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Achieving the Hydrogen Shot: Interrogating Ionomer Interfaces

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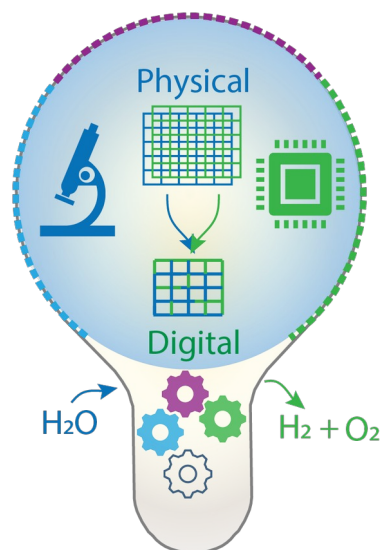
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To enable the hydrogen economy and decarbonize various sectors in our environment requires less expensive and more durable water electrolyzers, which can meet the Hydrogen Shot target. The key is to improve the ionomer interfaces in low-temperature water electrolyzers as rapidly as possible, but to do so requires a systematic and holistic campaign combining both experiments and theory. In this perspective, we discuss the issues of electrolyzers and needs for translational science. We then present the approach that the Energy EarthShot Research Center: Center for Ionomer-based Water Electrolysis is taking in hopes of inspiring the community with this approach that can be leveraged to multiple problems and technologies.



Keywords: Membrane, interface, durability, modeling, water

Highlights: One way to achieve the Hydrogen Shot goal of low-cost, clean hydrogen, is advancing research and development on the interfaces of water electrolyzers for both performance and lifetime. The Center for Ionomer-based Water Electrolysis is exploring new techniques and strategies to not only interrogate interfacial phenomena in water electrolyzers to increase efficiency and durability, but also a new paradigm related to synergistic, cojoined experimental and theoretical research.

Discussion:

1. Catalyst\ionomer interfaces are complex and not fully understood, but through investigating different interfaces and utilizing digital and physical twins, we can elucidate key mechanisms and understanding.
2. Understanding the dynamic double layer in electrochemical systems that use solid electrolytes is crucial to identifying and mitigating the controlling phenomena to enable increased performance and durability at the technology level.

3. Studying the time and length scales of interfacial changes can be a powerful tool to understand reaction mechanisms and changes in the electrolyzer performance and durability.

Both economic and environmental concerns motivate the transition from fossil fuels to renewable energy sources and associated energy vectors, with hydrogen being the simplest energy carrier. However, traditional water-splitting technologies are not yet cost effective, hence the impetus for the *Hydrogen Energy Earthshot* that is focused on producing clean hydrogen at \$1/kg_{H2} in 1 decade.¹ The most promising scalable technology for reaching this target is water electrolysis using low or zero carbon-emission electricity.^{1,2} In particular, low-temperature electrolysis using single-ion-conducting polymers (ionomers) provides one of the best opportunity for dynamic and modular (essential for renewable integration) operation, and offers system-efficiency gains via differential pressure operation. However, this technology is limited due to the need for expensive catalyst materials, thick and durable separators/membranes, and a lack of holistic understanding of the ion-conducting polymer (ionomer) interfacial phenomena (*e.g.*, oxygen evolution at the ionomer/catalyst interface)³. In fact, as DOE noted, a grand challenge for the field is to “*elucidate the structure, evolution, and chemistry of complex interfaces for energy- and atom-efficiency as they relate to electrolysis and degradation processes in hydrogen systems.*”⁴ While substantial effort has gone to exploring such phenomena for aqueous electrolytes, there is a need to understand fundamentally the distinct interface physics/chemistry of these complex ionomer systems and thus develop and identify new design principles. While this is not entirely a new problem with some previous work on looking at the interface between an ion-conducting solid and catalyst,⁵⁻⁹ new techniques and capabilities provide an unprecedented opportunity to increase understanding if accomplished in a concerted fashion; such understanding is essential for the innovation and maturation of hydrogen technologies. This lack of comprehension inhibits the

¹ With clean hydrogen being defined as hydrogen produced with a low carbon intensity (< 0.4 kgCO₂/kg H₂) based on full life-cycle assessment

design and tailoring of materials, assemblies, and conditions that promote efficient, durable, and cost-effective water electrolysis.

In ionomer-based water electrolysis, the ionomer serves as both the solid-electrolyte membrane (on the order of several micrometers, known also as an ion-exchange membrane) in the middle of the cell, preventing gas and electron crossover but allowing water and ion transport, and as ion-conducting thin-films (on the order of tens-to-hundreds of nanometers thick) that bind the electrocatalyst particles and form the 3D porous electrodes enabling high current densities (Figure 1). Ionomers have their own dependences on a range of operating and synthesis conditions including unknown durability stressors that can result in rare events and catastrophic failure.^{10,11} While ionomers respond to their environment¹² and control the local reaction environment,¹³ the dynamic and complex nature of the ionomer interfaces, especially with the electrocatalysts, is not understood, thus limiting electrolyzer improvements and achieving the Hydrogen-Shot goals. Such an understanding requires filling critical *knowledge gaps*, including:

- i)* the multiscale morphology of the materials and their evolution, operation, and degradation when taken far from equilibrium at high fluxes/currents,
- ii)* the transport and activity of the reactant and product species through ionomer-film structures and the associated ionic double layer including implications for catalyst reactivity/dissolution, and
- iii)* design rules for tailoring durable, high-performing catalyst/ionomer and ionomer/ionomer interfaces, looking at multiple length- and time-scales.

Specifically, it is not known how the physical and chemical bonding at the interface, and chemistry of the ionomer, control the overall transformation rate at the electrified interfaces due

to coupling of the chemical and mechanical forces over time that govern dynamic ionomer and interface morphology and ion activity. Addressing these gaps requires a targeted comprehensive effort towards interface discovery under relevant operating conditions, especially as most fundamental studies do not consider high-flux operation (1 to 4 A cm⁻²) and operating lifetimes to identify the durability of such materials.

Water Electrolyzers

Water electrolyzers that generate H₂ (and O₂) efficiently and at high rates require solid-state ionomer electrolytes that minimize ohmic losses, enable higher power densities, and prevent back-transport of produced H₂, thus allowing for *in-situ* pressurization and better dynamic operation, while maintaining high selective transport of the desired proton or hydroxide ions (Figure 1a). For example, liquid alkaline electrolyzers are proven technologies but cannot yet operate at the necessary high current densities (1 to 4 A cm⁻²) and dynamically with pressure differentials since they only use porous separators and liquid electrolytes.¹⁴ The ionomers also play a critical role as a binder and thin-film ion-conductor (Figure 1b) in the porous electrode, thereby allowing for dramatic increases in active electrocatalyst surface area and subsequently high fluxes and rates with minimum overpotential.

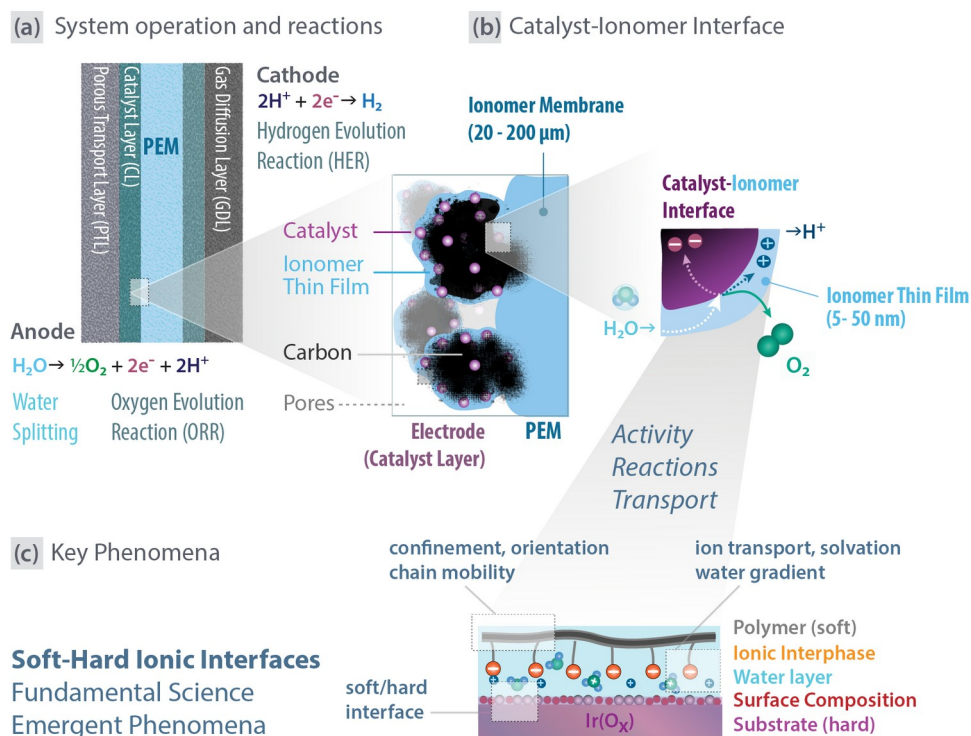


Figure 1. Schematic of multiscale nature of ionomer-based proton-exchange-membrane electrolyzer.

These motifs result in various interfaces (Figure 1c), all of which control different performance and durability aspects of the cell including ion, energy, and mass flows to and from the reaction interface and the resultant microenvironment.

Table 1. Acidic and alkaline electrolysis reactions

pH	Anode (OER)	Cathode (HER)
Acidic	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$	$2\text{e}^- + 2\text{H}^+ \rightarrow \text{H}_2$
Alkaline	$4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$

As shown in Table 1, hydrogen can be generated via either alkaline or acid reactions, where the former provide opportunities to use inexpensive catalysts,¹⁵⁻¹⁷ while the latter provides more efficient charge transfer but necessitates the use of Pt group metal (PGM) catalysts.¹⁸⁻²⁴ (with perhaps the optimal being a bipolar membrane arrangement in which the sluggish oxygen-evolution reaction (OER) is in alkaline, while the hydrogen-evolution reaction (HER) is in

acid).²⁵⁻²⁹ Typical operating conditions are $> 2 \text{ A cm}^{-2}$ with a pure-water feed and O_2 and H_2 occurring at the anode and cathode, respectively.^{30,31} The local strongly acidic conditions under which proton-exchange-membranes (PEMs) operate requires use of Pt and IrO_2 PGM catalysts at the cathode and anode, respectively. Hydroxide-exchange-membrane (HEM) water electrolyzers are a developing technology³² that allow for use of non-platinum catalysts, such as Ni metal and Ni/Co/Fe oxides.³³⁻³⁶ To date, HEM electrolyzers do not have comparable polarization performance or, more importantly, durability with respect to PEM electrolyzers, especially with pure water feeds.^{14,30} To compensate for these performance losses, most HEM electrolyzers use soluble supporting electrolyte, commonly carbonate or hydroxide, to improve conductivity, catalyst access, and increase durability.³⁷⁻⁴⁶ Although these technologies exist, and some work has been done to explore interfacial interactions, there is a scarcity of understanding. For example, despite significant efforts to evaluate experimentally and understand theoretically Pt-based catalysts in acidic medium, there remain gaps in our knowledge of how these catalysts perform and change during operation with ionomer thin-films, especially as liquid-cell measurements do not translate once integrated into porous electrodes.^{10,47}

Most ionomers are co-polymers of a neutral backbone containing a direct or tethered ion-containing group.⁴⁸⁻⁵⁰ Perfluorinated sulfonic-acid (PFSA) ionomers and their analogues are ubiquitous in acid-based electrolyzers, and considered a benchmark membrane separator. This is because of their *i*) conductivity, facilitated by protons dissociated from poly-ions (breaking/forming ionic bonds) to form water-ion bridges (hydrogen bonds), and *ii*) chemical-mechanical stability, due to stable polytetrafluoroethylene backbone enhanced by crystalline domains (covalent bonds).¹² For alkaline systems, HEMs with linear or aromatic backbones are

functionalized with quaternized ammonium (QA) cation groups, exchanged with OH⁻ anions.⁵⁰⁻⁵⁴ As such, all ionomers encompass covalent and ionic bonds, which provide them their functionality as the conducting solid electrolyte. Ion transport occurs at multiple length- and time-scales within the functional nanodomains of a mesoscale network, where the ions are traversing via dynamic fluctuations of water-ion molecules influenced by the polymer segmental motion. Studies have explored chemical stability via property changes under external stressors (e.g., conductivity decay in acid,⁵⁵⁻⁵⁷ or base,⁵⁸⁻⁶¹) but with limited information of morphological changes nor possible synergistic impacts of mechanical stressors, especially under relevant operating conditions. The ionic moieties also create an intermediate region between the neutral phase and ion-rich domains, thus creating an “*interphase*”¹² that must be understood for it will be sensitive to ionic identity and chemistry that could affect local mobility and transport.^{12,62-66} In thick ionomers (used as membranes), network connectivity of nanodomains exceeds characteristic hydrophilic/phobic domain lengths (5-10 nm), but in thinner ionomers on catalyst particles (<100 nm) confinement to characteristic domain lengths disrupt the bulk network formation and promotes confinement-driven orientation of domains, thereby exacerbating the interaction of the ionic moieties at interfaces with strong binding. It is this structural change with stronger binding that characterizes the *ionomer/electrocatalyst interactions* and hinders ion- and gas-transport function, thereby causing transport resistances. Such confinement also reduces mobility and increases in-plane stiffness in PFSA films,⁶⁷⁻⁶⁹ limits kinetic of swelling, and alters molecular orientation near the substrates,^{70,71} but the chemical structure and double-layer existence and effects at these interfaces are still unresolved.

In terms of degradation, there are various means of chemical attack typically from hydroxyl radicals that are generated by decomposition of hydrogen peroxide formed due to crossover of

reactant species (H_2 , O_2) across the membrane.^{12,72} In HEM electrolyzers, the main causes of degradation are nucleophilic attack by OH^- on solvated polar moieties and direct oxidation at the OER catalyst surface,⁷³ where oxygenated radicals may also play a role.⁷⁴ This problem motivates many new hydrocarbon-based HEM materials with rich side-chain chemistries.^{36,75–81} In any of the systems, mechanically induced degradation due to dehydration during reaction and gas evolution at the interface are concerns.¹²

Ionomer Interfaces and Scales

Low-temperature electrolyzers depend critically on the materials chemistry and engineering of reactive interfaces, where the transport and interfacial interactions control the overall rate of electrochemical transformation. These interfaces include structure/function relationships of the critical multicomponent ionomer interfaces (soft/fluid, soft/hard, soft/soft) for water electrolysis (*i.e.*, O_2 and H_2 evolution). The polymer interaction with the catalyst surface influences the electrocatalytic kinetics, water content, ionic transport, and the ionic double layer, even when the interaction forces are weak. Additionally, the double layer in electrochemistry plays a critical role, but very little work has been done to understand interfaces when solid ionomers are the electrolyte.⁸² Because the ion groups are fixed to the backbone with limited mobility, the interfacial capacitance, and hence local electric field, catalytic mechanisms, and ion activities are all probably different. These phenomena not only drive multiscale structural transitions but are also linked to dynamic segmental motion and multiscale deformation induced by the various strain gradients, fluxes, and environmental conditions/stimuli (temperature, humidity, pH, potential, *etc.*), which can be altered based on intrinsic chemistries (*e.g.* by synthesizing rubbery or stiff polymer backbone chemistries); the understanding of such linkages

is nascent. This knowledge gap is particularly prevalent in ionomer mechanical properties, for example in degradation due to creep, delamination, etc., that results in poor electrolyzer performance/durability, as well as confinement effects in the ionomer thin films that drastically alter their inherent properties.⁸³ Studying this region requires development of multimodal techniques to probe and elucidate mechanochemical deformation by quantifying the structure-deformation relationships during mechanical/electrochemical transformations.

The analysis and understanding of electrolyzers and the ionomer interfaces are exacerbated by their complexity, where concomitant phenomena occur across various length and time scales, as depicted in Figure 1. Thus, to tackle and optimize these technologies requires investigating the interface with different techniques that probe the various different length and time scales, which become more important when looking at a dynamic, non-equilibrium condition. These techniques include experimental and theoretical platforms that enable a comprehensive multimodal understanding around bulk and interfacial morphology, double-layer structure, local reactivity and transport including species adsorption, require in-depth insights of electrocatalyst/ionomer/water interfaces across length scales.

The dynamics and functioning of the interface evolution and performance can be studied with electromechanochemical, spectroscopic, microscopic, and computational tools to provide snapshots of structure and chemistry evolution as stressors are being applied to the interface across molecular (nm) to continuum ($> \mu\text{m}$) length scales. The length scales that the various chemical spectroscopic techniques probe needs to be matched to the structural systems microscopic length scales and furthermore coordinated to be the same across experimental platforms (*i.e.*, at best multimodal and identical location and at worst same materials and assembly and metadata). Additionally, the timescales for these phenomena span from

femtoseconds and picoseconds for chemical bond transformations to minutes for mass-transport processes and hours for degradation mechanisms. It is essential to understand the chemistry that drives structural transformations (and vice versa) and there is a need to capture how the interfacial chemistry changes as a function of time. Linking the chemical changes with morphological ones in PEM and HEM chemistries systematically highlights the differences in ionomer degradation pathways, and how they stem from the intrinsic surface chemistry interactions with the flexible side-chain moieties, resulting in different double-layer interactions and atomic and molecular environments that feedback to performance behavior and durability stressors.

CIWE's Approach

The above outlines the needs and directions for interrogating ionomer interfaces in water electrolyzers. To rise to this challenge requires a comprehensive, holistic multi-discipline approach such as that taken in the Energy Earthshot Research Center: Center for Ionomer-based Water Electrolysis (CIWE). The key is focusing on achieving the Hydrogen Shot via translational science, where the end goal informs the questions and boundaries wherein the fundamental science can be activated to answer. This approach enables systematic, yet surgical, experimental and theoretical strategies that provide physical insights into the most-critical properties of ionomers and impact on catalyst performance and the stability of both components. CIWE uses a nontraditional center approach of relatively limited material systems being the crosscut activity upon which the traditional crosscutting thrusts of characterization and modeling operate on. The structure of the center is shown in Figure 2, showing the various thrusts working together toward the Hydrogen Shot goal.

Investigating these relationships requires a holistic approach, focused not only on leveraging advanced multimodal characterizations and digital/virtual representations on systematic material systems (*e.g.*, PFSA and random or block-copolymer proton and hydroxide-conducting ionomers on various electrocatalysts) but also a convergent *digital-twins paradigm*,⁸⁴ wherein the physical and virtual worlds are brought together in a unity of theory and experiments to interrogate and interpret simultaneously, will help unravel these complex systems and improving electrolyzer performance and durability at lower cost. This gap is especially necessary to overcome the “small-data” problem endemic to these complex multicomponent interfaces and related phenomena, where experiments are often costly and span a limited range of the tremendous parameter space. The digital twin supplements the (necessarily limited) and sparse experimental findings with *in-silico* physics-based representations and virtual data that link disparate data sets and enable the virtual testing of materials (both real and hypothesized) and interfaces to identify knowledge gaps and provide parameter-space reduction. Thus, this approach enables synergistic interrogation and complementary data related to ionomer interfaces. This connectivity provides an unprecedented multiscale understanding of ionomer interactions at interfaces, and how they control, and can be tuned to improve, overall electrolyzer performance and durability. Thus, the approach accelerates the design-test-build-learn learning cycle of complex, hard-to-investigate systems.

The overall approach is accomplished through adaptive, hierarchical, physics-based models and experimental campaigns starting from simplified interfaces with known materials and expanding to multicomponent integrated assemblies as shown in Figure 2. Thus, studying bulk membranes and planar ionomer films on metallic substrates and building towards more-complex geometries and interfaces, longer timescales of degradation and stability, and then rapidly

transition to high flux and representative conditions. Key herein is to undergo systematic and relevant studies to elucidate specific governing principles and effects; thus, one focuses more on understanding using realistic material sets and designs rather than chasing pure high-performance material discovery. Finally, as advanced water electrolyzers operate at high fields and fluxes, we emphasize *in-machina* or *representative operando* studies, *i.e.* under conditions representative of the technologically relevant scales and conditions, with the aim to avoid artifacts common to fundamental studies and experimental setups. This approach requires an understanding of the fields and dimensionalities in the architectures such that edge effects, boundary conditions, or other phenomena do not dominate the *operando* response (*i.e.*, so it is representative of a system in practical use). Examples of **non** *in-machina* studies include *operando* experiments where ionic pathlengths alter the double layer such that it is not representative of a porous electrode, or studies where the energy flows and environmental conditions are controlled by the experimental architecture needed for experimental interrogation and not as they would be in a practical cell.

This approach streamlines the effort by establishing the feasibility of a new paradigm of research that relies on seamless physical and virtual experiments using hierarchical digital twins; pushing the frontier of investigation of soft/hard interfaces – especially those that are responsive and operate under high fluxes; pioneering a multiscale framework and concomitant model that will translate the basic-science knowledge to the critical applied problems facing water electrolysis; and demonstrating and exploring the synergy and complementarity of mechanics (stability) and electrochemistry (function) as a third leg of the understanding stool on this class of problems to go along with traditional simulations and spectroscopy and structure/function relationships. An example of this synergy is exploring the effect of pressure, as it is a variable

that influences multiple length scales, is an easy parameter to manipulate in experiments, and can be well studied in physical and computational models. Pressure, as not just an applied force but a thermodynamic state variable, is just one example where CIWE will provide new insights, techniques, and knowledge as we explore how it impacts chemical states of the bonding environment as well as impacts the ionomer morphology and directs gas-phase emergence. CIWE will bring pressure avenues to the more-traditional chemical-science community, and explore the interrelationships and interrogation methods of multiple simultaneous stressors, which is critical when looking at rare events and durability/degradation phenomena relevant to industry. Examples of these rare events are pinhole formation in the membrane, dissolution of the catalyst, shorting of the cell, and others that can have a significant impact on the performance and longevity of the cell.^{10,11,34} They are rare in nature either due to unplanned and unexpected operating excursions (e.g., exceeding limiting current density or rapid shut down) or just overcoming inherent large kinetic barriers (e.g., catalyst dissolution).

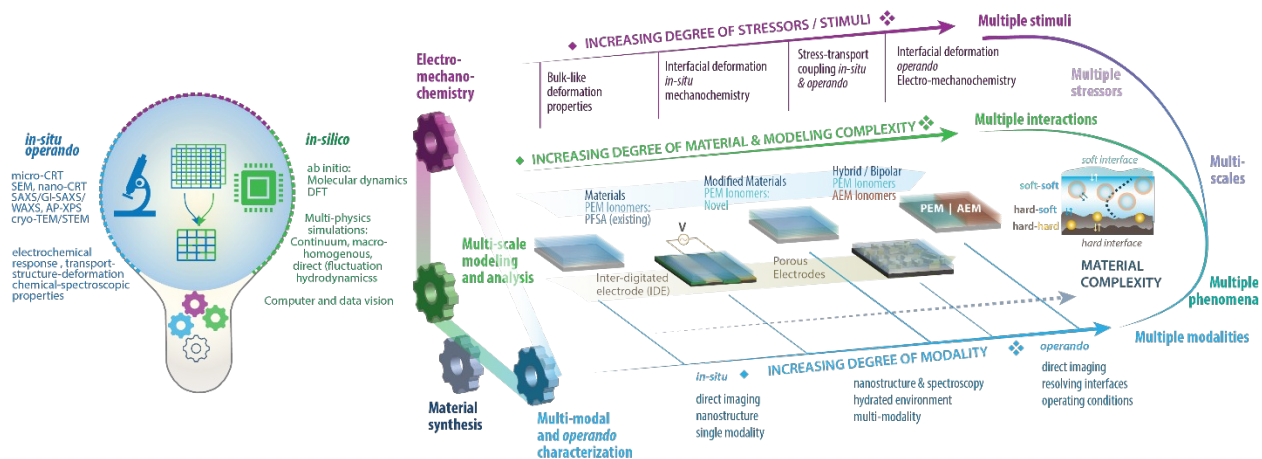


Figure 2: The structure and complexity of CIWE

Summary

To enable the hydrogen economy and decarbonize various sectors in our environment requires less expensive and more durable water electrolyzers, which can meet the Hydrogen Shot target. The key is to improve the ionomer interfaces in low-temperature water electrolyzers as rapidly as possible including ways to design, tune, and control them (e.g., adaptive materials, responsive interfaces, etc.). To do so requires a systematic and holistic campaign where we leverage advances in theoretical and experimental interrogation techniques that are brought together and jointly focused on exploration of relevant phenomena and interfaces. Thus, translational science, where the technology is driving the conditions and questions and fundamental science provides the answers, is paramount. Such a translational paradigm should be multidirectional and connected, ensuring rapid feedback between technology and science. The results and systematic approach of using digital twins, in-machina experiments, and multimodal data infrastructure and management, can also be leveraged for various related electrochemical devices, such as electrodialysis and electrosynthesis, to improve performance and durability, while lowering capital and operating expenses.

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Conflict of Interest Statement

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Authors Contributions

All authors contributed in the writing, editing, and formulation of the manuscript.

Data availability

Not applicable