Perspective Carbon Future

Failure mechanisms in PEM water electrolyzers

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Abstract: The failure of anode catalysts for the oxygen evolution reaction (OER) in proton exchange membrane (PEM) electrolyzers poses a significant barrier to their commercial deployment. In PEM electrolyzers, anode catalysts typically degrade due to the extremely oxidative environment and low local pH at the anode. Under these harsh conditions, catalysts may dissolve into the electrolyte, detach from the membrane, or become contaminated by impurities. These degradation processes are interconnected and complex, rather than isolated issues. Consequently, improving catalyst materials alone has only a limited impact on the overall system performance. In this perspective, we systematically review the causes of anode catalyst failure and their effects on PEM electrolyzer stability. We pay special attention to the limitations of current approaches, including material shortcomings, changes in electrode structure, and gaps in system-level strategies. A thorough understanding of these challenges is crucial. Achieving a stable anode for acidic OER requires deep insight into the failure mechanisms under real PEM operating conditions. By integrating advances in catalyst design, electrochemical characterization, engineering solutions, and data-driven methods, we can address these limitations effectively. This comprehensive approach is essential to accelerate development and enable widespread adoption of PEM electrolyzers.

Introduction:

Accelerating the development of clean, sustainable energy alternatives to fossil fuels is critical to mitigating climate change amid rising global energy demand[1, 2, 3]. Among emerging technologies, proton exchange membrane (PEM) electrolyzers stand out for hydrogen production due to their compact architecture, low internal resistance, and high energy efficiency[4, 5, 6, 7]. Despite their promise, the widespread deployment of PEM electrolyzers is hindered by high system costs and limited durability[8, 9]. In particular, the oxygen evolution reaction (OER) at the anode, an inherently sluggish four-electron process, requires high overpotential and suffers from low kinetics[10, 11, 12, 13]. These challenges are further exacerbated by the harsh operating conditions of the anode: high oxidative potential (~1.5 V vs. RHE) and extremely low local pH (0–2), especially under industrially relevant current densities (~2 A/cm^2). To withstand such conditions, commercial PEM systems rely almost exclusively on noble metal-based IrO_x catalysts, which are both expensive and scarce. Most current research attributes system failure primarily to Ru/IrO_x dissolution[14, 15, 16], focusing on optimizing Ru/Ir-based catalysts for improved stability and activity.

However, anode degradation is not a single-material issue; it is a complex, system-level challenge. In PEM electrolyzers, catalysts are applied directly onto the membrane, with a carbon paper gas diffusion layer (GDL) on the cathode side and a titanium porous transport layer (PTL) on the anode[17, 18, 19, 20]. Deionized water fed to the anode introduces several factors that contribute to performance loss, including[21]: dissolution of Ru/IrO_x under acidic and oxidative conditions; mechanical detachment of catalysts caused by oxygen bubble generation; continuous washing away of catalysts by the water flow; passivation of the PTL; contamination from impurities such as chloride ions in the feed water; and crossover of Ir/Ru species from the anode to the cathode, which can poison the Pt sites responsible for hydrogen evolution. In practical PEM electrolyzers, these degradation processes are not isolated but strongly interdependent. For example, impurity-induced (e.g., Fe^{3+}, Cl^- ions) passivation on the titanium PTL (TiO_2 layer, resistivity > 10^8 Ω cm) or catalyst surface increases interfacial resistance and local overpotential, which accelerates Ir/Ru oxidation and dissolution. The resulting structural weakening enhances bubble-induced detachment, while dissolved metal species can migrate to the cathode catalysts and redeposit on Pt/C surface, causing further blockage and current redistribution. Such feedback loops amplify local stresses and chemical instability, making it challenging to identify a single dominant failure mode. Therefore, understanding the synergistic interplay among chemical, electrochemical, and mechanical degradation pathways is crucial for developing durable PEM electrolyzers. Moreover, the interfacial processes and dynamic degradation mechanisms are still poorly understood, especially under realistic operating conditions involving high temperature, pressure, bubble formation, current flow, and local pH gradients.

This perspective proposes a systemic approach to understanding and mitigating anode catalyst failure in PEM electrolyzers. We argue that catalyst deactivation results from dynamic, interconnected physical, chemical, and electrochemical processes. To effectively address this challenge, researchers must move beyond isolated material improvements and focus on the interactions among the catalyst, membrane, water feed, and PTL. We emphasize the urgent need for: 1) advanced in-situ and operando characterization techniques to monitor catalyst restructuring, dissolution kinetics, and interfacial behavior in real time; 2) next-generation catalysts and PTLs engineered to withstand degradation under extreme operating conditions; and 3) improved predictive models for electrolyzer lifespan, grounded in a mechanistic understanding of failure pathways. We hope this perspective will inspire interdisciplinary collaboration, bringing together materials science, electrochemistry, fluid mechanics, and data science, to develop durable, cost-effective PEM electrolyzers and accelerate the global transition to clean hydrogen energy.

Reaction mechanisms

Under the acidic conditions, the acidic OER on Ru/IrO_x could proceed by two distinct pathways, both of which influence catalyst dissolution. In the adsorbate evolution mechanism (AEM), all O–O bond formation derives solely from water molecules [22, 23]. In contrast, in the lattice oxygen mechanism (LOM)[24, 25, 26], one oxygen atom originates from the Ru/IrO_x lattice and one from water (Fig. 1). This creates an oxygen vacancy, destabilizes the crystal framework, and exposes Ir sites in oxidation states >+4. These high-valence Ru/Ir centers are particularly prone to dissolution under acidic conditions. Although density functional theory (DFT) calculations predict both pathways, experimental validation is essential. In particular, oxygen-isotope labeling (e.g., ^{18}O tracing) can quantify the fraction of O_2 produced via lattice oxygen and correlate it with Ru/IrO_x stability. Experimental studies frequently use ^{18}O isotope labeling (e.g., via $H_2{}^{18}O$ or ^{18}O-enriched electrolytes) coupled with techniques like differential electrochemical mass spectrometry (DEMS) to distinguish these mechanisms by tracking the isotopic composition of evolved O_2 [4, 27, 28]. The contribution of lattice oxygen to the overall O_2 evolution strongly depends on the type of catalyst used for the OER and the potentials or cell voltage applied [4, 29]. Furthermore, measuring dissolution kinetics under controlled LOM activity will clarify how lattice participation accelerates degradation. Such insights are critical for guiding the rational design of next-generation, acid-stable OER catalysts for use in the PEM electrolyzers.

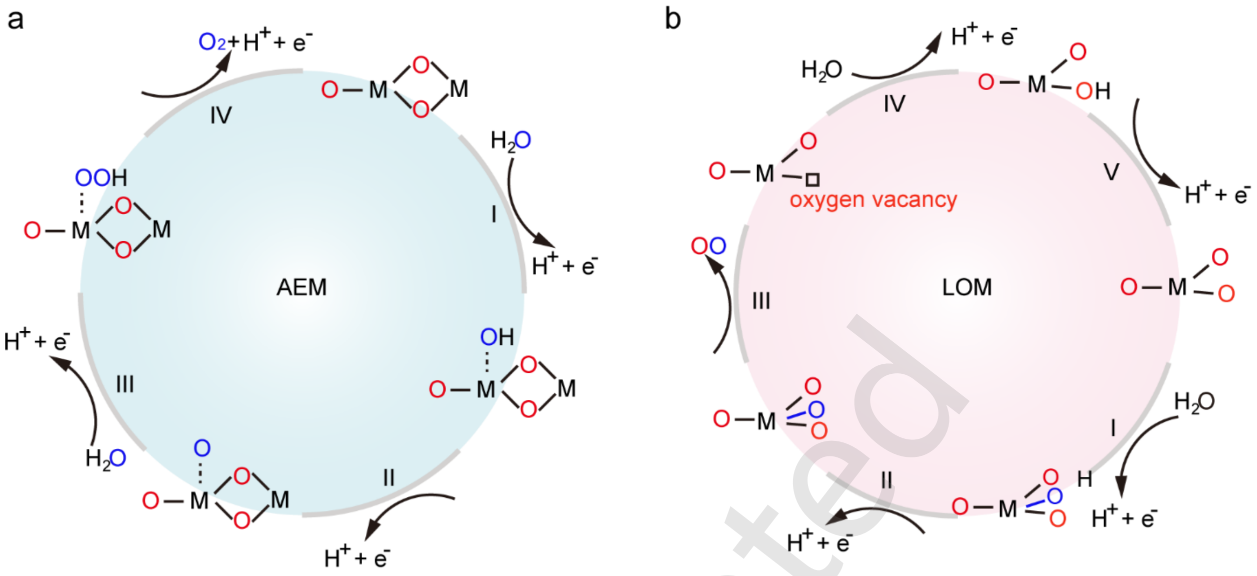

Fig. 1 Mechanisms of acidic OER. **a**, Adsorbate evolution mechanism (AEM) pathway. **b**, Lattice oxygen mechanism (LOM) pathway.

Oxidation potential

Under the harsh conditions of PEM electrolysis (pH < 2, E > 1.5 V vs. RHE), IrO_2 and RuO_2 active sites are driven into thermodynamically unstable high-valence states (Ir≥+5–6, Ru≥+5–6) that readily dissolve as soluble species, RuO_2 overoxidizes to RuO_4^{2-} and IrO_2 to IrO_3 (Ir^{+6}) with acidic protons further accelerating detachment from the lattice[30, 31, 32] (Fig. 2). Thermodynamic and experimental studies reveal distinct "corrosion threshold" potentials that RuO_4^{2-} formation becomes favorable near 1.4 V, above which RuO_2 dissolution rates increase sharply, whereas IrO_2 remains stable up to ~1.5 V but undergoes rapid IrO_3-mediated corrosion above ~1.6 V. Beyond these thresholds, dissolution rates rise exponentially, with each few hundred millivolts intensifying the progression from metal corrosion to high-valence oxide formation to complete solubilization.

Cyclic voltammetry (CV) serves as a key diagnostic, where anodic peaks for high-valence transitions (e.g., Ru^{+4}→Ru^{+6} at ~1.4 V)[33, 34] and accompanying dissolution-current spikes (monitored by on-line ICP–MS) mark the onset of catastrophic corrosion; repeated scans show diminishing and negatively shifted peaks, indicating defect accumulation and active-site loss. Rigorous CV screening, extending scans beyond 1.5–1.6 V, precisely defines each catalyst's "corrosion potential window," and only those with CV signatures anchored below the dissolution thresholds, through strategies such as dopant-induced redox suppression or protective architectures, can achieve both high acidic-OER activity and long-term stability.

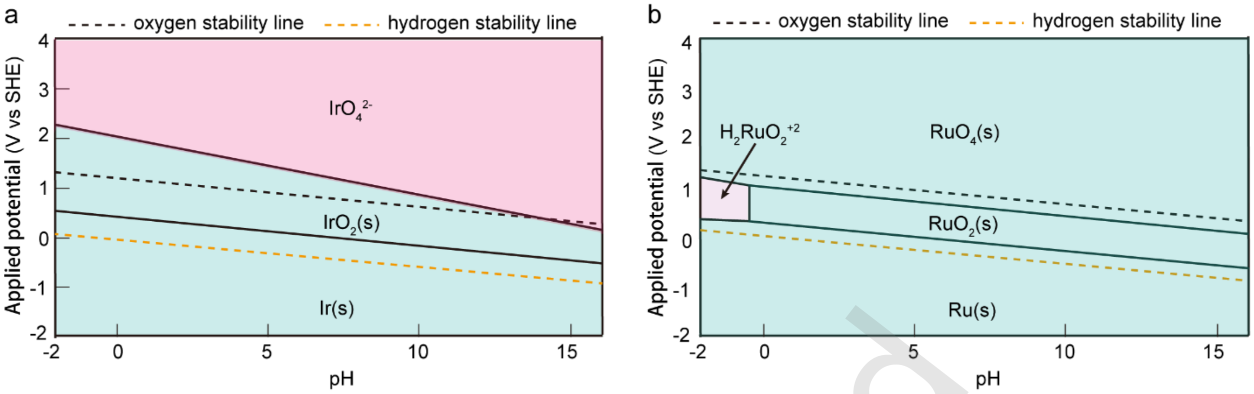

Fig. 2 Pourbaix diagrams of IrO_2 and RuO_2. **a**, Pourbaix diagrams of IrO_2. **b**, Pourbaix diagrams of RuO_2.

Catalysts detachment

In PEM electrolyzers, the dynamic reaction interface at the anode is a battlefield where oxygen evolution and mechanical destruction unfold simultaneously. The nucleation, growth, and detachment of O_2 bubbles, often treated as incidental byproducts, are powerful agents of catalyst layer degradation[35, 36, 37] (Fig. 3). As micron-sized bubbles form at active sites, their expansion exerts local shear stresses reaching 10^4–10^5 Pa, easily exceeding the binding energies that tether nanoparticles to the membrane (Fig. 3a). Detachment is equally destructive as capillary retraction forces generate microjets (~1 m/s) that act like nanoscale "hydraulic fracturing," prying nanoparticles from the surface. This mechanical assault is inseparably linked to electrochemical corrosion, producing a destructive synergy. Dissolution of high-valent metals such as $Ir^{>4+}$ hollows out the catalyst–support interface, cutting bonding strength by over 50%. Oxygen vacancy (Ov) clusters formed through the lattice oxygen mechanism concentrate stresses, magnifying bubble-induced damage by an order of magnitude. The result is a shelling–corrosion feedback loop as freshly exposed surfaces dissolve rapidly under high-potential acidic conditions, creating new bubble nucleation sites, accelerating particle loss, driving up overpotentials, and intensifying bubble activity—until the catalyst layer collapses. Recognizing this intertwined mechanical–chemical failure pathway reframes O_2 bubbles from passive products to active agents of decay, demanding that future PEM anode designs address bubble dynamics with the same urgency as intrinsic catalytic activity.

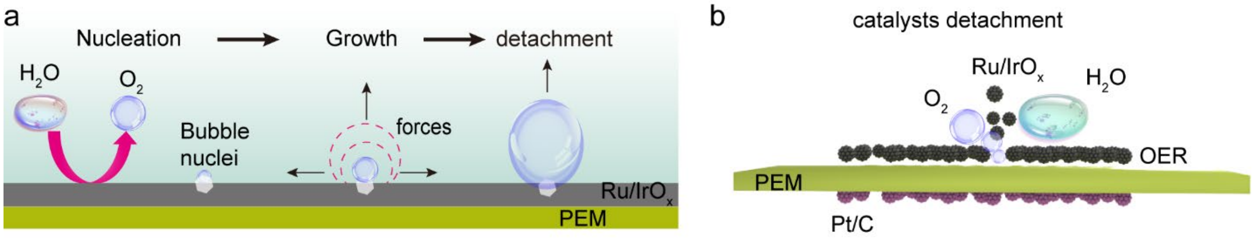

Fig. 3 Detachment of anode catalysts from the membrane caused by oxygen bubble generation. **a**, Oxygen bubble formation process at the anode catalysts layer. b, The formation and release of O_2 bubbles at the catalyst–membrane interface exert mechanical forces that lead to catalyst detachment.

Poisoning and contamination

In PEM water electrolyzers, chemical/electrochemical attack dominates membrane aging under high anodic potentials, oxygen-rich conditions, and pressure differentials. Oxygen crossover and partial reduction at the cathode generate H_2O_2, $HO_2\cdot$, and $HO\cdot$ radicals that cleave the PFSA backbone, causing end-chain "unzipping," functional-group loss, thinning, and ultimately pinholes and gas crossover (often tracked by increased fluoride release rate, FRR). Metal ions introduced during operation catalyze radical formation and further depress proton conductivity by exchanging with $–SO_3H$ sites. In the highly active anode of a PEM electrolyzer, trace impurities, often at only parts-per-million (ppm) levels, can be silent yet potent degraders, undermining catalyst stability through adsorption, active-site blockage, corrosion catalysis, or phase-change induction[38, 39, 40] (Fig. 4). These impurities may originate from feedwater (e.g., chlorine ions, sulfur dioxide, calcium and magnesium hardness ions) or systemic corrosion releasing metal ions such as $Fe^{2+/3+}$ and Cu^{2+}. In the harsh oxidative–acidic environment of the anode, even low concentrations can inflict severe damage. For example, at potentials above 1.3 V vs. RHE, Cl^- is oxidized to Cl_2 or hypochlorous acid (HClO)[41], which reacts with reactive oxygen species to attack the Ru/IrO_2 interface, forming an autocatalytic dissolution loop. Industrial data show that as little as 10 ppm Cl^- can accelerate Ir dissolution rates fivefold, causing catalyst layer delamination within hundreds hours. Similarly, $Fe^{2+/3+}$ and $Cu^{+}/^{2+}$ ions can adsorb onto active sites, blocking OH-binding positions crucial for the OER. At high potentials, these ions oxidize in situ to insulating oxides (e.g., Fe_2O_3), which blanket the surface and raise charge-transfer resistance. Hardness ions such as Ca^{2+} and Mg^{2+} further degrade performance by combining with phosphate impurities to form mineral scales (e.g., $Ca_3(PO_4)_2$) within porous electrodes, obstructing mass-transfer channels, inducing localized overheating, and accelerating support corrosion. Over time, these impurity-driven pathways amplify ROS flux to the membrane, accelerating PFSA chain scission, FRR rise, and H_2/O_2 crossover, eventually compromising cell safety and efficiency.

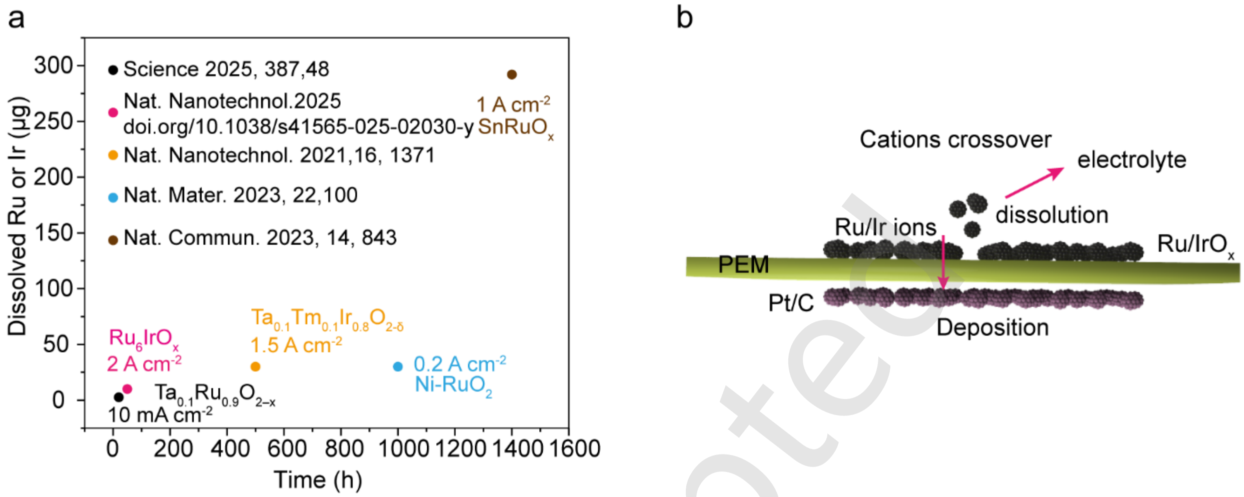

Fig. 4 Dissolution and migration of Ru/IrO$_x$ from the anode to the cathode. **a**, Quantification of dissolved Ru and Ir ions reported in representative acidic OER studies. The data highlight the extent of catalyst dissolution under various operating conditions, reflecting the stability differences among Ru- and Ir-based electrocatalysts. **b**, Side reactions in the anode chamber dissolve Ru/IrO$_x$, producing cations that migrate through the PEM and deposit on the cathode catalysts.

Anode support degradation

The MEA architecture defines where reactions and coupled transports occur. The PTL must balance water delivery and oxygen removal, while the catalyst layer requires an optimized pore structure and ionomer network to maintain continuous pathways for protons, electrons, and gases. Structural imbalance increases interfacial resistance and lowers efficiency. Carbon support materials face severe corrosion challenges under the extreme anodic potentials of PEM electrolyzers. When the potential exceeds ~1.0 V vs. RHE, the carbon framework undergoes irreversible oxidative corrosion via the reaction ($C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$)[14, 42]. Under industrial operating conditions, this process can be catastrophic: the support surface area may drop by up to 70% within just 24 hours, leading to agglomeration and detachment of catalyst particles, much like birds losing their nests. Simultaneously, the collapse of the support structure can produce cracks exceeding 5 μm in width within the electrode, enabling shear forces from gas bubbles to tear and further degrade the catalyst layer. For instance, Toyota's research[43] reports that carbon-supported Ru/IrO_2 anodes can lose up to 40% of their electrochemically active area after only 200 hours of operation at a high current density of 1.8 A cm^{-2}.

While titanium supports (PTL) offer superior corrosion resistance, they suffer from electrical conductivity loss due to surface passivation[44, 45] (Fig. 5). At high anodic potentials, a rutile titanium dioxide (TiO_2) layer (resistivity > 10^8 Ω cm) forms on the surface. This insulating film impacts anode performance in two critical ways. First, even a passivation layer only ~10 nm thick can raise the electrode–support interface impedance by more than two orders of magnitude, imposing an additional overpotential of ~200 mV. Second, by blocking electron conduction pathways, the passivation layer forces current to flow preferentially through unpassivated edge sites. These sites experience excessive local current densities, accelerating dissolution and initiating a chain reaction of "edge etching," which progressively deactivates the central active regions due to insufficient electron supply, ultimately leading to complete functional collapse of the catalyst layer.

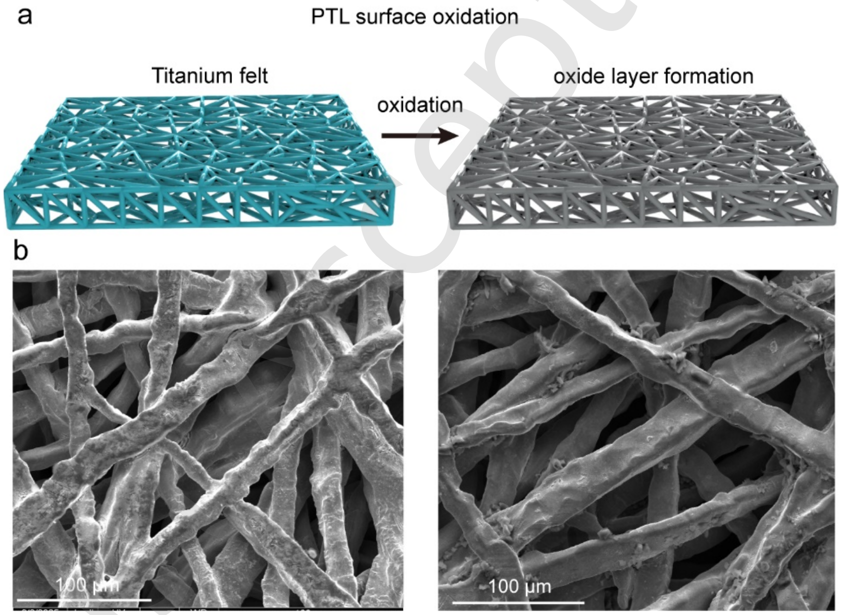

Fig. 5 Oxidation of the PTL surface layer. **a**, Over-oxidation of the PTL surface layer during the OER increases the resistance of the PEM electrolyzers. **b**, The scanning electron microscopy images of the commerical Pt@Titanium felt.

Additionally, the flow field acts as the highway for mass and heat management. Properly designed channels ensure uniform water supply and efficient removal of oxygen bubbles, preventing local dry-out and bubble-induced blockage of active sites. In contrast, uneven or overly narrow channels lead to mass transport limitations and localized overheating. Poor heat dissipation further accelerates membrane degradation and catalyst dissolution, shortening device lifetime. Ultimately, well-integrated flow field and PTL designs enable low voltage operation, uniform current distribution, and long-term durability. Achieving such synergy, through efficient and stable transport from macroscopic channels to microscopic pores, is essential to overcome the performance and cost barriers of PEM water electrolysis.

Stack-Level (Systemic) Failure

Catalysts decay, impurity-driven phenomena and component degradation cascade into stack-level failures through interconnected pathways. Catalyst layer delamination, mineral scale precipitation, insulating oxide formation, and membrane thinning produce non-uniform current distribution, local overheating, and mechanical stress on MEAs, PTLs, and seals. Corrosion products from PTLs or bipolar plates reintroduce metal ions, sustaining feedback loops that accelerate performance loss.

Gas crossover due to membrane cracks or thinning is detectable via abnormal OCV decay, back-pressure fluctuations, and elevated hydrogen in oxygen streams. Pre-failure indicators include rising FRR, increasing charge-transfer resistance (EIS), and measurable metal/halide content in effluent (ICP-MS). Impurity-related mechanisms remain underexplored: over 90% of academic studies rely on ultrapure water (<0.1 μS/cm), whereas industrial systems use feedwater ≤5 μS/cm, containing ppb-ppm impurities, leading to systematic overestimation of durability. Long-term operation causes dynamic accumulation of impurities at the membrane–electrode–gas interface, while synergistic effects (e.g., $FeCl_4^-$ formation from Cl^- and Fe^{3+}) distort the Ir lattice, producing nonlinear acceleration of degradation.

Operational factors, such as unstable power, inadequate water treatment, and poor BOP maintenance, exacerbate these effects, driving stack voltage rise, efficiency loss, and unplanned shutdowns. Together, impurity poisoning, ROS-driven membrane decay, and mechanical/structural defects define a coupled, system-level failure landscape, highlighting the need for impurity-aware durability testing, strict feedwater specifications, robust materials/coatings, and comprehensive monitoring to ensure long-term PEM electrolyzer operation.

Outlook

In this perspective, we would like to specify the key parameters and operating regimes that must be aligned to bridge the gap between laboratory-scale testing and practical PEM electrolyzer operation. We highlight that current density, cell voltage window, temperature, pressure, and electrolyte composition are the most critical factors governing degradation behavior. Laboratory studies often employ mild conditions (e.g., ≤100 mA cm^{-2}, ambient pressure, active surface area <5 cm^2), whereas industrial systems typically operate at 1–2 A cm^{-2}, 60–80 °C, >100 cm^2, and elevated pressures with dynamic load fluctuations. These discrepancies alter mass transport, bubble dynamics, and dissolution kinetics, leading to vastly different stability trends. We therefore recommend benchmarking catalyst performance under MEA-integrated, high-current, and transient operation to accurately capture degradation pathways and validate mechanistic models. Such alignment of testing parameters will enable meaningful translation of laboratory insights into device-relevant durability strategies and enhance the practical impact of future PEM anode research.

Our understanding of acidic OER catalyst deactivation under realistic PEM electrolyzer conditions remains incomplete. Advanced in situ techniques, such as synchrotron-based X-ray spectroscopy, electrochemical Raman, and DEMS performed in single-cell PEM setups with a window on the anode plate that allows to observe the anode catalysts/membrane interface, enable real-time observation of oxidation states, dissolution kinetics, and structural evolution under high temperature, pressure, and current load. The development of advanced diagnostic tools, such as cryogenic X-ray photoelectron spectroscopy (cryo-XPS), would enable more precise characterization of anode degradation processes. Integrating these data with electrochemical–mechanical–transport models allows quantitative evaluation of coupled degradation pathways, including dissolution, phase transition, bubble stress, and impurity adsorption. Together, these approaches not only reveal the dynamic feedback between local overpotential, mass transport, and mechanical stress but also guide the rational design of more stable catalysts, corrosion-resistant interfaces, and optimized operating protocols for durable PEM electrolyzers.

The durability limits of conventional Ru/Ir-based catalysts in high-potential, strong-acid environments are nearing saturation. Breakthrough materials are urgently needed. High-entropy alloys and oxides can enhance intrinsic stability through synergistic component interactions; two-dimensional materials such as MXenes offer corrosion resistance through their tunable electronic structure and high surface area; and biomimetic catalysts can draw inspiration from nature's photosynthetic systems. A particularly promising frontier is the design of high-entropy oxides [46, 47], which is characterized by their multi-principal cation compositions, representing a promising pathway toward unprecedented stability through high configurational entropy and synergistic lattice effects. Their intrinsic lattice distortion suppresses cation diffusion and ordering, thereby mitigating dissolution and phase segregation, the long-standing Achilles' heel of conventional binary oxides. The primary challenge, however, lies in achieving precise control over elemental composition and nanoscale homogeneity during synthesis, as local compositional inhomogeneity can generate structural weak points. The next breakthrough will require moving beyond empirical "kitchen-sink" formulations toward rationally designed high-entropy oxides in which specific elements fulfill well-defined roles: conductive species (e.g., Ir, Ru) to ensure electron transport, stabilizing elements (e.g., Ti, Zr) to reinforce structural integrity, and protective components (e.g., Cr) to form self-passivating surface layers. Integrating computational screening, such as DFT calculations for site-specific activity and dissolution energy, with advanced synthesis and in situ characterization will be essential for identifying optimal, multifunctional compositions and ultimately translating configurational entropy into functional stability. While non-precious metal catalysts remain attractive for cost reduction, their acidic OER stability must improve by at least one to two orders of magnitude. Achieving this goal demands novel protection strategies, including atomic-scale encapsulation and robust support–interface engineering.

Current accelerated stress test (AST) protocols fail to reflect the realities of industrial operation. A unified evaluation framework must be established—one that incorporates dynamic operating conditions (start–stop cycles, load fluctuations), impurity challenges (e.g., Fe^{3+}, Cl^-), 10,000-hour durability targets, and comprehensive multi-parameter in situ monitoring of performance decay, metal dissolution, and microstructural evolution. Mechanism-informed lifetime prediction models should integrate AST results with real-world failure modes, providing a quantitative basis for both material screening and electrolyzer design. Without such standardized benchmarks, the industrial adoption of advanced catalyst materials will remain slow and fragmented.

Addressing catalyst deactivation is inherently a multi-scale systems problem that demands interdisciplinary cooperation. Materials science must intersect with electrochemistry and surface science to elucidate atomic-level degradation pathways. Chemical and mechanical engineering can contribute by optimizing electrode architectures, such as three-dimensional supports resistant to bubble-induced mechanical stress, and by refining flow field designs for uniform mass transport. Computational science, including machine learning, should accelerate both the discovery of stable materials and the development of predictive multiscale models. Industry–academia partnerships are essential as industrial practitioners must articulate the key failure modes encountered in the field, while academic researchers focus on disruptive solutions, ensuring rapid translation from laboratory breakthroughs to commercially reliable electrolyzers. Both our group and other researchers in this field currently face a fundamental limitation: there is still no unified dataset that systematically decouples and quantifies all interacting failure pathways under identical operating conditions. This gap arises from differences in system coupling and heterogeneity, the strong sensitivity of degradation to operating potentials and conditions, and the limitations of existing characterization techniques. We hope that future studies will comprehensively analyze degradation processes under identical conditions to establish a quantitative failure-account map.

Conclusion

Anode catalyst deactivation is a central bottleneck limiting the economic viability of PEM water electrolysis. At its core lies the dynamic coupling of multiple failure modes under extreme operating conditions. Overcoming this challenge could dramatically lower lifecycle costs (CAPEX and OPEX), accelerate the deployment of green hydrogen technologies, and drive fundamental advances in electrocatalysis, interface science, and multiscale modeling. We call upon the global research community to unite advanced in situ diagnostics, disruptive material innovation, standardized evaluation protocols, and integrated engineering strategies. Through open and collaborative efforts, it is possible to initiate a new generation of efficient, durable, and cost-effective PEM electrolyzers, providing a decisive technological foundation for achieving global carbon neutrality.

Data availability

Not applicable.

Author contributions

H.W. supervised the project. H.W., S.H., and P.Z. jointly wrote and revised the manuscript.

Competing interests

The authors declare that there is no competing interest.

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