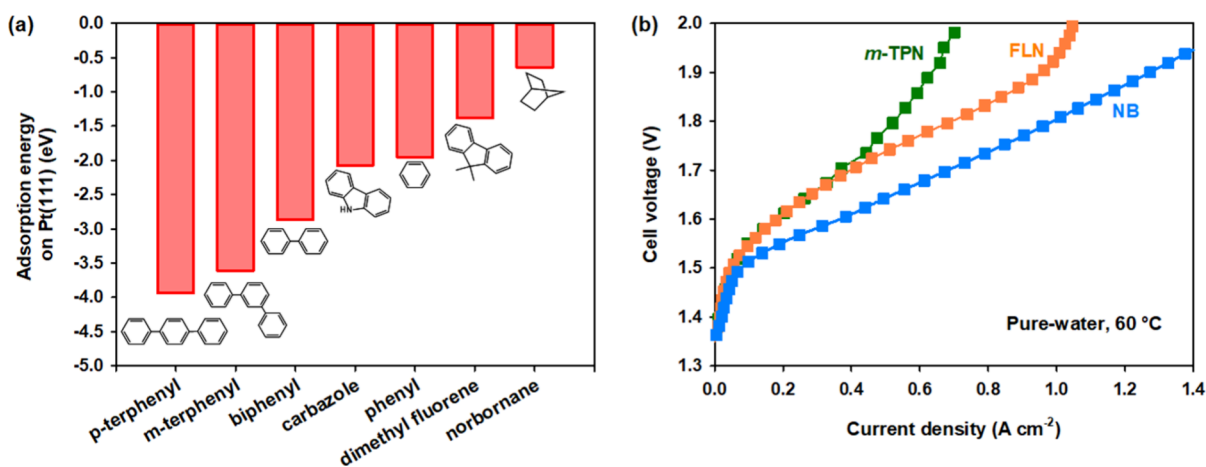


Figure 4. (a) Adsorption energy of ionomer fragments on Pt(111) surface calculated using optPBE-vdW functional.<sup>53</sup> (b) AEMWE performance comparison. Polarization curves of the MEAs using selected ionomers. All cells used the identical membrane (quaternized Diels–Alder polyphenylene) and catalysts (anode, IrO<sub>2</sub>, 2.5 mg<sub>IrO2</sub> cm<sup>-2</sup>; cathode, Pt/C 2.0 mg<sub>Pt</sub> cm<sup>-2</sup>). Reprinted with permission from ref 55. Copyright 2022 Wiley-VCH GmbH.

an efficient hierarchical structure that increases the tolerable volume fraction of water within the electrodes. Controlling water content can also ensure adequate localized pH levels for optimal catalyst OER activity. Therefore, there is a need to optimize the size and distribution of ionomer particles, catalysts, electrodes, and their integration into operational AEMWEs.<sup>49</sup>

Ensuring adequate localized pH levels for optimal electrochemical activity of OER catalysts is another consideration, necessitating precise design adjustments in ionomer particles, catalysts, electrodes, and their integration into operational AEMWEs.

The introduction of particulate ionomeric binders, with mean particle size of  $24.5 \pm 9.8 \mu\text{m}$ , was pioneered in AEM fuel cells by Mustain and co-workers<sup>45</sup> and has since been extended to AEM electrolyzers. These binders have showcased outstanding performance in fuel cells, achieving peak power densities of up to  $3.5 \text{ W cm}^{-2}$ ,<sup>50,51</sup> and demonstrating long-term stability (2,000 h).<sup>52</sup> In pure water-fed AEMWEs, they attained a current density of approximately  $1.0 \text{ A cm}^{-2}$  at 2 V,<sup>12</sup> surpassing conventional Zirfon-based liquid alkaline electrolyzers (Figure 3a). The AEMWE also exhibited promising durability, with a voltage degradation rate of only  $93.5 \mu\text{V h}^{-1}$  over 500 h (Figure 3b). However, further enhancements in the performance of particulate ionomer bonded MEAs are imperative for commercial viability. Addressing challenges related to the heterogeneous electrode structure, water transport, and localized pH for OER catalyst activity necessitates ongoing research and precision in design adjustments. The potential for cell failure under differential pressure conditions due to the inhomogeneous electrode structure remains an area for study and improvement.

**Ionomeric Binders with Low Adsorption Energy.** The electrochemical oxidation of ionomer fragments begins with ionomer adsorption. Therefore, one possible strategy involves minimizing ionomer adsorption by utilizing ionomers with low interaction energy. Aromatic groups, commonly found in hydrocarbon ionomer structures, tend to adsorb onto metal catalyst surfaces due to the interaction of their aromatic  $\pi$ -electrons with the electronic cloud surrounding metal atoms. Therefore, considerable research has focused on phenyl groups

with different structures, as their orientation on the metal catalyst surface significantly influences adsorption energy.

Figure 4a illustrates the adsorption energy of various phenyl groups and other ionomer fragments on the Pt(111) surface.<sup>53</sup> The fluorenyl group, characterized by a central fused five-membered ring between two phenyl-groups, exhibited the lowest adsorption energy,<sup>54</sup> attributed to its nonrotating backbone characteristics. Additionally, nonphenyl cyclo-olefins like norbornane demonstrated relatively low adsorption energy.

Figure 4b compares the performance of AEMWEs utilizing different ionomeric binders in the anode catalyst layer.<sup>55</sup> The MEA employing quaternized polynorbornene (NB) ionomer, known for its minimal adsorption, achieved the highest performance. Conversely, quaternized polyphenylene with a *meta*-terphenylene unit in the polymer backbone (*m*-TPN) showed the lowest performance. Quaternized polyfluorene (FLN) with a dimethyl fluorene unit exhibited performance between NB and *m*-TPN.

One significant advantage of this approach over particulate ionomer binders is the thin-film ionomer electrodes, which establish an optimal interface with nanoparticle catalysts without relying on corrosive liquid supporting electrolytes. However, it is important to note that the current top-performing AEMWEs employing this strategy have yet to reach practical performance levels compared to conventional PEMWEs. Additionally, stable long-term performance beyond even 200 h at high current density ( $>1 \text{ A cm}^{-2}$ ) has not been achieved. Another technical challenge involves fully isolating the AEM from OER catalysts, which can result in performance degradation due to electrochemical oxidation to some extent.<sup>56</sup>

**Competitive Adsorption.** Competitive adsorption is a strategy to introduce another species with a stronger adsorption energy that can mitigate the negative effects of ionomer adsorption. For example, consider the case of phenyl piperidinium ionomers. Two possible adsorption modes can be envisioned: either through the phenyl group on the backbone or the cationic piperidinium. Simple adsorption energy calculations on Pt(111) show that the piperidinium cation group has a higher adsorption energy ( $-4.36 \text{ eV}$ ) than the adjacent phenyl group in the piperidinium ( $-4.11 \text{ eV}$ ).<sup>55</sup> While these calculations overlook the details of the electrical

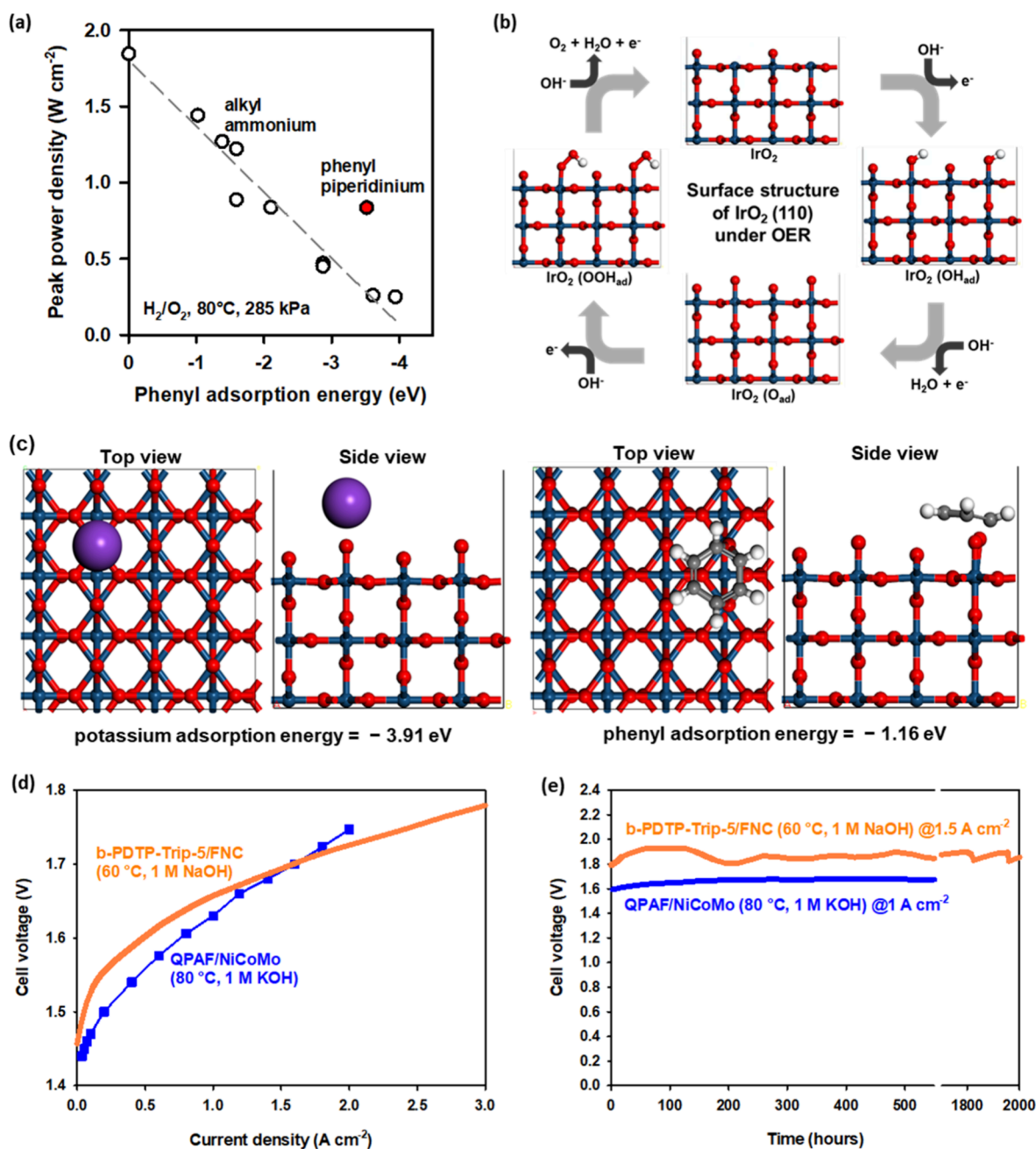


Figure 5. (a) Correlation between phenyl adsorption energy of HOR catalyst and AEMFC performance. Adapted with permission from ref 55. Copyright 2023 Wiley-VCH GmbH. (b) The surface structure of  $\text{IrO}_2(110)$  during the alkaline OER process. (c) Adsorption energy comparison of potassium ion (left) and benzene (right) on  $\text{IrO}_2(110)$  surface. The adsorption energy was calculated by density functional theory calculations based on Vienna ab initio simulation package (see detailed information in SI). (d) Performance and (e) durability of AEMWEs from the competitive adsorption approach. MEA1 (orange line): AEM, branched poly(aryl-co-aryl piperidinium) (b-PDTP-Trip-5) (thickness:  $20\ \mu\text{m}$ ); anode, Fe–Ni–Co (4.87 wt % Fe, 14.09 wt % Ni, 0.4 wt %) (FNC); cathode, PtRu/C ( $0.7\ \text{mg cm}^{-2}$ ). MEA2 (blue line): AEM, quaternized (arylene perfluoroalkylene) (QPAF) (thickness:  $25\ \mu\text{m}$ ); anode,  $\text{Ni}_{0.8}\text{Co}_{0.12}\text{Mo}_{0.08}\text{O}$ ; cathode, Pt/C with Nafion binder. Adapted with permission from ref 62. Copyright 2023 American Chemical Society, CC-BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>). Adapted with permission from ref 63. Copyright 2023 John Wiley and Sons.

double layer and solvation of the molecular species, if the trend holds true, AEM electrochemical devices employing phenyl piperidinium ionomers would be anticipated to outperform devices with other ionomers possessing a similar phenyl adsorption energy but without cationic group adsorption interference.

Figure 5a illustrates how competitive adsorption impacts the AEM fuel cell performance. It is noteworthy that AEM fuel

cells employing phenyl piperidinium containing ionomer exhibited relatively good performance. The state-of-the-art AEMWE performance from this approach, utilizing a branched poly(biphenyl piperidinium), achieves  $1.9\ \text{A cm}^{-2}$  at  $2.0\ \text{V}$  and  $>500\ \text{h}$  of stable performance ( $\sim 70\ \mu\text{V}/\text{hour}$  voltage increase) at  $1\ \text{A cm}^{-2}$ ,  $80^\circ\text{C}$  for pure water-fed PGM-free AEMWEs.<sup>57</sup>

Alkali cationic species may serve more effective competitive adsorption agents at the electrolyzer anode, given their

significantly higher adsorption energy at the operating anode potentials. Before the discovery of competitive adsorption with alkali cations, the practice of supplying supporting electrolytes was known to enhance AEMWE performance without a clear understanding of the underlying mechanism. AEMWEs utilizing potassium carbonate as a supporting electrolyte exhibit respectable performance, likely attributed to the strong adsorption of potassium, despite a decrease in local pH due to the electrolyte.<sup>58</sup> The optimal support electrolyte for AEMWEs is potassium hydroxide, which has recently suggested to release ionomer fragments from the catalyst surface<sup>59</sup> without significant reduction of local pH of the electrodes.

To investigate the possibility of the competitive adsorption effect with potassium hydroxide, we conducted adsorption energy calculations with the IrO<sub>2</sub> surface. As the KOH<sub>(aq)</sub> is fed in the anode while the potential is increased, OER process is accelerated, and the surface structure of IrO<sub>2</sub> changes to IrO<sub>2</sub> (O<sub>ad</sub>), which has been known as the most stable surface structure in typical alkaline OER conditions (Figure 5b),<sup>60</sup> allowing alkali metal cations to adsorb on the catalyst surface.<sup>61</sup> Figure 5c presents a comparison of the adsorption energy of potassium and phenyl groups, indicating that under the electrochemical potential of 2.1 V, the adsorption energy of a potassium ion on the surface of IrO<sub>2</sub>(110) (−3.91 eV) is much stronger than that of one phenyl group (−1.16 eV). Supplying a more concentrated KOH solution can more effectively prevent phenyl adsorption, as multiple potassium cations can occupy the adsorption site of a phenyl group. Current AEMWEs using this approach not only exhibit high performance at a practical level (Figure 5d) but also demonstrate longevity (Figure 5e).<sup>18,62,63</sup>

Unlike ionomer-free alkaline electrolyzers, this approach typically utilizes low concentrated KOH (≤1 M). Since competitive adsorption is employed, ionomers with low adsorption energy, such as quaternized polyfluorene or polynorbornene, are beneficial at a low KOH concentration (≤0.5 M). However, the benefits with higher concentration also depend on catalysts and their surface charge under operating conditions, so the optimum concentration should be determined by the individual ionomer-catalyst pairs. One clear disadvantage of this approach is the requirement for corrosive supporting electrolytes, which may accelerate material degradation over time, leading to the formation of salts, and complicating the electrolyzer system.

## SUMMARY AND OUTLOOK

In the past five years, extensive research has delved into understanding the factors influencing the performance and durability of AEMWEs, with a growing consensus emphasizing the crucial role of interactions between electrocatalysts and polymer electrolytes. Specifically, the electrochemical oxidation of ionomer fragments during undesirable adsorption has emerged as a critical challenge.

The approach employing competitive adsorption with a supporting liquid electrolyte stands out, demonstrating a practical level of performance and durability.

To address this, four distinct approaches have been explored: ionomer-free electrodes, particulate ionomers, the use of ionomers with low adsorption energy, and competitive adsorption. Each approach presents its own set of advantages and drawbacks at different levels of technical readiness. Notably, the approach employing competitive adsorption with a supporting liquid electrolyte stands out, demonstrating a practical level of performance and durability. Nonetheless, research efforts to address ionomer adsorption and electrochemical oxidation of ionomers should persist, as the ultimate objective for AEMWEs is to operate the cell in pure water, independent of supporting electrolytes.

The efficacy of AEMWEs in mitigating ionomer electrochemical oxidation can be further enhanced by integrating other methods, such as combining ion-solvating membranes with ionomer-bonded nanoparticle electrodes<sup>64</sup> or incorporating particulate ionomer with a flowing low concentration of KOH electrolyte.<sup>65</sup> Innovative ideas and their implementations to mitigate ionomer electrochemical oxidation is on going. For example, a recent paper reports the introduction of a passivated layer (2–3 nm thick of HfO<sub>x</sub>) that allows hydroxide ion transport but shows undesirable ionomer adsorption.<sup>66</sup>

Several challenges persist for the AEMWEs employing the current approaches. There is a need to demonstrate the performance and durability of AEMWEs at high current densities (≥2 A cm<sup>−2</sup>) and operating temperatures (≥80 °C), especially advantageous for PGM-free catalysts. Validating the ability to operate under differential pressure, particularly with the relatively thin AEMs (≤50 μm thick) employed in current high-performing AEMWEs, is crucial.<sup>67</sup> Optimizing the concentration of supporting electrolytes becomes imperative for balanced performance and durability. Additionally, a comprehensive techno-economic analysis is warranted to determine the feasibility of PGM-free or low PGM hydrogen evolution catalysts.

A notable advantage of AEMWEs lies in their potential to eliminate degraded perfluoroalkyl substances from the MEAs. Given the stringent regulations surrounding perfluoroalkyl substances, ongoing efforts to develop wholly hydrocarbon membranes and ionomers become imperative. Recent strides in AEMWE research, focusing on minimizing undesirable catalyst-ionomer interactions, not only hold tremendous promise in providing a cost-effective and environmentally friendly alternative to PEMWEs but also guide the development of hydrocarbon-based ionomers for other electrochemical devices such as CO<sub>2</sub> electrolyzers.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acseenergylett.4c00832>.

Calculation of electrode local pH, synthetic process of materials and computational details for the adsorption energy (PDF)

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## Author Contributions

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## Notes

The authors declare the following competing financial interest(s): S.W.B. has patents pending on advanced electrode architectures for durable anodes in AEMWE. Other authors declare no competing interests.

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