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Review Article

The roles of interfacial water in electrocatalytic water splitting across diverse electrolyte environments

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ABSTRACT

Electrocatalytic water splitting is central to green hydrogen production, yet its efficiency is increasingly governed by both active-site energetics and the nanoscale water layer at the electrode-electrolyte interface. Interfacial water directly influences water dissociation, proton and hydroxide transport, and catalyst stability. Its mechanistic roles, however, are fundamentally electrolyte-dependent, varying across alkaline, acidic, and neutral conditions and further diverging between the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), with seawater serving as a representative case in which additional ionic perturbations are superimposed on the alkaline and neutral baselines. In this review, we systematically examine how the distinct functions of interfacial water vary with the electrolyte environment. For each, we analyze how the electrolyte chemistry dictates the core function of interfacial water, survey the corresponding catalyst design strategies, and identify the mechanistic principles linking interfacial water structure to catalytic performance. We emphasize that an effective strategy in one environment may be irrelevant in another, and that catalyst design must target the electrolyte-specific roles of interfacial water rather than following a universal approach. We conclude by outlining a forward-looking agenda that spans standardized in situ characterization, electrolyte-specific quantitative descriptors, and device-level translation, and by distilling three prioritized research directions for converting these electrolyte-specific principles into practical catalyst design.

Keywords: interfacial water, hydrogen-bond network, electrocatalytic water splitting, electrolyte environment.

1.Introduction

Renewable-driven water electrolysis for green hydrogen production is a cornerstone technology on the path to global deep decarbonization.[1, 2] Electrocatalyst design has long been guided by the Sabatier principle, which uses the adsorption free energies of reaction intermediates as the central descriptors for optimizing intrinsic active-site activity.[3] A growing body of experimental and theoretical evidence, however, has shown that optimizing the electronic structure of a catalyst alone cannot fully explain or predict its performance under realistic operating conditions. Both HER and OER occur within the nanoscale catalyst-electrolyte interface, where the local physicochemical environment directly governs reaction kinetics and overall energy efficiency.[4, 5] Interfacial water at the catalyst-electrolyte boundary is increasingly recognized as a critical factor that governs catalytic performance.[6-8] Importantly, interfacial water engineering accounts for what adsorption-energy optimization alone cannot explain, and many leading catalysts now tune both simultaneously.

Interfacial water refers to the thin water layer spanning only a few molecular diameters at the electrode-electrolyte interface, a region conventionally divided into the inner Helmholtz plane, the outer Helmholtz plane, and the adjacent diffuse layer, in which water molecules and hydrated ions adopt arrangements distinct from those of bulk water. Rather than serving as an inert solvent, it exists as ordered molecular ensembles subject to the dual regulation of the solid surface and the interfacial electric field, adopting specific orientational arrangements and hydrogen-bond configurations. Bulk water possesses an isotropic, dynamically fluctuating hydrogen-bonding network. As water approaches the charged electrode, the interfacial electric field and the surface orient the water dipoles and reorganize this network, so the near-surface water is no longer equivalent to bulk water and is instead resolved into several spectroscopically distinct populations.[9, 10] These species, together with water bound in ion hydration shells, are further governed not only by the bulk pH but also by the electrode potential, the surface charge and potential of zero charge, the electric-field strength, the identity and ionic strength of the cations and anions, the water activity, the surface hydrophilicity, and specific adsorption, and their relative populations interconvert as the potential is shifted. The electrolyte-specific distinctions developed below should therefore be read as tendencies established under the cited conditions rather than as absolute categories. By deconvoluting the O-H stretching band in in situ Raman and surface-enhanced infrared absorption spectra, interfacial water can be resolved into four distinct configurations, namely tetrahedrally coordinated water ($4\text{-HB}\cdot\text{H}_2\text{O}$, $\sim 3200\text{ cm}^{-1}$), doubly hydrogen-bonded water ($2\text{-HB}\cdot\text{H}_2\text{O}$, $\sim 3400\text{ cm}^{-1}$), dangling O-H water (~ 3600 to 3700

cm^{-1}), and cation-hydrated water ($\text{M}^+\cdot\text{H}_2\text{O}$, $\sim 3600\text{ cm}^{-1}$). [11-13] The two higher-frequency populations, dangling O-H and cation-hydrated water, are only weakly hydrogen-bonded and dissociate readily, and both are features of the interfacial environment rather than of the bulk. They overlap spectrally near 3600 cm^{-1} but are physically distinct, the dangling O-H being a surface species whose O-H group is free of hydrogen bonding, while the cation-hydrated water is water in the hydration shells of electrolyte cations. Because of this spectral overlap, the two are often merged under a single umbrella term, free water, which is nevertheless applied inconsistently across the literature, sometimes referring to the dangling O-H, sometimes to the cation-hydrated water, and sometimes to the entire high-frequency band without distinguishing the two. Accordingly, an increase in the free-water population is widely reported to correlate positively with catalytic activity. [14] This correlation is not universally beneficial, because increasing the weakly hydrogen-bonded population disrupts the rigid hydrogen-bond network and may simultaneously weaken the connectivity required for efficient proton transport via the Grotthuss mechanism. [15] These band positions and intensities are, however, not universal, because they depend on the surface selection rules, the applied potential, the ion identity, and the deconvolution model, and are further modulated by electric-field-induced Stark shifts. Interfacial water additionally exhibits orientational ordering absent in bulk water, with the H-down configuration most effectively promoting O-H bond cleavage. [9, 11] This orientational tuning of water dissociation, however, has been established almost exclusively in alkaline media. Whether the same orientation-activity coupling persists in proton-rich, proton-poor, or chloride-rich electrolytes is far from obvious. The evidence surveyed in this review demonstrates that it does not, and that interfacial water performs fundamentally distinct mechanistic roles depending on the chemistry of the electrolyte. The central thesis of this review is therefore that catalyst design must target these electrolyte-specific functions rather than following a universal approach.

Existing reviews have addressed important facets of this topic, yet none has systematically compared interfacial water function across electrolyte environments. Tang et al. surveyed the multifaceted roles of interfacial water across diverse electrocatalytic reactions, providing a broad but reaction-oriented overview, [6] and Huang et al. examined interfacial water modulation in the context of water-participating electrocatalytic hydrogenation, focusing on a specific reaction class. [16] Wu et al. classified interfacial water regulation strategies by catalyst engineering tactics such as crystal-structure modulation, surface modification, and active-site construction, providing a strategy-oriented framework. [5] Guo et al. similarly organized the discussion around active-site

engineering, focusing on catalyst structural design rather than electrolyte-specific function.[17] A systematic comparison of the distinct mechanistic roles that interfacial water plays in different electrolyte environments, however, remains conspicuously absent. In this review, we first establish how proton activity and half-reaction set the intrinsic function of interfacial water across alkaline, acidic, and neutral conditions for both the HER and the OER. We then treat the remaining electrolyte-specific components as perturbations superimposed on this baseline. Seawater, whether used directly near pH 8.2 or deliberately alkalized, retains a neutral-to-alkaline character, so its distinct behavior stems from its non-pH components, namely Cl^- , Mg^{2+} , and Ca^{2+} , rather than from the bulk pH. Buffer anions likewise restructure the interfacial hydrogen-bond network in neutral electrolytes, and ionomers impose a locally acidic microenvironment in acidic membrane electrode assemblies. Across all these environments we identify the mechanistic principles that link interfacial water structure to catalytic performance (Figure 1). We conclude by outlining a forward-looking agenda that spans standardized in situ characterization, electrolyte-specific quantitative descriptors, and device-level translation, and by distilling three prioritized research directions.

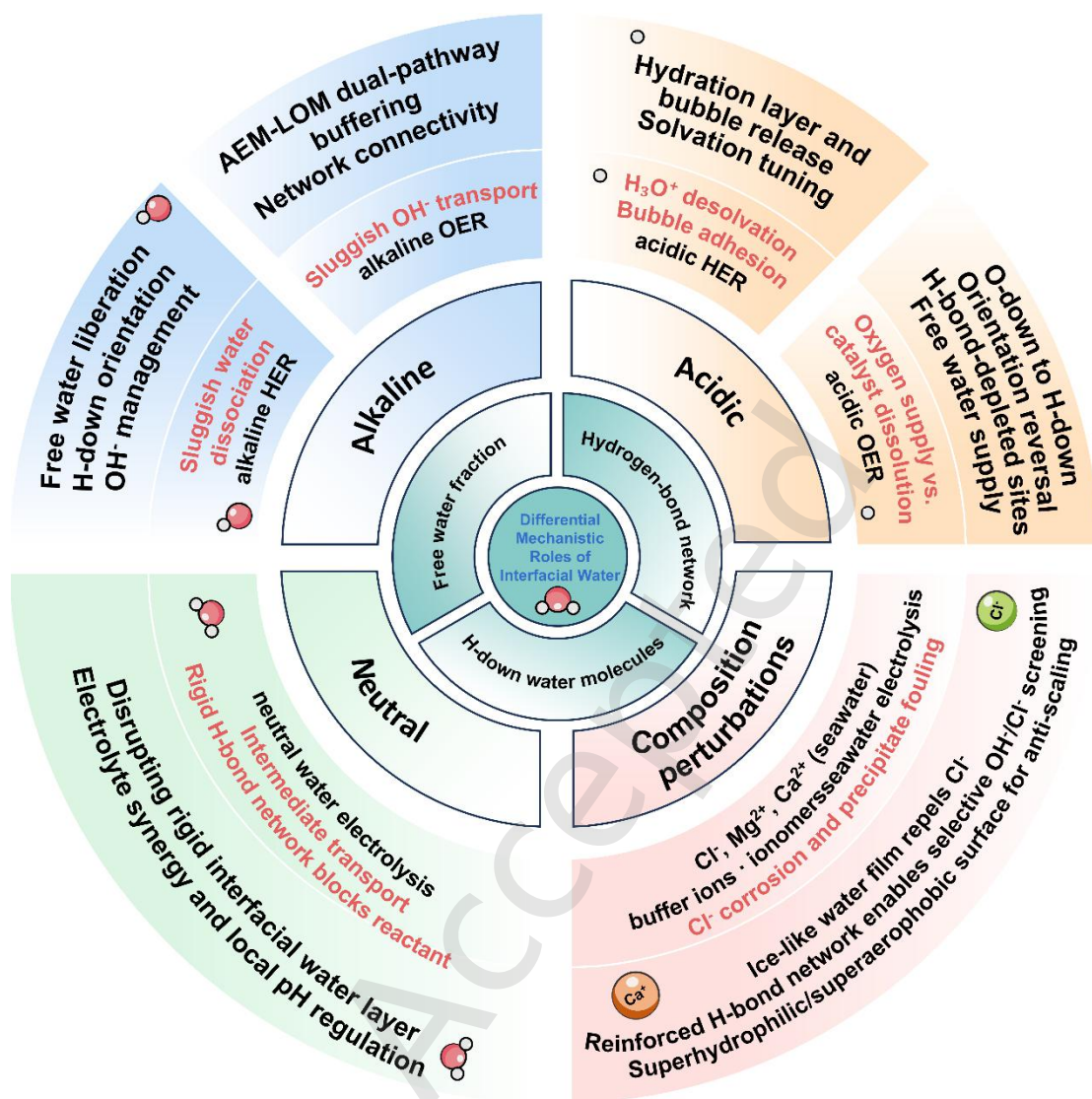


Figure 1. Schematic overview of the distinct roles of interfacial water and the corresponding catalyst design strategies across the alkaline, acidic, and neutral environments, together with the electrolyte-specific composition perturbations (seawater Cl⁻, Mg²⁺, Ca²⁺; buffer ions; ionomers) that act on these baselines.

2. Roles and modulation strategies of interfacial water across electrolyte environments

The structural features and mechanistic roles of interfacial water differ fundamentally across electrolyte environments. In alkaline media, interfacial water acts as the proton donor for HER (Figure 2a), dissociating in situ to generate adsorbed hydrogen (H^*); in acidic media, by contrast, the abundant H^+ in the bulk means that O-H bond cleavage of water is no longer required for proton supply, yet interfacial water still governs proton solvation, desolvation, and proton transport through proton relays (Figure 2b); in neutral media, the rigid interfacial hydrogen-bond network severely constrains both water dissociation and intermediate transport (Figure 2c). In seawater electrolysis, interfacial water must additionally function as a protective barrier against chloride corrosion and precipitate fouling (Figure 2d).[18-20] These electrolyte-specific roles, which further diverge between HER and OER within the same electrolyte, create an urgent need for catalyst design strategies tailored to the target environment. Even within a single electrolyte, the core functions of interfacial water in HER and OER are often fundamentally distinct. We therefore treat alkaline and acidic environments separately according to reaction type. Beyond optimizing the Gibbs free energy of adsorption at active sites, the intrinsic structural design of the catalyst also precisely modulates interfacial water, enabling water-molecule activation, hydrogen-bond network restructuring, and synergistic optimization of the electric double-layer microenvironment, without relying on complex electrolyte additives.[4, 5]

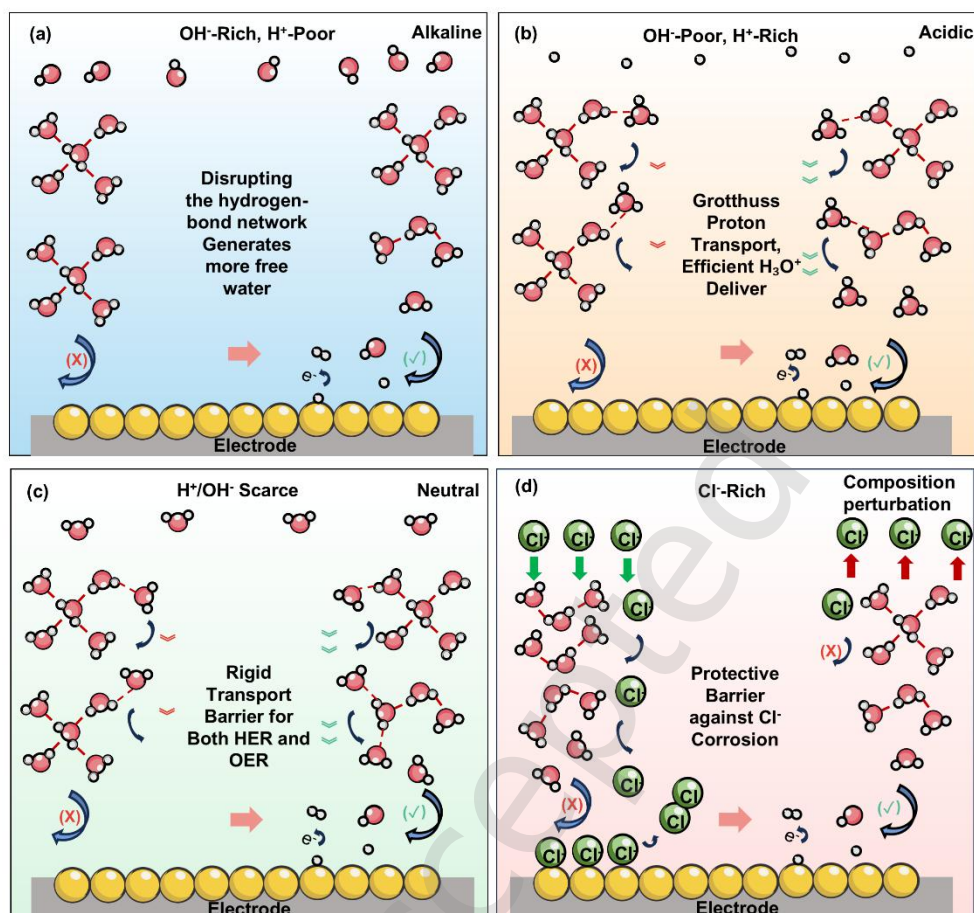


Figure 2. Schematic comparison of interfacial water functions across the alkaline, acidic, and neutral environments, and of the composition perturbations (illustrated by seawater Cl⁻ enrichment) superimposed on this baseline. (a) Alkaline environment: free water liberated from the rigid hydrogen-bond network serves as the proton donor for HER. (b) Acidic environment: a moderately disrupted hydrogen-bond network facilitates H₃O⁺ solvation and Grotthuss proton transport. (c) Neutral environment: the dense hydrogen-bond network forms a rigid transport barrier that suppresses water dissociation and intermediate transport, and must be disrupted to restore reactant and product mobility. (d) Composition perturbation (illustrated by seawater Cl⁻ enrichment). Cl⁻ accumulates near the interface, where an ordered interfacial water film functions as a protective barrier that repels Cl⁻ while permitting OH⁻ transport.

2.1 Alkaline environment

Alkaline water electrolysis represents the most extensively studied electrolyte medium, in which there are essentially no free protons and interfacial water becomes the proton donor for the hydrogen evolution reaction (HER). In the Volmer step ($\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}^\bullet + \text{OH}^-$), a proton is transferred directly

from interfacial water to the surface as adsorbed hydrogen (H^*) through O-H bond cleavage, with hydroxide released as the co-product, a route that has no counterpart in acidic media.[21-23] Simultaneously, the high OH^- concentration generates a strong interfacial electric field that produces rich and well-resolved vibrational spectroscopic fingerprints, making alkaline environments the most thoroughly characterized among these electrolyte environments surveyed in this review.[5, 9] Despite operating in the same electrolyte, alkaline HER and alkaline OER impose fundamentally distinct demands on interfacial water. HER requires rapid water dissociation kinetics and efficient proton transport, whereas OER relies on interfacial water as both an OH^- transport medium and a carrier that fine-tunes the binding energetics of multiple reaction intermediates ($^*OH$, $^*O$, $^*OOH$).[24, 25] These two half-reactions share a common physical medium, the interfacial hydrogen-bond network, whose structure must strike a delicate balance between being sufficiently disrupted to liberate weakly hydrogen-bonded water for dissociation and sufficiently connected to sustain proton and hydroxide transport.[15, 26]

2.1.1 Alkaline HER: water as the proton donor

Alkaline HER proceeds via the Volmer-Heyrovsky or Volmer-Tafel mechanism. The Volmer step ($H_2O + e^- \rightarrow H^* + OH^-$) supplies the adsorbed hydrogen, and its efficiency is governed by four distinct sub-processes, namely water dissociation (cleavage of the O-H bond), proton transfer to the surface (formation of H^*), H adsorption energetics, and removal of the OH^- product.[24, 27] The structure and activation state of interfacial water molecules are central to the first three of these.[22, 23] Three complementary strategies have emerged to accelerate this step. These include disrupting the hydrogen-bond network to liberate free water, orienting interfacial water into the H-down configuration, and managing the OH^- product through either rapid removal or cooperative reuse. Each strategy is examined in the following discussion.

(1) Liberating free water

The dissociation activity of interfacial water directly dictates the rate of $^*H$ supply. Water molecules embedded in a strongly hydrogen-bonded network are resistant to O-H bond cleavage because the bond is stabilized by hydrogen bonding, whereas free water, being less constrained and structurally more flexible, can markedly lower the energy barrier of the Volmer step. Cui et al. demonstrated this strategy in a W_1O/NiS heterointerface system. In situ Raman spectra reveal that on pristine NiS, the O-H stretching region is dominated by the 4-HB- H_2O band, indicative of a rigid hydrogen-bond network; upon incorporation of oxygen-coordinated W single atoms, the free water

peak grows markedly with increasing cathodic potential, while the 4-HB·H₂O contribution diminishes (Figure 3a-b). Quantitatively, the free-water to 4-HB·H₂O area ratio on W₁O/NiS is nearly twice that on NiS across the entire potential window (Figure 3c), confirming that the local electric-field perturbation generated by interfacial charge redistribution at the W₁O-NiS junction effectively weakens hydrogen-bond coupling among water molecules and liberates free water for accelerated Volmer-step kinetics.[28] Wu et al. reported a complementary approach using Ru nanoparticle-decorated Raney Ni, where Ru sites simultaneously enriched cation-hydrated K⁺·H₂O and lowered the water-dissociation barrier.[29] These strategies share a common principle, namely that disrupting the rigid hydrogen-bond coupling of interfacial water liberates free water and accelerates proton supply for the Volmer step.

(2) Orienting water into the H-down configuration

Beyond increasing the free water population, the molecular orientation of interfacial water is another critical factor governing water dissociation efficiency. Shah et al. have shown on Pt single-crystal surfaces that the H-down configuration functions as a reaction switch for alkaline HER by shortening the charge-transfer distance and facilitating electron injection into the O-H antibonding orbital.[30] Tuning interfacial water into this H-down orientation therefore represents a central catalyst design objective. Yuan et al. constructed a PtO_x/NiO heterointerface in which the high-valence PtO_x component generates a strong interfacial dipole field. DFT calculations reveal that this dipole field originates from electron accumulation near PtO_x and depletion near NiO, which together produce an enhanced local dipole moment (Figure 3d). AIMD simulations confirm that this dipole field reorients interfacial water molecules into the H-down configuration, with a substantially smaller H₂O adsorption angle and shorter H-to-surface distance relative to metallic Pt/NiO (Figure 3e). The resulting H-down orientation markedly lowers the water dissociation barrier compared with Pt/NiO (Figure 3f), while the partially oxidized Pt state simultaneously shifts the H adsorption free energy toward thermoneutral, to -0.02 eV versus 0.42 eV on Pt/NiO (Figure 3g). This dual optimization, dipole-driven water orientation and valence-tuned H binding, collectively accelerates alkaline HER kinetics.[31] Cai et al. further advanced this orientational control strategy by constructing IrRu dual single-atom sites (DSACs) on a CoP support. The electronegativity difference between Ir and Ru generates an atomic-scale local electric field that polarizes interfacial water molecules into an asymmetric H-down geometry (Figure 3h).[32] DFT calculations quantify the consequence of this reorientation, showing that the H₂O dissociation barrier decreases from 0.91 eV on pristine CoP to 0.68 eV on IrRu DSACs

(Figure 3i).[32]

(3) Managing the OH⁻ product

The dissociation of interfacial water generates not only H but also OH⁻, which can accumulate at the active site and block subsequent water dissociation if not effectively managed.[33] Han et al. addressed this issue using a composite of Mo single atoms and Ru nanoclusters, in which the interfacial water network shuttles OH⁻ away from the oxophilic Mo dissociation sites toward adjacent Ru clusters for H₂ evolution.[34] Chen et al. took the opposite approach, demonstrating through in situ Raman spectroscopy on Au@Ru core-shell nanoparticles that OH⁻ can be retained at the surface as a cooperative participant. The full-range spectra simultaneously capture OH⁻ alongside interfacial water and two distinct adsorbed H species across the entire HER potential range (Figure 3j), and Gaussian deconvolution of the O-H stretching region resolves the three canonical interfacial water configurations coexisting with these species (Figure 3k). This spectral coexistence reveals that OH⁻ is not merely a site-blocking adsorbate but an integral component of the interfacial hydrogen-bond network. On high-valence RuO_x surfaces, moderately adsorbed OH⁻ serves as a proton acceptor, forming a hydrogen bond with an adjacent water molecule and facilitating its O-H bond cleavage, while hydrated Na⁺ ions drawn closer to the surface further lower the Volmer-step barrier. The applicability of these approaches depends on the surface chemistry. On oxophilic surfaces, rapid OH⁻ removal via the interfacial water network prevents active-site poisoning, whereas on noble metal surfaces with moderate OH binding, retaining OH as a proton acceptor converts a potential poison into a catalytic asset.[18]

In summary, the core objectives of interfacial water modulation in alkaline HER can be distilled to accelerating water dissociation kinetics and optimizing proton transport channels.

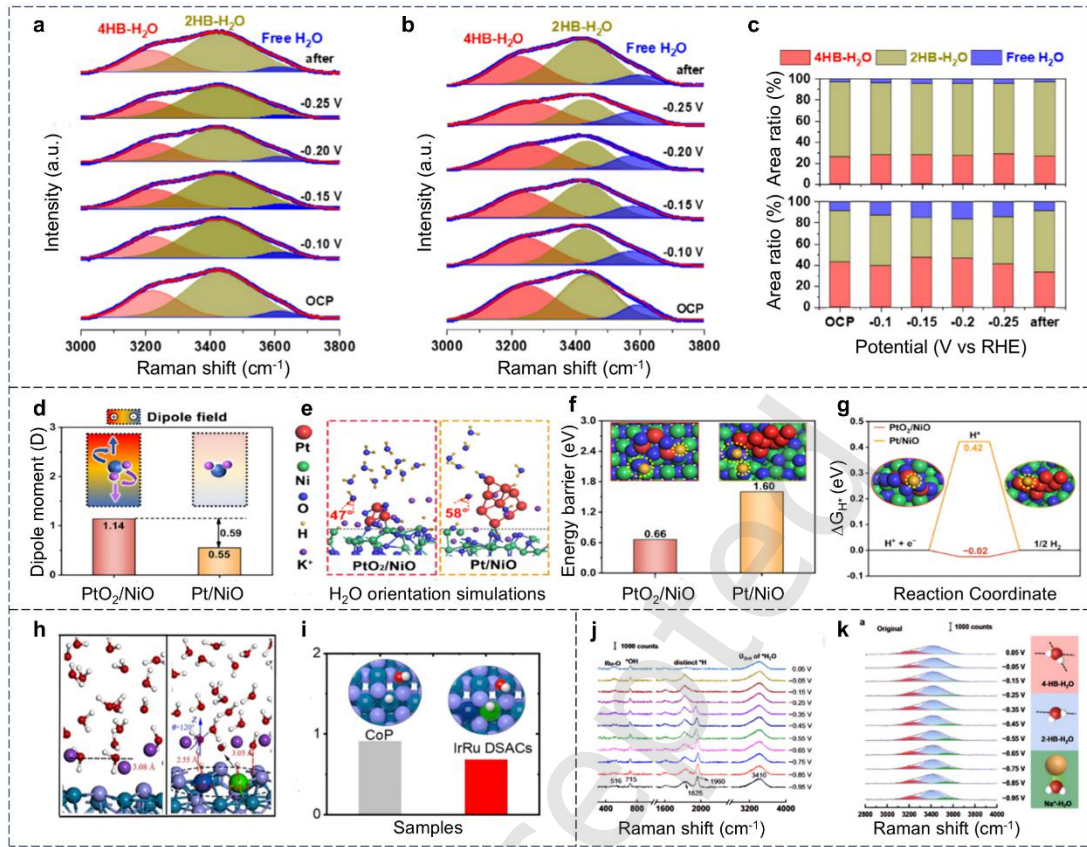


Figure 3. Strategies for tuning interfacial water orientation and managing OH^- in alkaline HER. In situ Raman spectra of interfacial water on NiS (a) and $\text{W}_1\text{O}/\text{NiS}$ (b) at varied potentials. (c) Free-water to 4-HB- H_2O area ratios on NiS and $\text{W}_1\text{O}/\text{NiS}$. Reproduced from Ref [28]. (d) Calculated dipole moments of PtO_2/NiO and Pt/NiO , with a schematic of dipole field-induced H_2O orientation regulation. (e) AIMD-simulated H_2O adsorption configurations on PtO_2/NiO and Pt/NiO . (f) DFT-calculated H_2O dissociation barriers. (g) H adsorption free energies on PtO_2/NiO (-0.02 eV) and Pt/NiO (0.42 eV). Reproduced from Ref [31]. (h) Schematic of Ir-Ru atomic-scale local electric field polarizing interfacial water into H-down geometry. (i) DFT-calculated H_2O dissociation barriers on CoP (0.91 eV) and IrRu DSACs (0.68 eV). Reproduced from Ref [32]. (j) In situ Raman spectra of alkaline HER on Au@Ru surfaces. (k) Gaussian deconvolution of the O-H stretching region into 4-HB- H_2O , 2-HB- H_2O , and $\text{Na}^+ \cdot \text{H}_2\text{O}$. Reproduced from Ref [18].

2.1.2 Alkaline OER: water as the OH^- transport medium

In contrast to alkaline HER, alkaline OER involves a four-electron transfer process with multiple reaction intermediates ($^*\text{OH}$, $^*\text{O}$, and $^*\text{OOH}$) undergoing sequential adsorption and conversion, rendering its kinetics far more sluggish than those of HER.[25] The role of interfacial water in alkaline OER is fundamentally distinct from that in HER. In HER, interfacial water acts as the sole proton donor

and the modulation focus lies in accelerating water dissociation. In OER, by contrast, the rate-determining step depends on the catalyst, the applied potential, the surface coverage, and the operative mechanism; O-O coupling (through $*O + OH^- \rightarrow *OOH$ in the AEM, or through lattice-oxygen involvement in the LOM) is rate-limiting on many oxide catalysts. Consequently, the function of interfacial water as both an OH^- transport medium and a carrier of reaction intermediates becomes the central factor governing catalytic efficiency.[35]

(1) Accelerating OH^- transport

Bulk OH^- must reach the active sites to achieve efficient transport, and this transport occurs through a combination of diffusion down concentration gradients, electromigration in the interfacial electric field, and structural (Grotthuss-type) proton-hopping diffusion along the hydrogen-bond network.[35] However, OH^- in alkaline solutions tends to form a hypercoordinated solvation structure, which impedes proton transfer from water molecules to OH^- and renders the diffusion rate of OH^- nearly half that of H^+ . [26] Breaking the rigid hydrogen-bond network and constructing well-connected OH^- transport channels therefore represents an important direction in catalyst design. Huang et al. demonstrated this principle in a CoN/HfO₂ heterostructure, in which the interfacial built-in electric field induced a ligand-field distortion that drove the Co²⁺ center from octahedral to tetrahedral coordination.[36] In situ ATR-SEIRAS spectra show that on CoN/HfO₂, the $K^+ \cdot H_2O$ component grows markedly with increasing anodic potential while the 4-HB·H₂O contribution progressively diminishes (Figure 4a-c). Quantitatively, the $K^+ \cdot H_2O$ population on CoN/HfO₂ exceeds that on pristine CoN across the entire potential range (Figure 4d), and the 4-HB·H₂O to 2-HB·H₂O area ratio decreases correspondingly (Figure 4e).[36] The tetrahedral Co²⁺ center enhances electron delocalization through its partially occupied t_2 orbitals, which weakens hydrogen-bond coupling among interfacial water and enriches $K^+ \cdot H_2O$ near the surface. A complementary approach introduces strongly electronegative ligands to directly enhance network connectivity. Li et al. incorporated F ligands at the pore edges of Fe-Ni(OH)₂, where F atoms form stronger hydrogen bonds with interfacial water than surface OH groups, accelerating synchronous proton transfer that accompanies OH^- diffusion and boosting the OER turnover frequency nearly two orders of magnitude.[37] In both cases, the increase in cation-hydrated water promotes OH^- transport not merely by disrupting the rigid network but by enhancing its connectivity. This demands a precise balance between liberating free water and preserving network pathways.[38,39]

(2) Buffering AEM and LOM through interfacial water

Beyond OH^- transport, the greater complexity of OER lies in the fact that the adsorption strengths of the subsequent $^*\text{O}$ and $^*\text{OOH}$ intermediates are likewise subject to fine regulation by hydrogen-bond interactions with interfacial water.[40] Excessively strong adsorption impedes product desorption, while overly weak adsorption destabilizes the intermediates, making it imperative to simultaneously optimize interfacial water dissociation and intermediate adsorption energetics.[41] Li et al. addressed this challenge by modifying FeNiOOH with arginine, a zwitterionic molecule whose guanidinium and carboxylate groups form dynamic hydrogen bonds with interfacial water. In situ Raman spectra with Gaussian deconvolution reveal a persistent dominance of $4\text{-HB}\cdot\text{H}_2\text{O}$ on pristine FeNiOOH across the OER potential range (Figure 4f),[42] whereas on Arg@FeNiOOH , the high-frequency modes associated with free water grow markedly with increasing anodic potential (Figure 4g).[42] Semi-quantitative analysis of spectral weights shows that on FeNiOOH , free water contributes only marginally even at elevated potentials (Figure 4h), while on Arg@FeNiOOH its apparent spectral weight rises from approximately 45 percent at open-circuit potential to over 70 percent at 1.8 V (Figure 4i).[42] This interfacial water restructuring has direct mechanistic consequences. ATR-SEIRAS spectra show that pristine FeNiOOH exhibits only a single band near approximately 1100 cm^{-1} , corresponding to the OOH intermediate of the conventional AEM pathway (Figure 4j), whereas Arg@FeNiOOH exhibits an additional absorption feature near approximately 1230 cm^{-1} assignable to the $^*\text{OO}$ species characteristic of the LOM pathway (Figure 4k).[42] This dual spectral signature demonstrates that arginine coordination enables the cooperative operation of AEM and LOM on a single catalyst surface. The liberated free water serves a dual function. On O-M-O units it accelerates OH^- supply for the AEM pathway, and on N-M-O motifs it replenishes the oxygen vacancies generated by lattice oxygen consumption along the LOM pathway. The interfacial water layer thus acts as a hydrogen-bond buffer that couples the two pathways and mitigates the activity-stability trade-off.[42-44]

Collectively, the core objectives of interfacial water modulation in alkaline OER lie in accelerating OH^- supply and transport while simultaneously optimizing the adsorption energetics of reaction intermediates.[45] Catalyst design can address these objectives through two parallel routes. The first disrupts the rigid hydrogen-bond network and introduces polar ligands to enhance OH^- transport. The second leverages dual-mechanism synergy to achieve simultaneous optimization of water dissociation and intermediate adsorption.[45] In contrast to alkaline HER, where proton supply serves as the central theme, interfacial water engineering in alkaline OER is more heavily weighted toward OH^-

transport and intermediate management. The two half-reactions complement each other, and their interfacial water modulation strategies together address the full scope of alkaline water splitting.

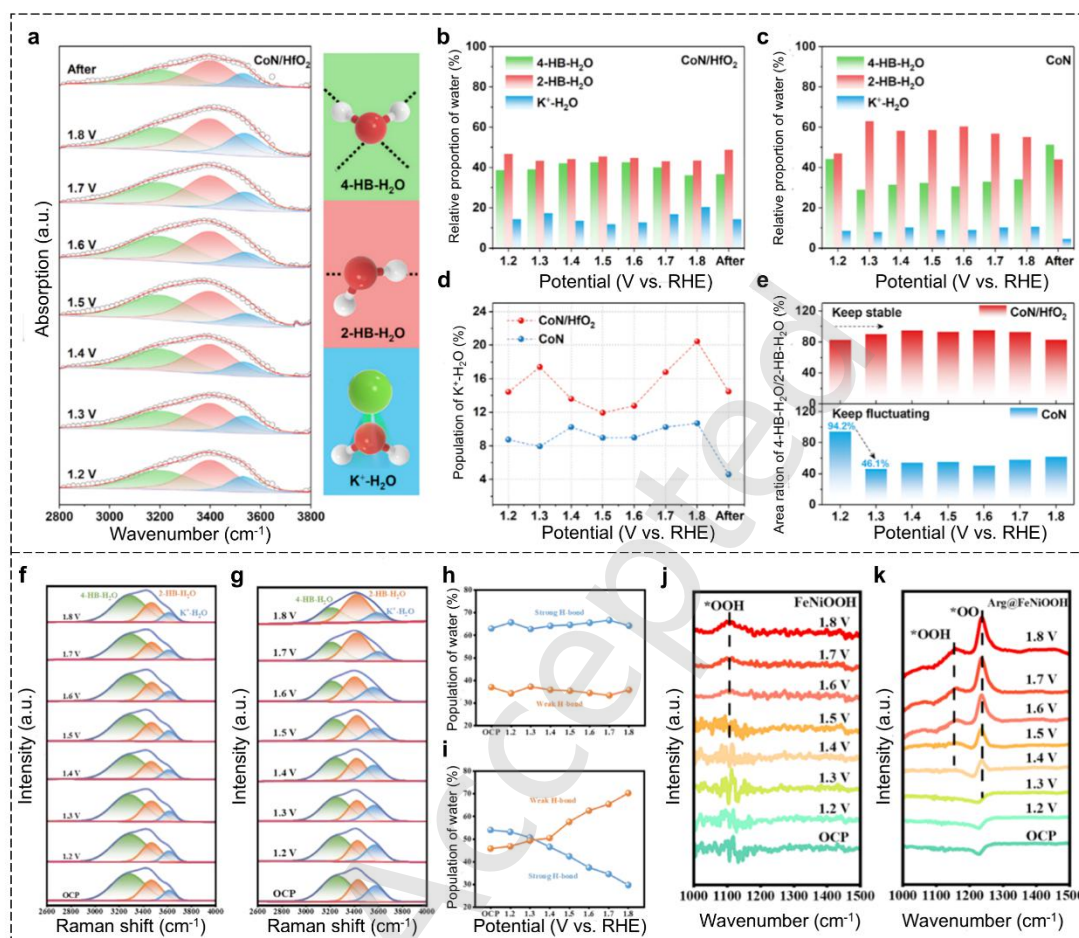


Figure 4. Interfacial water modulation for alkaline OER. (a) In situ ATR-SEIRAS spectra of interfacial water on CoN/HfO₂ in 1.0 M KOH. Proportions of water types on CoN/HfO₂ (b) and CoN (c). (d) K⁺·H₂O proportions on CoN/HfO₂ and CoN at varied potentials. (e) 4-HB·H₂O to 2-HB·H₂O area ratios. Reproduced from Ref [36]. (f) In situ Raman deconvolution of the O-H stretching region on FeNiOOH. (g) Corresponding deconvolution on Arg@FeNiOOH. Quantitative populations of strongly and weakly hydrogen-bonded water on FeNiOOH (h) and Arg@FeNiOOH (i). (j) ATR-SEIRAS spectrum of FeNiOOH at 1.50 V vs. RHE, showing the OOH intermediate of the AEM pathway. (k) ATR-SEIRAS spectrum of Arg@FeNiOOH, showing an additional *OO intermediate confirming AEM and LOM coexistence. Reproduced from Ref [42].

2.2 Acidic environment

Acidic water electrolysis, particularly proton exchange membrane water electrolysis (PEMWE), represents the industrially most relevant platform for green hydrogen production, yet interfacial water research in acidic media remains less developed than in alkaline environments. Two defining

characteristics distinguish the acidic environment. The first is a high concentration of H^+ (typically 0.1-0.5 M H_2SO_4 or HClO_4) and a correspondingly low OH^- activity. Under these conditions, the role of interfacial water undergoes a fundamental transformation relative to alkaline environments. In acidic HER, interfacial water no longer serves as the proton donor; it instead functions as the solvation medium for H_3O^+ , still participating in proton relay and desolvation, governing proton transport from the outer Helmholtz plane to the electrode surface through the Grotthuss mechanism.[14, 15] In acidic OER, interfacial water assumes a dual and paradoxical role, as it is simultaneously the sole oxygen source for the reaction, since bulk OH^- is virtually absent, and the primary mediator of catalyst degradation, capable of attacking surface lattice oxygen through O-down nucleophilic attack or polarizing metal-oxygen bonds via hydrogen bonding to facilitate metal dissolution.[46] The two half-reactions thus impose fundamentally different demands. Acidic HER revolves around proton management, encompassing H_3O^+ solvation, transport, and H_2 product detachment, whereas acidic OER must navigate a trilemma of ensuring adequate oxygen supply, preventing water from attacking the lattice, and shielding vulnerable metal sites from dissolution. The experimental characterization of interfacial water in acidic media presents distinct challenges relative to alkaline environments. The corrosive electrolyte and strong H_3O^+ absorption complicate operando spectroscopic measurements, and the local superacidity generated by PFSA ionomers in PEMWE devices further alters the interfacial water structure in ways not captured in standard three-electrode cells.[47] The following two subsections separately discuss the mechanistic roles of interfacial water and the corresponding catalyst design strategies for acidic HER and acidic OER.

2.2.1 Acidic HER: water as the H_3O^+ solvation medium

In acidic HER, the high concentration of H^+ in the bulk electrolyte reduces the Volmer step to a proton discharge process ($\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H} + \text{H}_2\text{O}$), meaning that water no longer needs to dissociate to supply protons, although it still mediates proton relay and desolvation.[48] The catalytic bottleneck therefore shifts from O-H bond cleavage to two distinct challenges. The first is ensuring efficient delivery of H_3O^+ from the outer Helmholtz plane to the active site through the interfacial hydrogen-bond network. The second is facilitating the timely release of H_2 product to prevent bubble-induced active-site blocking at high current densities.[45]

(1) H_3O^+ solvation and proton delivery

Under acidic conditions, the excess proton exists not as a discrete H_3O^+ cation but as a fluctuating hydrated species that interconverts between the Eigen (H_9O_4^+ , a hydronium coordinated by

three waters) and Zundel (H_5O^{2+} , a proton shared between two waters) configurations, around which interfacial water forms a solvation shell through the hydrogen-bond network.[26] Wu et al., using AIMD simulations, revealed that the hydrogen-bond network in the acidic electric double layer is far more connected than its alkaline counterpart.[14] The excess proton resides in the OHP and, via a continuous and ordered hydrogen-bond network, delivers protons to water molecules in the IHP through potential-dependent Grotthuss-type interconversion between the Eigen and Zundel forms; these protons subsequently undergo the Volmer reaction at the electrode surface.[15] This solvation structure directly influences both the migration rate of H_3O^+ to the active sites and the energetic cost of H^+ desolvation from its hydration shell prior to adsorption. Li et al. demonstrated a strategy for tuning this solvation structure in Na_xWO_3 , where embedded Na^+ ions disrupt the rigid interfacial water layer and reconfigure the local hydrogen-bond network.[49] In situ FTIR spectra at -0.95 V vs. RHE reveal that on pristine WO_3 , interfacial water is dominated by a strongly hydrogen-bonded ice-like layer; upon Na^+ intercalation, a distinct band corresponding to isolated H_3O^+ emerges, while the signal of the rigid water network diminishes (Figure 5a, b).[49] The quantitative proportions of interfacial water configurations extracted from these spectra confirm that Na_xWO_3 exhibits a markedly higher fraction of isolated H_3O^+ relative to WO_3 , accompanied by a larger electrochemically active surface area (Figure 5c). The potential-dependent evolution of these populations further shows that the isolated H_3O^+ fraction on Na_xWO_3 increases progressively as the potential shifts cathodically (Figure 5d), demonstrating that Na^+ enriches the electronic states of the WO_6 octahedra and dynamically breaks the rigid ice-like water structure in the IHP.[49] The resulting interfacial water configuration simultaneously provides a moderate $^*\text{H}$ adsorption strength, because the weakened hydrogen-bond coupling between water molecules and $^*\text{H}$ shifts $^*\text{H}$ binding toward thermoneutral. This dual optimization of proton supply and $^*\text{H}$ adsorption energetics collectively accelerates the Volmer step.[49, 50]

(2) Hydration-layer-mediated H_2 release

Beyond proton delivery, efficient HER at practical current densities also requires the timely removal of the H_2 product. At high current densities, H_2 bubbles nucleate and adhere to the electrode surface, directly blocking active sites and impeding H_3O^+ mass transport. The resulting additional overpotential can account for 7 to 25 percent of the total HER overpotential.[51] The continuous interfacial water film on superhydrophilic electrode surfaces serves as a hydration barrier layer between the bubbles and the electrode. Zhang et al. demonstrated this concept on CoP catalysts, where

UV/ozone treatment induced a crystalline-to-amorphous surface transition, flipping the wettability from partially hydrophobic to superhydrophilic and superaerophobic.[52] High-speed video snapshots capture the stark contrast. On pristine CoP, H₂ bubbles remain pinned to the surface and grow to large diameters before detaching; on UV-treated CoP, bubbles slide freely across the surface and release at much smaller sizes (Figure 5e).[52] Bubble probe AFM measurements reveal the mechanistic origin of this behavior. A clear jump-in event occurs on CoP at approximately 1.5 nN, signaling bubble attachment driven by hydrophobic attraction, whereas only repulsive forces are detected on UV-CoP even at forces exceeding 30 nN (Figure 5f, g).[52] Stokes-Reynolds-Young-Laplace model analysis confirms that this hydrophobic attraction dominates bubble adhesion, and that the hydration layer introduced by surface amorphization weakens it by increasing the effective separation between the gas bubble and the solid surface. This substantially lowers the bubble detachment energy barrier, enabling bubble release at smaller sizes and higher frequencies. The strategy proved effective under strongly acidic conditions. UV-CoP delivered lower HER overpotentials than Pt/C at current densities exceeding 78 mA cm⁻² (Figure 5h). Self-healing superaerophobic coatings have achieved comparable performance at pH 1, further confirming the generality of this approach.[53]

In summary, interfacial water regulation in acidic HER revolves around proton management, optimizing the hydrogen-bond network to ensure efficient H₃O⁺ transport and discharge, while the interfacial hydration layer facilitates timely H₂ product detachment, together achieving a coupled supply-detachment synergy.

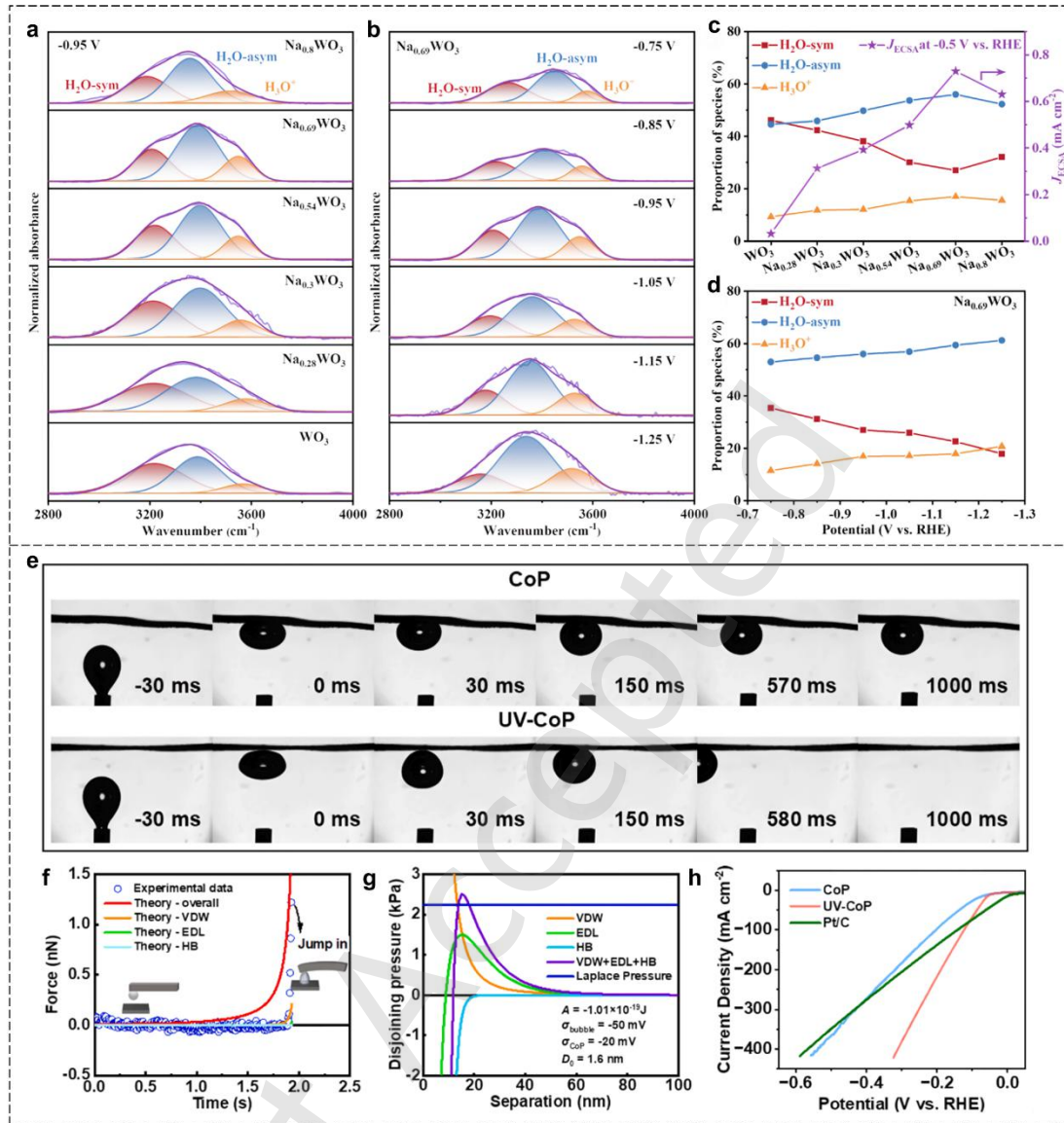


Figure 5. Interfacial water modulation for acidic HER. (a, b) In situ FTIR spectra on WO_3 and Na_xWO_3 at -0.95 V vs. RHE in 0.5 M H_2SO_4 . (c) Interfacial water configuration proportions and ECSA values. (d) Configuration proportions on $\text{Na}_{0.69}\text{WO}_3$ at varied potentials. Reproduced from Ref [49]. (e) High-speed video snapshots of H_2 bubble adhesion on CoP and free-sliding on UV-CoP. (f, g) Bubble probe AFM force curves with SRYL model fitting. (h) HER polarization curves, showing UV-CoP outperforming Pt/C above 78 mA cm^{-2} . Reproduced from Ref [52].

2.2.2 Acidic OER: water as the oxygen source and degradation mediator

In acidic OER, the rate-determining step, whose identity depends on the catalyst, the applied potential, and the mechanism, is often the formation of $^*\text{OOH}$ from $^*\text{O}$ and H_2O ($^*\text{O} + \text{H}_2\text{O} \rightarrow ^*\text{OOH} + \text{H}^+ + \text{e}^-$), which requires interfacial water to dissociate and supply the oxygen; interfacial water is thus the sole oxygen source under conditions where bulk OH^- is virtually absent.[54-56] This dependence

creates an intrinsic vulnerability, because the same interfacial water molecules that sustain oxygen evolution can also attack surface lattice oxygen through O-down nucleophilic attack, triggering the lattice oxygen mechanism (LOM) and subsequent metal dissolution, or polarize metal-oxygen bonds via hydrogen bonding to directly facilitate metal center protonation and detachment.[46] Catalyst design for acidic OER must therefore address not a single challenge but a trilemma. It must ensure adequate oxygen supply, preventing water from attacking the lattice, and shielding vulnerable metal sites from dissolution.

(1) Increasing free water supply

In acidic electrolytes, strong intermolecular interactions among water molecules generate a dense hydrogen-bond network that hinders water migration to and dissociation at active sites, a key microscopic origin of the sluggish kinetics of acidic OER.[57] Free water, liberated from the constraints of the H-bond network, accesses the catalyst surface and dissociates more readily; thus, increasing the proportion of interfacial free water represents a central strategy for accelerating acidic OER kinetics. Deng et al. approached this challenge through the lens of hard-soft acid-base (HSAB) theory, introducing hard Lewis acid oxides (ZrO_2 , TiO_2 , HfO_2) onto RuO_2 surfaces to capture free water molecules (acting as hard bases) and reconfigure the interfacial hydrogen-bond network.[58] AIMD simulations combined with in situ ATR-SEIRAS and Raman spectroscopy revealed that on pristine RuO_2 , interfacial water is dominated by a dense 4-HB- H_2O network; upon Lewis acid incorporation, the hydrogen-bond network is restructured, driving a directional evolution from rigid 4-HB- H_2O toward free water (Figure 6a, b).[58] Critically, the spectral weight of weakly hydrogen-bonded water on ZrO_2 - RuO_2 remained nearly constant even in the high-potential regime, whereas that on pristine RuO_2 was rapidly depleted, demonstrating that the Lewis acid sites enable dynamic replenishment of free water to continuously supply the catalytic sites with oxygen sources (Figure 6c). This design principle, which disrupts the rigid hydrogen-bond network while preserving sufficient connectivity for sustained water delivery, was further validated in a PEMWE device and corroborated by Ga doping and other p-block metal doping strategies.[14, 58]

(2) Reversing water orientation from O-down to H-down

Once an adequate free water supply is secured, the next challenge is controlling how water molecules interact with the catalyst surface. On pristine RuO_2 surfaces, interfacial water predominantly adopts an O-down orientation, in which the O atom readily launches a nucleophilic attack on surface non-bonded oxygen, generating oxygen vacancies that trigger LOM and ultimately

lead to Ru dissolution and deactivation.[46] Tuning interfacial water into the H-down orientation, in which the H atom faces the catalyst surface, can suppress lattice oxygen loss.[59] Zhu et al. reported an interstitial B-doped RuO_2 catalyst in which the B-O-Ru structure generates a local electric field that inverts the orientation of interfacial water. AIMD simulations of the first-layer water molecules reveal that on pristine RuO_2 , interfacial water adopts an O-down configuration with an O-to-surface distance of 2.74 Å, favorable for nucleophilic attack on surface non-bonded oxygen (ONB); on B- RuO_2 , by contrast, water molecules flip to an H-down orientation with an H-to-surface distance of 2.92 Å, thereby suppressing the O-down attack pathway (Figure 6d).[46] The water dipole orientation distribution along the surface normal direction quantifies this reversal. On RuO_2 , a sharp positive $\cos \theta$ peak indicates predominant O-down orientation, whereas on B- RuO_2 , a series of negative $\cos \theta$ peaks emerge, with 58.75 percent of interfacial water molecules adopting the H-down configuration (Figure 6e).[46] The local electric field induced by interstitial B simultaneously flips interfacial water from O-down to H-down, suppressing nucleophilic attack on ONB, while B itself inhibits ONB formation, thereby preventing lattice oxygen loss and structural collapse during acidic OER (Figure 6f).[46] This work established a complete design chain of non-metal doping, local electric field, water orientation reversal, and LOM suppression.

For catalysts in which complete LOM suppression is unattainable, an alternative is to manage its consequences. If lattice oxygen is inevitably consumed, the oxygen vacancies must be rapidly backfilled before they accumulate and trigger structural collapse.[59] Li et al. proposed a dynamic oxygen replenishment mechanism (DORM) in W-doped NiCo_2O_4 spinel. Quantitative deconvolution of the O-H stretching band from in situ Raman spectra reveals that W- NiCo_2O_4 maintains a markedly higher spectral weight of free water at the interface, whereas pristine NiCo_2O_4 accumulates predominantly rigid 4-HB- H_2O structures (Figure 6g).[60] This restructuring of the interfacial hydrogen-bond network enhances water mobility and promotes more efficient proton-donating configurations. The oxophilic W^{6+} dopants serve a dual function (Figure 6h). They activate lattice oxygen for the OER while simultaneously accelerating water dissociation to generate OH intermediates that rapidly backfill the oxygen vacancies created by lattice oxygen consumption, converting LOM from a destabilizing factor into an integral part of a reversible catalytic cycle.[60, 61]

(3) Constructing H-bond-depleted sites

Beyond controlling water orientation, an even more fundamental approach is to regulate whether interfacial water adsorbs onto specific surface sites at all. The dissolution of transition metal

oxides in acid is initiated by water molecules polarizing metal-oxygen bonds through hydrogen bonding. When interfacial water forms H-bonds with surface lattice oxygen, electron density is drawn from the M-O bond into the H-bond, weakening the M-O linkage and facilitating protonation and detachment of the metal center.[54] Constructing a hydrogen-bond-depleted microenvironment, defined as local surface regions where interfacial water adsorption is thermodynamically unfavorable, therefore represents a direct strategy for suppressing the initial step of metal dissolution.

Wang et al. further validated this concept in La and Ca-co-doped Co_3O_4 catalysts.[62] The key to creating such a microenvironment lies in selecting dopants with intrinsically weak affinity for water. La^{3+} , with its fully occupied $5s^2 5p^6$ valence shell, possesses no empty orbitals capable of accepting electron density from the oxygen lone pairs of water molecules; as a result, water adsorption onto La sites is thermodynamically disfavored. This prediction was directly confirmed by atomic-resolution imaging, as large-scale STM images reveal that La atoms substitutionally occupy Co sites within the monolayer Co_3O_4 -like film (Figure 6i); upon H_2O dosing, water molecules adsorb readily on pristine Co sites, whereas the regions surrounding La dopants remain strikingly adsorbate-free, as evidenced by both high-resolution STM and nc-AFM imaging (Figure 6j-l).[62] This direct visual evidence establishes that La sites function as local water-repellent islands on the catalyst surface. The spectroscopic and theoretical evidence further quantifies the impact of this site-specific water exclusion. DFT calculations reveal that the energy barrier for Co-O bond cleavage nearly doubles on a hydrogen-bond-depleted surface relative to a hydrogen-bond-rich surface (Figure 6m). This site-specific water exclusion is accompanied by a marked suppression of rigid 4-HB· H_2O in favor of weakly hydrogen-bonded configurations and a systematic decrease in interfacial hydrogen-bond density along the surface normal direction, as shown by AIMD simulations. Together with Ca doping, which stabilizes the Co_3O_4 lattice, this strategy achieves a marked suppression of Co leaching under acidic OER conditions by shielding vulnerable Co-O bonds from the H-bond-mediated polarization that initiates dissolution.

To summarize, the modulation logic of acidic OER revolves around oxygen-source supply and catalyst self-protection. Interfacial water acts as both the sole oxygen source and the mediator of dissolution reactions, demanding a delicate balance between supply and protection.

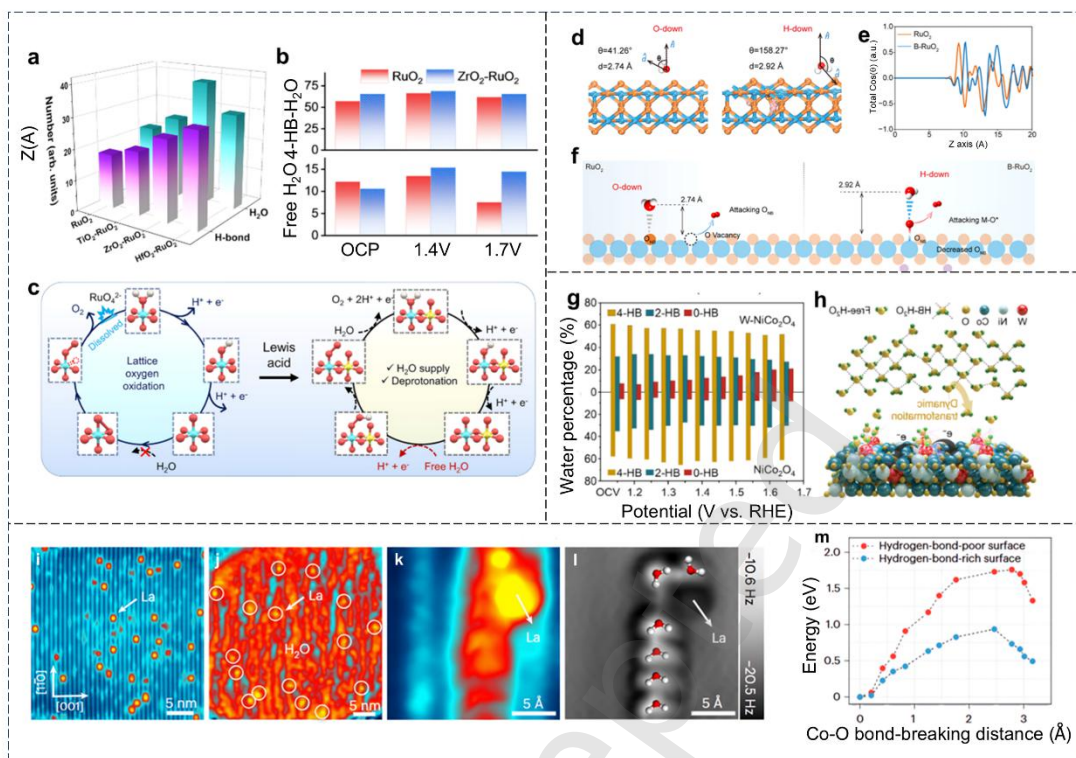


Figure 6. Interfacial water modulation strategies for acidic OER. (a) Average H-bond numbers and H_2O counts at the catalyst interface. (b) Interfacial water structure percentages. (c) Schematic of Lewis acid-mediated free H_2O supply and deprotonation. Reproduced from Ref [58]. (d) AIMD-simulated first-layer water configuration on B- RuO_2 (H-down) and RuO_2 (O-down). (e) Water dipole orientation distributions. (f) Schematic of the B-O-Ru local electric field mechanism. Reproduced from Ref [46]. (g) Interfacial water distribution on W- NiCo_2O_4 and NiCo_2O_4 . (h) DORM schematic. Reproduced from Ref [60]. (i) STM image of La substitution in monolayer Co_3O_4 . (j-l) STM and nc-AFM images showing absent water adsorption on La sites. (m) DFT-calculated Co-O cleavage barriers on H-bond-poor and H-bond-rich surfaces. Reproduced from Ref [62].

2.3 Neutral environment

Neutral-pH water electrolysis occupies a distinct position among these electrolyte environments surveyed in this review. Unlike alkaline and acidic media, where either OH^- or H^+ is abundant, neutral electrolytes contain extremely low concentrations of both species (typically $\sim 10^{-7}$ M at pH 7).[63, 64] Under these conditions, the interfacial electric field weakens considerably compared with extreme-pH regimes, and water molecules near the electrode surface tend to form an even more rigid and densely interconnected hydrogen-bond network, which severely constrains both water dissociation efficiency and intermediate transport.[13, 65] Interfacial water in neutral environments thus functions primarily

as a transport barrier that must be disrupted, rather than as a proton donor or solvation medium as in alkaline and acidic HER, respectively. Although both half-reactions share this rigid interfacial water network as a common kinetic bottleneck, they diverge in an important respect. Neutral HER is limited primarily by the suppression of water dissociation and hindered interfacial transport of H_2O and OH^- intermediates, whereas neutral OER faces the additional challenge of local acidification induced by the OER process itself. The consumption of OH^- during oxygen evolution causes a local pH drop near the catalyst surface, which simultaneously suppresses OH^- supply and narrows the stability window of non-noble-metal catalysts.[66, 67] From a characterization standpoint, neutral environments present a distinct difficulty. The inherently weak interfacial electric field under low ionic strength conditions renders water vibrational signatures considerably more difficult to resolve than in alkaline or acidic media, and dedicated in situ spectroscopic studies under neutral-pH conditions remain conspicuously scarce.[63, 68]

2.3.1 HER: heterointerface engineering for water layer disruption

In neutral HER, the rigid interfacial water layer constitutes the primary factor limiting catalytic activity. AIMD simulations and in situ SERS studies have shown that interfacial water molecules on Ru surfaces are interconnected by a dense hydrogen-bond network, which suppresses the interfacial transport of $^*\text{H}_2\text{O}$ and $^*\text{OH}$ and hinders both the exposure and regeneration of active sites.[69]

To address this central bottleneck, heterointerface engineering has emerged as an effective strategy for disrupting the rigid hydrogen-bond network.[70] Chen et al. designed a $\text{Ru}/\text{Nb}_2\text{O}_5$ heterojunction catalyst that provides a particularly well-characterized example. AIMD simulations reveal that on pristine Ru, interfacial water molecules form a densely interconnected hydrogen-bond network; upon incorporation of Nb_2O_5 , the electron-rich O regions of the oxide disrupt this network by altering the molecular orientation of interfacial water, breaking hydrogen-bond connectivity and increasing the free water content in the vicinity of Ru sites (Figure 7a, b).[65] Quantitatively, the average number of hydrogen bonds per interfacial water molecule decreases substantially on $\text{Ru}/\text{Nb}_2\text{O}_5$ relative to both pristine Ru and Nb_2O_5 (Figure 7c).[65] This restructuring is experimentally corroborated by in situ Raman spectroscopy, which shows an enhanced dangling O-H population and a shift of the O-H stretching band toward higher wavenumbers on $\text{Ru}/\text{Nb}_2\text{O}_5$, directly signaling an increase in free water (Figure 7d, e).[65] DFT calculations further demonstrate that the weakened hydrogen-bond network simultaneously shifts the $^*\text{H}$ adsorption free energy toward thermoneutral (Figure 7f), achieving a dual optimization of water dissociation and $^*\text{H}$ binding energetics.[65] Sun et al.

exploited the synergistic interplay between RuSe_x clusters and Ru single atoms (RuSe_x-RuNC) to regulate interfacial water in neutral HER. On RuNC alone, the rigid interfacial water layer severely impedes the transport of H₂O and OH intermediates between the active sites and the bulk electrolyte (Figure 7g). Upon incorporation of RuSe_x, the chalcogenide clusters disrupt the dense hydrogen-bond network at the interface, creating transport channels that facilitate H₂O supply to and OH removal from the neighboring RuNC sites (Figure 7h). Operando ATR-SEIRAS spectra in neutral phosphate buffer directly capture this restructuring. On RuNC, the O-H stretching region is dominated by low-frequency bands characteristic of strongly hydrogen-bonded, ice-like water across the entire HER potential range (Figure 7i), whereas on RuSe_x-RuNC, the νO-H band shifts progressively to higher wavenumbers with increasing cathodic potential, signaling a dynamic weakening of the hydrogen-bond network and an enrichment of weakly hydrogen-bonded water (Figure 7j). This interfacial water restructuring drastically boosts the mass activity of the catalyst.[13]

2.3.2 OER: electrolyte-ion synergy for network restructuring

In neutral OER, the rigid hydrogen-bond network similarly obstructs water molecules from accessing active sites, while the local acidification induced by the OER process itself further deteriorates the interfacial microenvironment. Unlike HER, neutral OER faces an additional challenge, because the consumption of OH⁻ during the reaction causes a local pH drop near the catalyst surface, which simultaneously suppresses the subsequent supply of OH⁻ and narrows the stability window of non-noble-metal catalysts.[66, 67]

The catalyst-plus-electrolyte integrated modulation strategy represents an effective design paradigm for tackling this dual challenge. Building on the foundational discovery of an in situ formed oxygen-evolving catalyst in neutral phosphate-buffered water by Kanan and Nocera,[71] Liu et al. discovered that the simultaneous introduction of borate and fluoride ions into the neutral electrolyte generates a strong synergistic effect.[72] The radial distribution profiles of the anions reveal that F⁻ preferentially accumulates in the inner Helmholtz plane, where it disrupts the rigid hydrogen-bond network of interfacial water; this creates access channels through which borate ions subsequently penetrate into the same region and arrange into a hierarchically ordered ionic structure (Figure 7k).[72] The statistical analysis of hydrogen-bond populations under different electrolyte compositions and applied potentials confirms that the F⁻/borate combination restructures the interfacial hydrogen-bond network more effectively than either anion alone (Figure 7l). This structural reorganization intensifies the local electric field and accelerates proton transfer at the electrode

surface, boosting the OER activity of $\text{Co}(\text{OH})_2$ catalysts by nearly an order of magnitude.[72] Although this example operates through electrolyte engineering rather than intrinsic catalyst design, the mechanistic principle it reveals points directly toward a catalyst-level strategy. Two factors explain why such catalyst-level strategies remain scarce in neutral OER. The weak interfacial electric field under the low ionic strength of neutral media provides a weaker handle for restructuring water through the surface alone, so electrolyte anions of high charge density, such as F^- and borate, have been the more effective and more tractable route. The same weak field also renders the interfacial water signatures difficult to resolve, which has hindered the verification of catalyst-level effects and further biased the field toward electrolyte engineering. A catalyst-level analogue of the F^- /borate synergy would integrate the two functions on the catalyst surface, pairing a bond-breaking fluorinated ligand that disrupts the rigid hydrogen-bond network with a structure-ordering phosphate or borate moiety that simultaneously buffers the local pH, so that no electrolyte additive is required.

Overall, the design strategies for HER and OER in neutral media converge on a single overarching objective, namely restructuring the rigid, dense interfacial water layer into a dynamic and flexible network that facilitates reactant supply and product desorption.[63, 68] It should be noted, however, that the interfacial-water-focused mechanistic evidence in neutral electrolytes remains considerably thinner than in alkaline and acidic environments, because the weaker interfacial electric field under neutral conditions renders water vibrational signatures more challenging to resolve, and the causal chain from catalyst structure to interfacial water restructuring is less rigorously established here than in the environments discussed earlier. Strengthening this evidence base through dedicated in situ spectroscopy under neutral-pH conditions represents an important direction for future work.[63, 68]

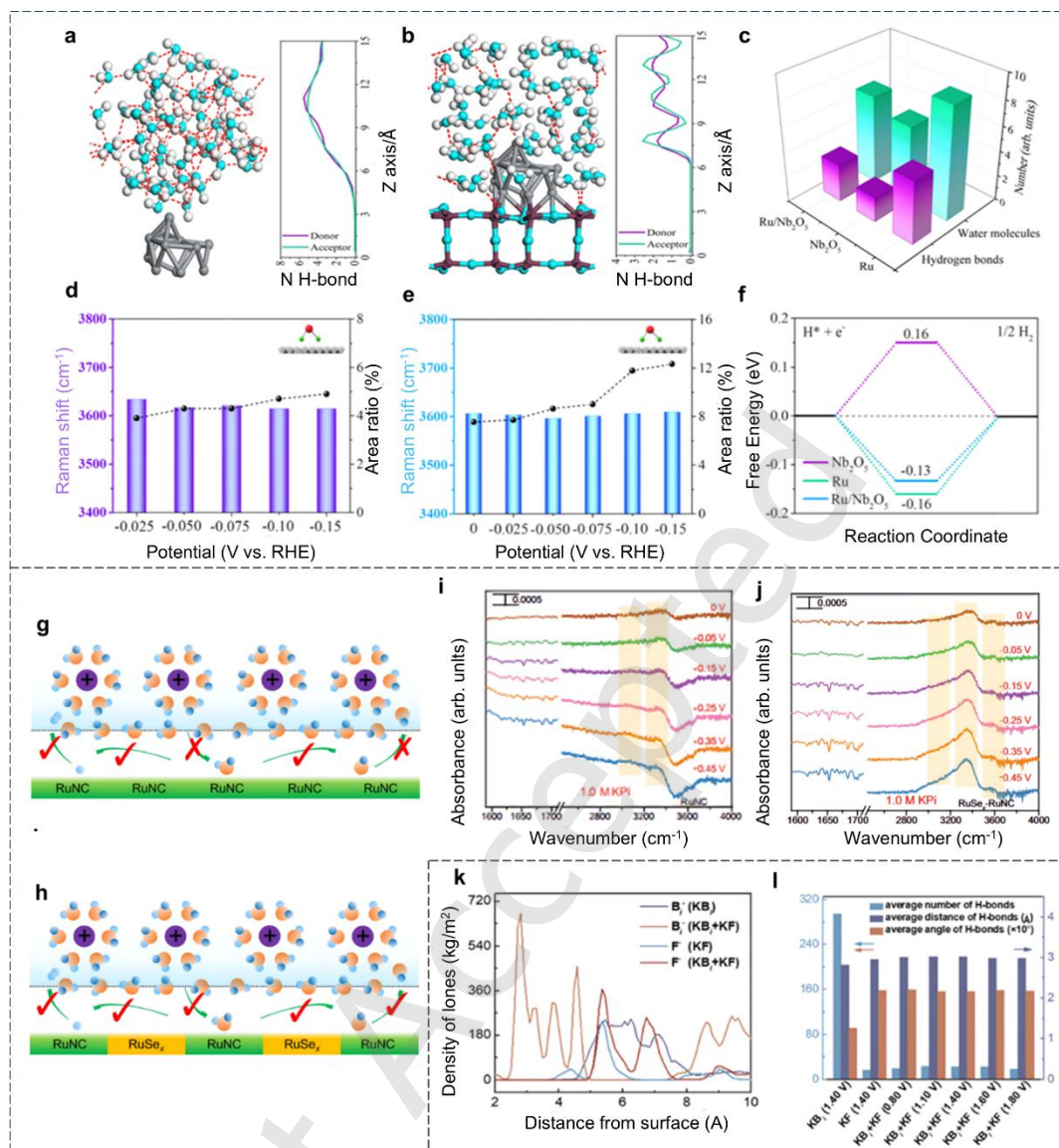


Figure 7. Interfacial water modulation in neutral media. AIMD snapshots of interfacial water on Ru (a) and Ru/Nb₂O₅ (b). (c) Average H-bond numbers for Ru, Nb₂O₅, and Ru/ Nb₂O₅. (d, e) Raman shift and area ratio of dangling O-H bonds. (f) $\Delta G(H)$ vs. $\Delta G(H-O-H)$ relationship. Reproduced from Ref [65].

Schematic of neutral HER on RuNC (g) and RuSe_x-RuNC (h). Operando ATR-SEIRAS spectra of RuNC (i) and RuSe_x-RuNC (j) in 1.0 M KPi. Reproduced from Ref [13]. (k) Radial distribution of borate and fluoride anions. (l) H-bond population statistics under varied conditions. Reproduced from Ref [72].

2.4 Seawater electrolysis

Seawater electrolysis retains the neutral-to-alkaline character of the environments discussed above but superimposes a set of non-pH composition perturbations on this baseline. Seawater, whether used directly near pH 8.2 or deliberately alkalized, contains Cl⁻ at approximately 0.5 M, which triggers catalyst corrosion and the parasitic chlorine evolution reaction (CIER) at the anode, while

dissolved cations such as Ca^{2+} and Mg^{2+} readily form hydroxide precipitates in the locally alkaline cathodic environment.[73-76] These added components endow interfacial water with protective functions that have no counterpart in pure-water electrolysis, namely suppressing Cl^- migration toward the electrode, constructing a corrosion-resistant microenvironment, and preventing precipitate fouling of active sites.[77-79] Whereas in the alkaline, acidic, and neutral environments above the organizing principle is the intrinsic HER-versus-OER divergence of interfacial water, seawater electrolysis adds a second, composition-driven layer, in which the organizing principle becomes the nature of the threat being countered. Interfacial water combats Cl^- corrosion through two complementary mechanisms, a physical barrier effect provided by ordered water films and a chemical sieving effect conferred by differential hydrogen-bond affinity for OH^- over Cl^- , while resisting precipitate fouling through hydration repulsion sustained by superhydrophilic and superaerophobic surface engineering.[19, 20] The characterization of interfacial water in seawater introduces additional complexity, since dissolved ions generate spectral interference that complicates the deconvolution of interfacial water signals, and operando measurements must capture the dynamic competition between Cl^- repulsion and OH^- supply. The following two subsections separately discuss these protective roles, namely anti- Cl^- corrosion and anti-precipitation fouling.

2.4.1 Physical barrier and chemical sieving against chloride

The equilibrium potential of the chlorine evolution reaction (ClER) at the anode lies close to that of the OER, resulting in fierce competition between the two.[73,74] Interfacial water combats Cl^- attack through two complementary protective mechanisms.

The first is the physical barrier effect. Yuan et al. employed electrochemically driven dynamic migration and re-adsorption of phosphorus in phosphate-doped Co-Ni-Fe layered double hydroxide (CNFPO) to enrich high-charge-density phosphate groups on the surface.[79] Semi-quantitative analysis of spectral weights of interfacial water species reveals that CNFPO exhibits a markedly higher apparent spectral weight of 4-HB· H_2O relative to the phosphate-free CNFO control (Figure 8a), directly confirming that surface phosphate groups organize interfacial water molecules into a highly ordered, ice-like water film through electrostatic templating. MD simulations further show that this ordered water film substantially increases the effective distance of Cl^- from the catalyst surface compared to H_2O , effectively blocking Cl^- migration toward the electrode (Figure 8b). Critically, in situ Raman monitoring after a 100-hour stability test demonstrates that the interfacial water species populations on CNFPO remain virtually unchanged (Figure 8c), confirming that the ice-like water barrier is

dynamically maintained during long-term operation.[79]

The second is the chemical sieving effect.[80] Oxyanions (SO_4^{2-} , MoO_4^{2-} , PO_4^{3-} , etc.) generated through catalyst surface reconstruction can reinforce the interfacial hydrogen-bond network, transforming it into a selective molecular sieve.[77, 80] Yu et al. discovered that SO_4^{2-} generated through surface reconstruction on NiFeS catalysts substantially increases the 4-HB·H₂O to free-H₂O intensity ratio relative to the control system (Figure 8d), indicating a denser and more ordered interfacial hydrogen-bond network.[77] Density distribution profiles obtained from MD simulations reveal the functional consequence of this reinforced network, showing that OH^- accumulates preferentially near the catalyst surface, while Cl^- is excluded to greater distances, and the hydrogen-bond distribution follows the same spatial pattern as that of OH^- (Figure 8e), confirming that the reinforced network selectively accommodates OH^- over Cl^- . DFT calculations provide the thermodynamic basis for this discrimination. The hydrogen-bond energy of interfacial water follows the order $\text{OH}^- > \text{H}_2\text{O} > \text{Cl}^-$ (Figure 8f), meaning that the network is energetically biased to accept OH^- while rejecting Cl^- . [77] The chemical sieving effect, whether achieved through in situ generated oxyanions or through surface-anchored Lewis-base species such as silicates, converts the interfacial hydrogen-bond network into a selective barrier that energetically favors OH^- over Cl^- . A conceptually related strategy exploits surface Lewis-base sites to directly reconstruct the interfacial hydrogen-bond network to exclude Cl^- . Silicate species anchored on $\text{Ni}(\text{OH})_2$ surfaces have been shown to preferentially enrich OH^- at the interface and restructure the hydrogen-bond network within the electrochemical double layer, simultaneously repelling Cl^- and mitigating local acidity.[81]

Physical barrier and chemical sieving represent two complementary mechanisms by which interfacial water resists Cl^- corrosion. The former blocks Cl^- migration through steric hindrance and electrostatic repulsion exerted by the ice-like ordered water film. The latter achieves OH^-/Cl^- selectivity through the differential hydrogen-bond affinity of the interfacial network. Together, they provide effective corrosion protection for the anode in seawater electrolysis.

2.4.2 Hydration repulsion against precipitate fouling

Ca^{2+} and Mg^{2+} present in seawater readily form $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ precipitates in the locally alkaline environment generated by cathodic HER, covering active sites and blocking gas transport channels.[73, 74] In this context, interfacial water modulation serves a dual function. It promotes the rapid detachment of H_2 bubbles to reduce precipitation nucleation sites, while the hydration repulsion force facilitates the removal of already-formed precipitates from the surface.[78]

Oxycation and polymer functional layer strategies have demonstrated outstanding effectiveness in anti-precipitation fouling.[82] Sun et al. constructed an ordered interfacial water network through sulfonic acid and amine groups in a PANI-derived copolymer (SAE-Co), endowing the electrode with both superhydrophilic and superaerophobic character.[78] Captive bubble measurements and contact angle tests confirm the simultaneous superhydrophilicity and superaerophobicity of SAE-Co (Figure 8g). Bubble probe AFM measurements reveal that the gas bubble adhesive force on SAE-Co is dramatically lower than that on the unmodified AE-Co control (Figure 8h, i), directly demonstrating that the ordered hydration layer weakens bubble adhesion and facilitates bubble release at smaller sizes.[78] This sustained interfacial water film further prevents direct nucleation of Mg^{2+} and Ca^{2+} on the electrode surface. The practical impact is visually captured during natural seawater electrolysis at 1.0 A cm^{-2} , where the SAE-Co surface remains largely free of precipitates and H_2 bubbles, whereas the AE-Co surface is heavily covered by $Mg(OH)_2$ precipitates and adherent bubbles (Figure 8j, k).[78] The ordered hydration layer thus combats precipitation fouling through two parallel mechanisms. The superhydrophilic surface sustains a continuous water film that prevents direct contact between cations and the electrode surface, and the hydration repulsion force weakens the adhesion of any precipitates that may form, enabling their removal under hydrodynamic shear.[83, 84]

In conclusion, interfacial water modulation in seawater electrolysis shoulders functional demands far exceeding those in pure-water environments. The physical barrier and chemical sieving mechanisms jointly establish a dual defense against Cl^- corrosion, while superhydrophilic and superaerophobic surface engineering effectively combats precipitate fouling. Future design of seawater electrolysis catalysts is shifting from a singular focus on activity toward the tripartite optimization of activity, selectivity, and stability, achieved through the synergistic modulation of interfacial water.

One cross-cutting pattern emerges from the electrolyte-by-electrolyte comparison above. Across these electrolyte environments surveyed in this review, interfacial water performs functions that are not merely different in degree but opposite in kind. It serves as a proton donor in one environment and a proton solvation medium in another; an oxygen source and a degradation mediator in another; a rigid transport barrier in one and a protective shield in another. These functional inversions mean that a strategy optimized for one environment may be irrelevant or even detrimental in another.

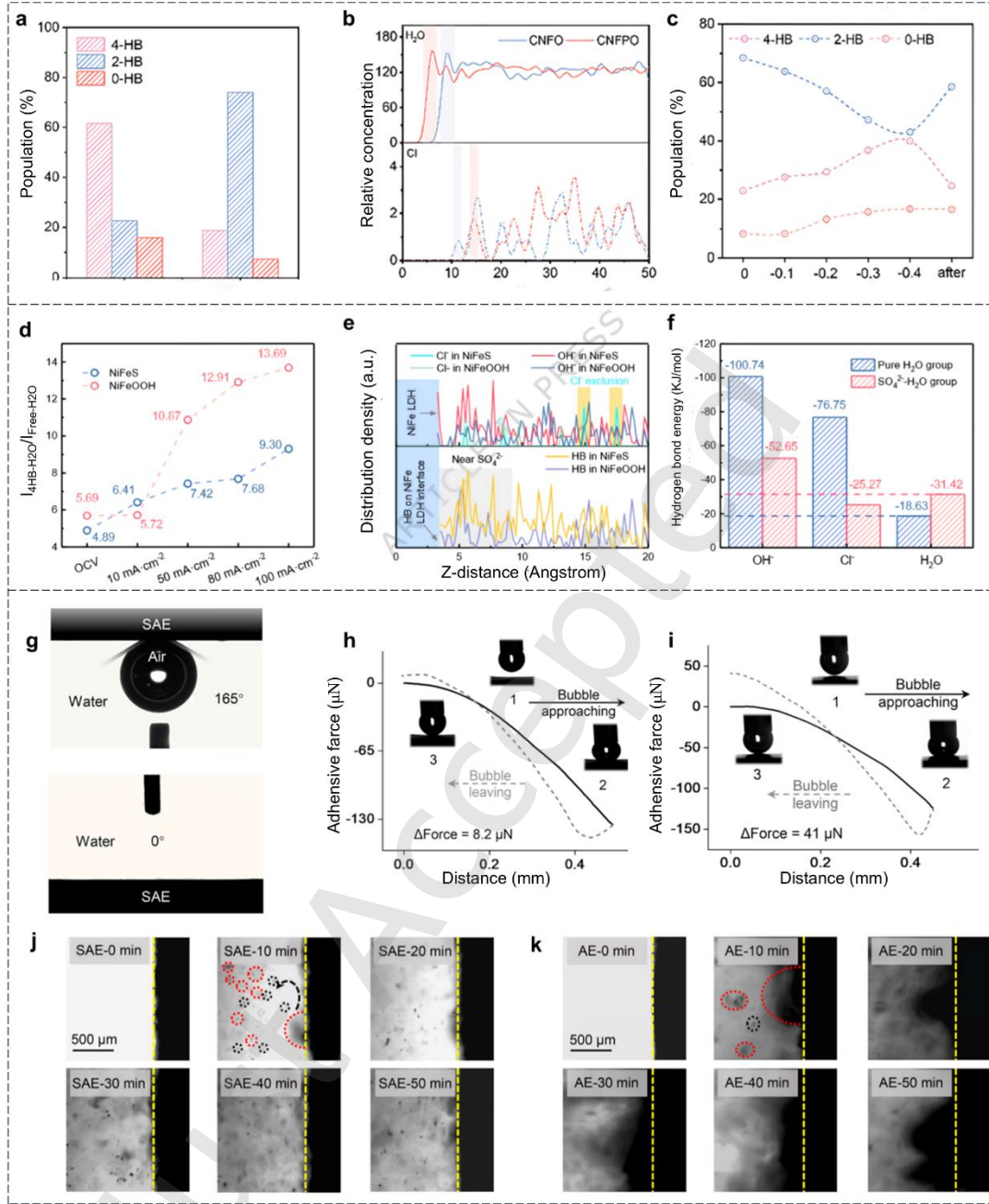


Figure 8. Interfacial water strategies in seawater electrolysis. (a) Interfacial water populations on CNFPO and CNFO. (b) H₂O and Cl⁻ distance distributions from MD simulations. (c) Water populations on CNFPO after 100 h stability test. Reproduced from Ref [79]. (d) 4-HB·H₂O to free-H₂O intensity ratio. (e) Density profiles of OH⁻, Cl⁻, and H-bonds. (f) H-bond energies toward OH⁻, H₂O, and Cl⁻. Reproduced from Ref [77]. (g) Captive bubble and contact angle measurements for SAE-Co. Gas bubble adhesion force on SAE-Co (h) and AE-Co (i). Photographs of Mg(OH)₂ precipitates and H₂ bubbles on SAE-Co (j) and AE-Co (k) at 1.0 A cm⁻². Reproduced from Ref [78].

3. Summary and Outlook

Interfacial water has evolved from a silent bystander into a key participant that dictates electrocatalytic performance. This review has systematically surveyed its distinct mechanistic roles across alkaline, acidic, neutral, and seawater electrolysis. The central insight is that the ideal interfacial water structure lies in balance rather than in extremes. It must moderately disrupt the rigid hydrogen-bond network to liberate free water for accelerated dissociation, while preserving sufficient network connectivity for efficient proton and hydroxide transport, and this balance must be achieved in an electrolyte-specific manner. The core proposition emerging from this cross-environment comparison is that catalyst design must target the specific roles of interfacial water in the intended electrolyte medium.

3.1 In situ characterization across electrolyte environments

At the characterization level, the quality and availability of in situ interfacial water data are highly uneven across electrolyte environments, and this unevenness reflects both the physical difficulty of each environment and where the field has concentrated its effort. Alkaline media provide the richest spectral fingerprints because the strong interfacial electric field generated by the high OH^- concentration yields well-resolved O-H stretching features, and this environment has accordingly accumulated the most extensive in situ Raman and SEIRAS evidence.[5, 9] Acidic environments, despite their industrial relevance to PEMWE, present greater experimental challenges, because the corrosive electrolyte and the strong H_3O^+ absorption complicate the acquisition of reliable operando spectra, and the local superacidity generated by PFSA ionomers further alters the interfacial water structure in ways not captured in standard three-electrode cells.[47] Neutral environments face the opposite problem, because the inherently weak interfacial electric field under low ionic strength conditions renders water vibrational signatures considerably more difficult to resolve, and dedicated in situ studies under neutral-pH conditions remain conspicuously scarce.[63, 68] Seawater electrolysis introduces additional spectral interference from dissolved ions, which further complicates the deconvolution of interfacial water signals.[19] The differing research maturity across these environments is therefore a direct consequence of these factors, and the depth of each section of this review reflects the available evidence rather than an artificial balancing of these environments. Closing this gap requires electrolyte-adapted characterization strategies, including ultrafast pump-probe spectroscopy to capture femtosecond hydrogen-bond dynamics,[85, 86] nanoscale infrared platforms such as AFM-IR to map interfacial water heterogeneity across single active sites,[87] and multimodal

in situ setups that simultaneously acquire Raman, infrared, and X-ray absorption signals with cross-validation by AIMD simulations.[87] A related caveat concerns quantification. Across the literature surveyed here, the areas of deconvoluted O-H sub-bands are almost universally equated with the relative molecular populations of interfacial water species. This convenient practice nevertheless conflates spectral weight with molecular abundance, because band areas are not generally proportional to population given differences in Raman cross sections, infrared absorption coefficients, and the adopted fitting constraints. Reported fractions are therefore best read as apparent spectral weights rather than absolute populations, and more rigorous quantification will require isotope-substitution (D_2O) controls to assign overlapping O-H features unambiguously, constrained multi-peak fitting, and cross-validation against molecular simulations.

3.2 Toward quantitative descriptors across electrolyte environments

At the theoretical level, interfacial water research must move beyond the qualitative observation that higher free water fractions correlate with better activity, and toward a set of quantitative descriptors specific to each electrolyte environment.[6, 7] Because interfacial water plays a different role in each environment, the most informative descriptor also differs. In alkaline media, the free water fraction and the Stark tuning rate, namely the potential-dependent shift of the O-H stretching frequency that gauges the interfacial electric field, capture water-dissociation kinetics in the HER, while the cation-hydrated-water fraction tracks OH^- transport in the OER.[9, 11, 36] In acidic media, the isolated H_3O^+ fraction reflects proton delivery in the HER, whereas the hydrogen-bond-depleted surface area and the oxygen replenishment rate capture the oxygen-supply versus self-protection competition in the OER.[49, 60, 62] For neutral media, the average hydrogen-bond coordination number of interfacial water at the IHP may be the single most predictive descriptor, given that the rigid network is the dominant bottleneck.[13, 65] In seawater electrolysis, the Cl^- exclusion efficiency, quantified by the spatial separation between the Cl^- density and the catalyst surface from MD simulations, defines a performance parameter that has no counterpart in pure-water environments.[77, 79]

Each candidate descriptor nevertheless carries its own conditions of applicability and current limitations. The free water fraction is informative only where free water is the rate-limiting reactant, namely alkaline HER and acidic OER,[9, 11] and its extraction is sensitive to the deconvolution model and to the spectral overlap between dangling O-H and cation-hydrated water near 3600 cm^{-1} , so reported values are best treated as semi-quantitative, as discussed in the Introduction. The Stark

tuning rate further requires potential-resolved in situ spectra and is most reliably interpreted on well-defined surfaces, where the field response is not convoluted with surface heterogeneity.[9] The cation-hydrated-water fraction, which tracks OH⁻ transport in alkaline OER, is subject to the same spectral-overlap limitation as the free-water fraction, because cation-hydrated water and dangling O-H both contribute near 3600 cm⁻¹ and are difficult to separate unambiguously.[36] The isolated H₃O⁺ fraction is informative only in strongly acidic electrolytes and must be extracted from in situ infrared or Raman spectra in which the isolated H₃O⁺ band is distinguishable from the strongly hydrogen-bonded water signal.[49] The hydrogen-bond-depleted surface area is specific to acidic OER, in which water-mediated lattice dissolution is the dominant degradation channel, but it currently lacks a direct operando probe and is inferred from atomic-resolution imaging and AIMD simulations on a limited set of model oxides.[62] The oxygen replenishment rate, which quantifies how rapidly the oxygen vacancies generated by lattice-oxygen consumption are backfilled, is likewise specific to acidic OER and is currently inferred from the time-resolved evolution of the free-water population together with AIMD simulations, rather than from a direct operando probe.[60] The average hydrogen-bond coordination number is conceptually the most direct descriptor of the neutral-electrolyte bottleneck, but it is also the least validated, because the weak interfacial electric field in neutral media renders the underlying spectral signatures difficult to resolve.[13, 65] The Cl⁻ exclusion efficiency is uniquely defined for seawater, yet it must still be correlated with measurable selectivity metrics, such as Faradaic efficiency and the absence of hypochlorite products, before it can serve as a predictive quantity.[77, 79] Working toward such a set of electrolyte-specific descriptors, and integrating it with high-throughput AIMD simulations and machine learning, would accelerate rational catalyst screening and reduce reliance on trial-and-error approaches.[88-90] It is worth clarifying the logical relationship between these interfacial water descriptors and the adsorption energy descriptors of the Sabatier principle, which are complementary rather than subsuming or merely correlated. An adsorption free energy such as $\Delta G(H)$ is an outcome governed by both the intrinsic electronic structure and the local environment, and restructuring the interfacial water is often the very mechanism by which $\Delta G(H)$ is shifted toward thermoneutral. PtO_x/NiO is a concrete example,[31] in which the interfacial dipole field reorients water into the H-down configuration and simultaneously shifts $\Delta G(H)$ from 0.42 eV on Pt/NiO to -0.02 eV on PtO_x/NiO, so the interfacial water descriptor and the adsorption energy descriptor describe the same mechanism from two complementary perspectives.

3.3 Industrial translation across electrolyte environments

At the industrial application level, the functions of interfacial water differ not only among electrolyte chemistries but also among electrolyzer architectures, and this dual dependence must be explicitly addressed.[91] In PEMWE, the locally superacidic microenvironment created by PFSA ionomers places interfacial water under more aggressive conditions than those in standard three-electrode cells.[47] In AEMWE, Donnan exclusion and alkaline-stable ionomer chemistry impose distinct solvation environments that affect OH^- transport in ways that remain poorly understood.[92, 93] In conventional AWE, the large electrode gap means that ohmic drop may dominate over interfacial water kinetics under certain operating regimes, and the relative importance of interfacial water engineering versus cell-level transport optimization must be carefully evaluated. Seawater electrolysis at industrial current densities introduces an additional dimension, namely the dynamic competition between Cl^- repulsion and OH^- supply at the anode, and between precipitate removal and H_2 detachment at the cathode, must be maintained not over hours but over thousands of hours.[94] A progressive research paradigm, spanning from model interfaces to operating membrane electrode assemblies and from activity-centric optimization to holistic evaluation of activity, selectivity, stability, and cost, will be essential to translate the electrolyte-specific strategies surveyed in this review into practical water electrolysis technologies.

Beyond conventional water electrolysis, the principles of interfacial water modulation hold considerable promise for broader application. Extending these strategies to unconventional water sources such as industrial wastewater and salt-lake brine, as well as to CO_2 reduction, organic electrosynthesis, photocatalysis, and thermal catalysis, represents an important frontier.[95, 96] In each emerging system, defining the functional identity of interfacial water and devising targeted modulation strategies will be essential for expanding the scope and impact of interfacial water science.

Taken together, the three levels discussed above point to three prioritized research directions. The first and most urgent is the quantitative standardization of interfacial water characterization, whereby isotope-substituted D_2O controls, constrained multi-peak fitting, and cross-validation against molecular simulations are consolidated into a community-wide protocol that converts reported O-H sub-band areas into absolute water populations comparable across laboratories and electrolyte environments. The second is systematic descriptor validation, whereby the candidate descriptors proposed in Section 3.2 are benchmarked against a common set of catalysts under standardized conditions and integrated with machine learning to establish quantitative structure-performance relationships. The third is device-level translation, whereby the electrolyte-specific strategies surveyed

here are implemented in membrane electrode assemblies that sustain activity, selectivity, and stability at industrial current densities over thousands of hours, with particular attention to the dynamic Cl^-/OH^- competition in seawater. With the steady advancement of in situ characterization techniques, the gradual establishment of quantitative activity descriptors, and the progressive refinement of interfacial water management in industrial electrolyzers, interfacial water science is transitioning from passive understanding to active design, from model environments to real devices, and from single reactions to multi-scenario applications. Through deep interdisciplinary integration across experimental techniques, theoretical calculations, materials design, and environmental engineering, interfacial water modulation holds great promise to become a cornerstone strategy for overcoming the technological bottlenecks in electrocatalytic water splitting and propelling the large-scale production of green hydrogen.

Author contributions

Z.G., L.X., and C.Y. conceptualized the review. Z.G. conducted the literature survey, designed the figures, and wrote the manuscript. L.X. and C.Y. revised the manuscript and supervised the project. L.X. obtained financial support. All authors participated in the discussion and approved the final manuscript.

Conflict of interest

The authors declare no competing financial interest.

Data availability

No primary research results, software or code has been included and no new data were generated or analyzed as part of this review.

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