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Mini Review

RuO₂-based nano-heterojunctions as functional interfacial reactors for acidic oxygen evolution

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Abstract

RuO₂ shows high acidic OER activity as Ir-free catalysts, but this feature also induces lattice-oxygen overactivation, Ru overoxidation, dissolution, and irreversible reconstruction and consequent limited stability. Heterojunctions engineering has emerged as an effective strategy to improve acidic OER catalysts by coupling chemically distinct components besides doping. However, previous studies have mainly emphasized heterostructure construction and performance enhancement, while the atom-level interfacial functions that govern acidic OER activity and stability have been somewhat overlooked. In this review, RuO₂-based heterojunctions are proposed as functional interfacial reactors rather than simple multicomponent composites for acidic OER. Heterointerfaces regulate acidic oxygen evolution through five interconnected functions: electronic coupling, oxygen spillover and redox buffering, interfacial water/proton microenvironment regulation, dual-site cooperation, and balanced lattice-oxygen redox. These functions are individually elucidated using representative Ru-based heterojunctions, including Ru/RuO₂, RuO₂/LiCoO₂, ZrO₂-RuO₂, RuO₂/MoO₃, and RuO₂-CeO₂, to reveal how specific interfacial structures regulate charge redistribution, Ru-O covalency, oxygen-species migration, water/proton dynamics, and cooperative O-O bond formation, thereby enhancing OER activity while suppressing Ru overoxidation and dissolution. This review should also be inspiring for designing Core/shell or loaded RuO₂-based catalysts, and thus provides fundamental understanding for designing durable, low-noble-metal acidic OER catalysts for PEMWE.

Keywords : RuO₂ nano-heterojunctions; atomic heterointerface; Acidic oxygen evolution; Interfacial reactor; PEM water electrolysis

1.Introduction

Electrocatalytic water splitting powered by renewable electricity offers a promising route toward sustainable hydrogen production and energy storage. Among various water-electrolysis technologies, proton-exchange membrane water electrolysis (PEMWE) has attracted particular attention because of its compact cell configuration, high current-density capability, high gas purity,

rapid dynamic response, and compatibility with intermittent renewable-energy sources [1, 2]. However, the anodic oxygen evolution reaction (OER) remains the principal kinetic and durability bottleneck for PEMWE. Acidic OER involves a sluggish four-electron proton-coupled electron-transfer process and proceeds under strongly acidic and highly oxidizing potentials [3, 4]. Under such harsh conditions, efficient OER catalysis requires not only rapid water activation, oxygenated-intermediate conversion, and O-O bond formation, but also sustained resistance to metal overoxidation, lattice oxygen loss, oxygen-vacancy accumulation, cation dissolution, and irreversible structural reconstruction. Therefore, practical PEMWE anodes must simultaneously deliver low overpotentials, high-current-density operation, and long-term structural durability [5-7].

Current acidic OER catalysts are still largely dominated by Ir- and Ru-based oxides. IrO₂ is widely regarded as the benchmark catalyst because of its relatively high corrosion resistance under acidic conditions; however, its relatively low intrinsic activity, high cost, and limited abundance substantially hinder its large-scale deployment. RuO₂, in contrast, exhibits superior intrinsic OER activity and comparatively lower cost, making it one of the most attractive alternatives to Ir-based catalysts [5, 8]. Nevertheless, Ru-based oxides suffer from a pronounced activity-stability dilemma. Strong Ru-O covalency and highly redox-active lattice oxygen can lower the energetic barriers of OER elementary steps and accelerate reaction kinetics, but these same features may also promote excessive Ru oxidation, lattice oxygen participation, oxygen-vacancy formation, surface reconstruction, and eventual Ru dissolution as soluble high-valent species [9]. Non-noble-metal [10, 11] oxides, including Co-, Mn-, Fe-, and Ni-based materials, provide another opportunity to reduce noble-metal consumption or even develop noble-metal-free acidic OER catalysts. However, these materials are generally more vulnerable to cation dissolution, phase transformation, and structural collapse under acidic and highly anodic conditions [12, 13]. Thus, simply optimizing a single active phase often fails to satisfy the simultaneous requirements of catalytic activity, structural stability, and resource efficiency.

This limitation originates from the intrinsic coupling between catalytic reactivity and structural degradation. Increasing metal-oxygen covalency, activating lattice oxygen [14-16], introducing vacancies, or promoting unconventional OER pathways can accelerate oxygen

evolution, but excessive oxygen-sublattice activation may trigger irreversible oxygen loss, vacancy accumulation, metal overoxidation, and framework destabilization. Therefore, the rational design of acidic OER catalysts should not aim to maximize local oxygen activity indiscriminately [5, 6]. Instead, oxygenated-intermediate adsorption, lattice oxygen redox, and metal oxidation/dissolution should be maintained within an optimized operational window, where oxygen species remain sufficiently reactive for rapid OER while the metal-oxygen framework retains structural integrity.

Heterojunctions engineering offers an effective route to address the intrinsic limitations of single-component catalysts. By coupling chemically and electronically distinct domains, heterointerfaces can integrate catalytically active motifs, electronically regulating units, oxygen-buffering domains, and proton-transfer microenvironments within one architecture. Representative Ru-based acidic OER heterojunctions, such as $\text{RuO}_2/\text{LiCoO}_2$ [17], $\text{ZrO}_2\text{-RuO}_2$ [18], $\text{RuO}_2/\text{MoO}_3$ [19], $\text{RuO}_2\text{-CeO}_2$ [20], and Ru/RuO_2 [21], have demonstrated that intimate heterointerfaces can regulate charge redistribution, oxygen-species migration, interfacial water organization, cooperative active sites, and structural evolution under anodic polarization. Related non-Ru systems, including IrO_x/TiN [22], $\text{IrO}_x/\text{t-ZrO}_2$ [23] and $\text{CdO-CO}_{3-x}\text{Cd}_x\text{O}_4$ [24], further indicate that these interfacial functions are not restricted to Ru-centered catalysts. Importantly, the catalytic value of a heterojunctions does not arise merely from the coexistence of two materials. A physical mixture may alter surface area, conductivity, wettability, or mass transport without generating an electronically and chemically coupled reaction zone [25]. Likewise, homogeneous doping, solid-solution formation, simple surface decoration, and conventional support effects should not automatically be classified as functional heterointerfaces. A genuine acidic OER heterojunctions requires chemically or structurally distinguishable domains, intimate interfacial contact, measurable interface-specific coupling, and a catalytic consequence that exceeds the additive behavior of the individual components.

Accordingly, heterointerfaces should be regarded as more than static phase boundaries or conventional band-alignment regions [26]. Under acidic OER conditions, they can act as dynamic interfacial reaction zones in which electron transfer [21], oxygen migration [23], water/proton organization [27], cooperative reaction pathways, lattice oxygen redox, and corrosion processes

are simultaneously coupled. This perspective shifts heterojunctions design from simple material integration toward the deliberate construction of interfaces with programmed catalytic functions. Despite substantial progress, current studies on acidic OER heterointerfaces remain fragmented. Many reports are organized according to material composition, structural morphology, or apparent performance enhancement [28-30], whereas the specific catalytic functions performed by heterointerfaces are often discussed separately and lack a unified mechanistic framework [31-34]. Existing reviews have summarized acidic OER catalysts from the perspectives of Ru/Ir-based oxides, non-noble-metal systems, defect engineering, doping, morphology modulation, support effects, or general heterostructure design[5, 8, 35-38]. These reviews have established important structure-performance and structure-mechanism relationships, and provide a comprehensive basis for understanding how different material-design strategies regulate acidic OER behavior. However, interfacial phenomena such as charge redistribution, oxygen-species migration, interfacial water/proton regulation, and cooperative O-O bond formation are generally discussed within individual material systems or modification strategies, rather than being organized according to the operation-relevant functions generated at chemically coupled interfaces.

The distinction of the present review therefore lies not in heterojunctions engineering itself or in the identification of individual interfacial phenomena, but in reorganizing these previously dispersed mechanistic observations into a RuO₂-centered, operation-relevant functional interfacial framework. Whereas previous reviews predominantly address what catalyst compositions, structural motifs, or modification strategies improve acidic OER performance, the present review focuses on what function is generated at a chemically coupled interface, what evidence supports the assignment of that function, and how it regulates both catalytic turnover and degradation. Accordingly, we move beyond conventional structure-performance correlations and establish a framework that connects identifiable interfacial motifs and coupling characteristics with their dominant catalytic functions, and further relates these functions to mechanistic descriptors, Ru overoxidation, lattice degradation, dissolution, and PEMWE-relevant durability. Thus, the conceptual advance of this review lies in shifting from a material/strategy-centered description of heterostructures toward a function-oriented and design-oriented framework for RuO₂ interfaces.

In this review, we establish a RuO₂-centered atomic-scale functional interfacial reactor

framework for understanding and designing nano-heterojunctions catalysts for acidic OER [8, 39]. Rather than regarding heterojunctions as simple physical mixtures or multicomponent assemblies, we consider genuine functional heterointerfaces to consist of chemically distinguishable domains in intimate contact, where interfacial coupling under operating conditions gives rise to catalytic behavior beyond the additive contributions of the individual components. Within this framework, RuO₂-based heterointerfaces regulate acidic OER through five interconnected functions: electronic coupling, oxygen spillover and redox buffering, interfacial water/proton microenvironment regulation, dual-site cooperation, and balanced lattice-oxygen redox (Fig. 1). These functions collectively optimize reaction kinetics while redistributing localized oxidative stress, thereby enabling dynamic corrosion buffering and interface stabilization during prolonged operation. Accordingly, this review is organized around a structure-coupling-function-outcome relationship, using representative Ru-based heterojunctions to elucidate how specific interfacial motifs regulate catalytic activity, Ru overoxidation, lattice degradation, and dissolution. Key future directions are further highlighted, including the operando identification of active interfaces, atomic-level control of interfacial motifs, the rational design of core-shell and supported RuO₂ catalysts, and validation under PEM water electrolysis conditions. Through this function-oriented perspective, this review provides a unified mechanistic foundation and practical design strategy for developing highly active and durable Ru-based acidic OER catalysts.

Heterojunctions as Functional Interfacial Reactors for Acidic OER

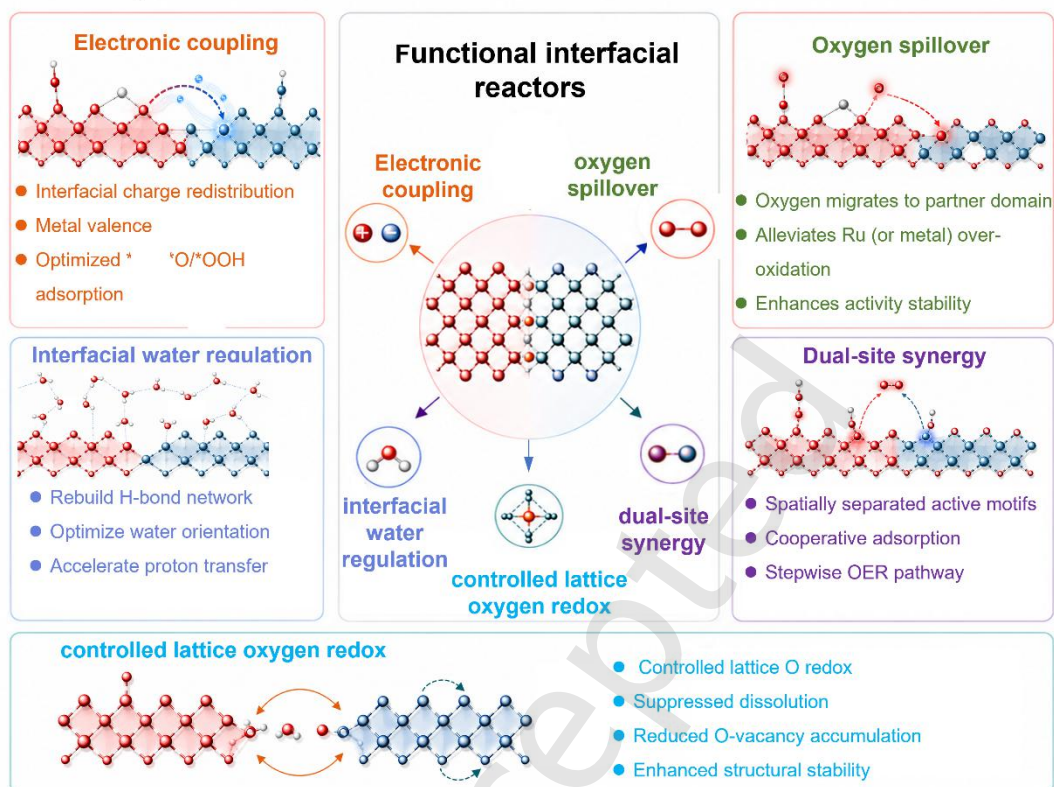


Figure 1 Functional heterointerface as interfacial reactors for acidic OER. Heterointerfaces regulate acidic OER through five key functions: electronic coupling, oxygen spillover/redox buffering, interfacial water/proton regulation, dual-site cooperation, and balanced lattice-oxygen redox.

2. Defining Functional Heterointerface for Acidic OER

The term “heterostructure” is broadly used in electrocatalysis to describe materials containing multiple components, phases, structural domains, or dimensional building blocks [26]. However, compositional complexity alone does not establish a catalytically meaningful heterojunction. Under acidic OER conditions, two components may coexist as a physical mixture, a uniformly doped phase, a solid solution, a surface-decorated material, or a conventional catalyst-support architecture without forming a chemically coupled interfacial reaction zone. Importantly, an improvement in apparent OER activity alone cannot verify interfacial catalysis, because changes in surface area, conductivity, wettability, or catalyst utilization may produce similar performance trends.

In this review, a functional heterojunction for acidic OER is defined as an interfacial catalytic architecture comprising at least two chemically, structurally, or coordinatively distinguishable

domains in intimate contact, where the interface generates an operation-relevant coupling and a catalytic consequence that cannot be reproduced by the isolated components or by a composition-matched physical mixture [26, 35]. Such coupling may arise from interfacial bond formation, charge redistribution, local electric fields, lattice strain, oxygen-species exchange, or cooperative reaction pathways. Thus, the defining feature is not merely the presence of a phase boundary, but the emergence of an interface-specific function under acidic OER conditions [22].

A functional heterojunction should satisfy four interconnected criteria[19, 26]. First, the coupled domains must be structurally or chemically distinguishable, as established by spatially resolved microscopy, diffraction, local coordination analysis, or complementary spectroscopic probes. Second, the domains must form an intimate and catalytically accessible interface rather than coexist as isolated particles. Third, the interface should induce a measurable perturbation in local electronic structure, coordination environment, oxygen-redox behavior, interfacial water structure, or reaction kinetics beyond that expected from the individual components. Finally, the interfacial architecture, or its dynamically reconstructed derivative, must remain relevant under operating conditions. This requirement is critical because acidic OER can induce dissolution, phase segregation, surface reconstruction, and the formation of transient active structures that differ substantially from the as-prepared catalyst [16, 40-42].

Accordingly, a convincing assignment of functional heterojunction catalysis requires a structure-coupling-function-outcome relationship [16, 42]. Structural evidence should establish the identity and contact of the coupled domains; electronic or chemical evidence should reveal interface-specific interactions; and catalytic evidence should demonstrate that the resulting function alters reaction kinetics, pathway selection, or degradation behavior. Whenever possible, these conclusions should be supported by composition-matched physical-mixture controls, interface-density-dependent comparisons, and operando or post-operando characterization. Ex situ X-ray [41, 43] photoelectron spectroscopy shifts or improved current densities alone are insufficient to establish a functional interface.

This definition also clarifies the boundary between functional heterointerface and related catalyst categories. Homogeneously doped materials and solid solutions should generally be regarded as local coordination or electronic-structure regulation when distinct interfacial domains

are absent [44]. Likewise, isolated single-atom decoration, molecular functionalization, and simple surface coatings should not automatically be classified as heterointerface. Catalyst-support architectures are included only when the support directly participates in charge transfer, oxygen migration, interfacial water regulation, local electric-field generation, or structural stabilization [45, 46]. Similarly, reconstructed interfaces should be considered functional only when their formation and catalytic relevance can be verified under, or after, acidic OER operation [47].

This distinction is particularly important for acidic OER, where nominally similar multicomponent materials may operate through fundamentally different mechanisms. For example, metal/oxide and oxide/nitride interfaces such as Ru/RuO₂ and IrO_x/TiN can exhibit direct interfacial coordination and charge redistribution, whereas oxide/oxide architectures such as ZrO₂-RuO₂ may generate bridge-mediated electronic perturbations and differentiated oxygenated-intermediate chemistry. In contrast, a uniformly doped RuO₂ lattice should not be designated as a heterojunction unless distinguishable domains and an interface-specific catalytic function are experimentally established.

Once these structural and mechanistic criteria are satisfied, functional heterointerface can be classified according to their dominant interfacial role. Although partial mechanistic overlap exists among some of the five interfacial functions, each function is defined by a distinct primary role. Accordingly, each representative catalyst is assigned to one dominant function based on the interfacial process that is most directly supported by the available evidence and provides the principal mechanistic link between interface structure and catalytic outcome. Other concurrent effects are discussed as secondary or coupled functions. In this review, five coupled functions are considered: electronic coupling, oxygen migration and redox buffering, water/proton microenvironment regulation, dual-site cooperation, and balanced lattice-oxygen redox. These functions are not mutually exclusive. Charge redistribution can alter oxygen affinity and water adsorption; oxygen buffering can regulate lattice-oxygen activity; and dual-site cooperation can redistribute the oxidative burden otherwise concentrated on a single metal-oxygen motif. The following sections examine how these interfacial functions govern catalytic activity, oxidative degradation, and long-term structural stability in acidic OER.

Despite the potential advantages discussed above, heterojunctions construction does not

inherently guarantee improved acidic OER stability. A functional heterointerface requires not only intimate contact between chemically distinct components, but also effective interfacial coupling and sufficient structural stability during operation. Weakly coupled components may behave primarily as physical mixtures without generating meaningful interfacial regulation, whereas inappropriate or excessive coupling may lead to undesirable interfacial effects, such as unfavorable charge redistribution, excessive interdiffusion, or destabilization of the Ru-O framework. Moreover, the non-RuO₂ component may undergo dissolution, phase segregation, or reconstruction under strongly acidic and oxidative conditions, resulting in partial or complete loss of the initially designed interface. In such cases, the stabilization effect of heterojunction construction may be limited. Therefore, the presence of a heterostructure alone should not be regarded as evidence of a beneficial interfacial effect; operation-relevant coupling, structural persistence, and a direct relationship with degradation behavior must be established.

In this review, mechanistic assignments are evaluated according to the nature and strength of the available evidence. The conclusions derived from operando/in situ spectroscopy, isotope-labeling measurements, and other working-state characterization are treated as direct experimental evidence. Atomic-scale interpretations based on DFT/AIMD calculations, such as charge redistribution, adsorption energetics, vacancy formation, and migration barriers, are regarded as theory-supported mechanisms. Interfacial processes that are consistent with the DFT evidence but have not been directly observed are explicitly identified as mechanistic inferences.

3. Five Interfacial Functions for Acidic OER Regulation

3.1 Electronic Coupling: Regulating Charge Distribution and Intermediate Adsorption

Electronic coupling is a key pathway through which heterointerfaces regulate acidic OER reactivity [26]. When chemically distinct domains with different work functions, electronegativities, Fermi levels, or metal-oxygen covalencies are brought into intimate contact, interfacial charge redistribution can arise through orbital hybridization, interfacial bonding, or built-in electric fields [48]. This electronic perturbation can alter the local valence state, coordination environment, metal-oxygen bonding characteristics, and adsorption energetics of key oxygenated intermediates, including *OH, *O, and *OOH [49]. Its function is therefore not simply

to increase or decrease the electron density at active metal centers, but to establish an optimized electronic environment that preserves the reactivity required for water activation and intermediate conversion while limiting excessive metal oxidation and destabilization of the metal-oxygen framework. In terms of evidentiary support, operando/in situ spectroscopic measurements can directly establish potential-dependent changes in Ru valence, coordination, or electronic states, whereas the direction and spatial distribution of interfacial charge transfer are generally further interpreted using DFT-derived charge-density differences, Bader-charge analysis, or electronic density-of-states calculations.

A representative example of dynamically regulated electronic coupling is the RuO₂/LiCoO₂ heterointerface reported by Wang et al [17]. RuO₂ nanoparticles were tightly anchored on LiCoO₂ nanosheets, where the initial interfacial interaction transferred electron density from the LiCoO₂ support to Ru sites and provided electronic compensation for the RuO₂ domain. Under acidic OER potentials, partial extraction of interlayer Li⁺ induced dynamic reconstruction of the support, transforming the initial RuO₂/LiCoO₂ interface into a RuO₂/Li_{1-x}CoO₂ interface (Fig. 2(a)). This process did not eliminate the interfacial electronic interaction; instead, it continuously adjusted the charge distribution across the interface. As shown in Fig. 2(b), the calculated Bader charge of Ru increased from 6.457 e in bare RuO₂ to 6.626 e in RuO₂/LiCoO₂, confirming electron transfer from the LiCoO₂ support to the RuO₂ domain. After partial delithiation, the Ru charge decreased moderately to 6.584 e, but remained higher than that of bare RuO₂. In parallel, the charge associated with Co sites decreased from 7.962 e in pristine LiCoO₂ to 7.751 e in RuO₂/LiCoO₂ and further to 7.647 e in RuO₂/Li_{1-x}CoO₂, indicating progressive electron depletion of the support during interfacial reconstruction. These results reveal a dynamically balanced charge-transfer process rather than a static electron-donation effect. Such dynamic electronic regulation moderately weakens Ru-O covalency while retaining sufficient electronic compensation at Ru sites. Operando XAS showed that the Ru-O bond in RuO₂/LiCoO₂ gradually elongated under anodic polarization, whereas that in bare RuO₂ became substantially shortened. Meanwhile, the Ru oxidation state increased only moderately in the heterostructure but rose sharply in bare RuO₂. The dynamically reconstructed Li_{1-x}CoO₂ interface therefore suppresses excessive Ru oxidation and lattice-oxygen activation while preserving favorable *OOH formation energetics. This case

demonstrates that a heterointerface can function as a dynamically responsive electronic regulator, continuously tuning the Ru–O bonding environment during acidic OER rather than acting merely as a static support or electron reservoir.

Cheng et al [21]. constructed a dopant-free Ru/RuO₂ metal/oxide heterostructure featuring an intimately matched Ru (100)/ RuO₂ (110)-type interface. Unlike a simple physical mixture of Ru and RuO₂, the metal/oxide junction induced directional electron transfer from metallic Ru toward the adjacent RuO₂ domain and established a built-in potential gradient across the interface. This charge redistribution lowered the effective oxidation state of interfacial Ru centers, modified Ru 4*d*-O 2*p* hybridization, and partially populated Ru-O antibonding states, thereby moderating Ru-O interactions and optimizing the adsorption of oxygenated intermediates. As illustrated in (Fig. 2(c) and 2(d)) the interfacial electronic perturbation lowered the calculated kinetic barriers for both the adsorbate evolution mechanism (AEM) and lattice oxygen mechanism (LOM), while rendering lattice oxygen participation more accessible. More importantly, the electron-enriched RuO₂ domain exhibited a reduced tendency toward further anodic oxidation, thereby suppressing the formation of high-valent soluble RuO₄ species. This electronic stabilization was accompanied by accelerated interfacial charge transfer and substantially enhanced catalytic performance, with an overpotential of 182 mV at 10 mA cm⁻² and stable operation for over 270 h at 100 mA cm⁻² in 0.5 M H₂SO₄. This study identifies metallic Ru not as a secondary inactive phase, but as an interfacial electron reservoir that regulates the working state of adjacent RuO₂ active sites and thereby reconciles catalytic reactivity with resistance to oxidative dissolution.

An oxide/oxide interfacial analogue is provided by Liao et al [50], who constructed a ZrO₂/RuO₂ heterointerface through an inter-doping strategy. Atomic-resolution microscopy identified ZrO₂ (111)/ RuO₂ (110) phase boundaries, while dual-edge XANES/EXAFS analysis revealed local Zr-O-Ru coordination motifs at the interfacial region. As summarized in Fig. 2(e)-2(h), this bridged linkage acts as an interfacial electronic relay rather than rendering ZrO₂ an independent catalytic center. Compared with either pristine RuO₂ or a physical ZrO₂/RuO₂ mixture, the integrated heterostructure exhibited reciprocal electronic shifts, with reduced Ru and more oxidized Zr species, consistent with charge redistribution from Zr-containing domains toward interfacial Ru sites. This electronic perturbation slightly weakened Ru-O bonding and shifted the

Ru d-band center closer to the Fermi level, thereby optimizing the adsorption and conversion of oxygenated intermediates. DFT calculations further identified Ru as the primary active center and showed that Ru sites associated with Zr-O-Ru bridges favor $^*\text{OH}$ formation and reduce the $^*\text{O}$ to $^*\text{OOH}$ conversion barrier by approximately 0.70 eV relative to conventional O-Ru-O sites. Meanwhile, the strengthened Zr-O framework was proposed to moderate excessive lattice-oxygen involvement and mitigate destructive structural evolution under anodic polarization. Consequently, the bridge-mediated Zr-O-Ru electronic coupling enabled a low overpotential of 137 mV at 10 mA cm^{-2} and stable acidic OER operation for 655 h. This work highlights that oxide/oxide heterointerfaces can regulate Ru-site reactivity not only through phase-level contact, but also through atomically localized metal-oxygen-metal bridges that couple optimized intermediate binding with improved resistance to oxidative degradation.

Collectively, these examples establish interfacial charge-transfer regulation as more than a static electron-donation or electron-withdrawing effect. Metal/oxide, oxide/oxide, and dynamically reconstructed heterointerfaces employ distinct structural motifs-including built-in potential gradients, support-mediated charge compensation, and atomically localized metal-oxygen-metal bridges-to redistribute electron density around Ru active sites. Such electronic coupling regulates the Ru valence state and Ru-O covalency, thereby tuning the adsorption and conversion energetics of $^*\text{OH}$, $^*\text{O}$, and $^*\text{OOH}$ while avoiding both excessive Ru oxidation and uncontrolled lattice-oxygen activation. Importantly, the objective of heterointerface design is not to maximize charge transfer in one direction, but to maintain a dynamically balanced electronic state in which metal-oxygen bonds remain sufficiently reactive for efficient OER turnover yet sufficiently robust against oxidative dissolution and structural degradation. Therefore, interfacial charge regulation provides a fundamental route for linking heterojunctions structure to optimized catalytic reactivity and long-term durability in acidic OER.

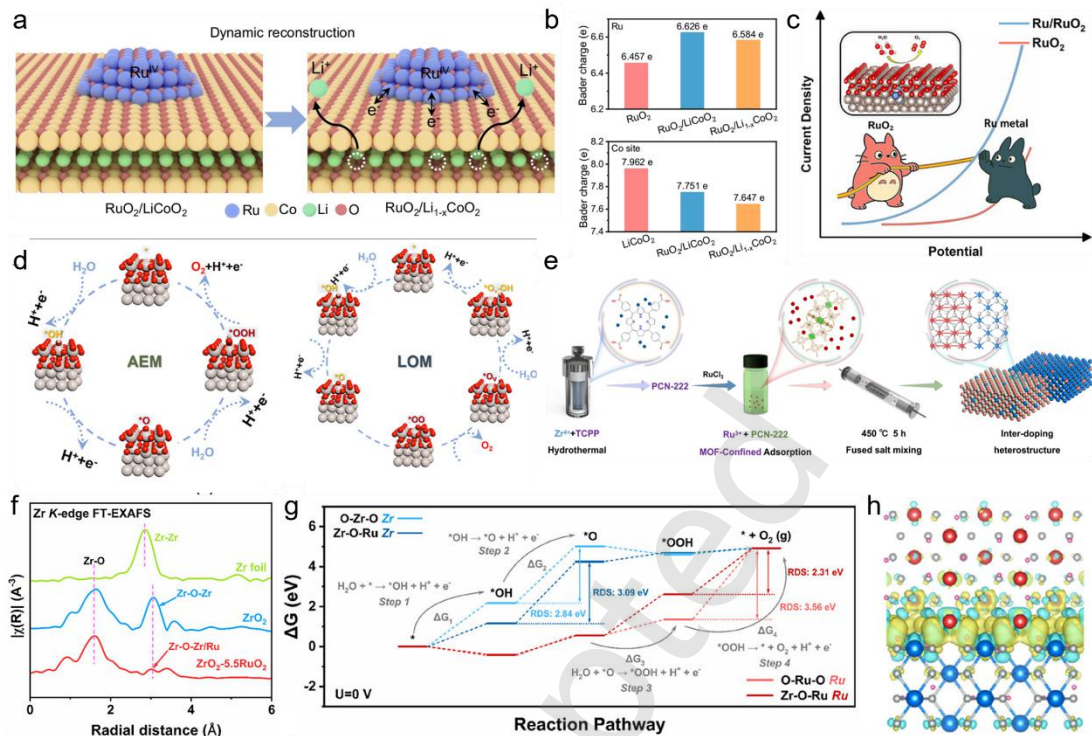


Figure 2 Interfacial Electronic Regulation in Ru-Based Heterojunctions Catalysts. (a), Schematic illustration of dynamic reconstruction at the $\text{RuO}_2/\text{LiCoO}_2$ interface during OER, accompanied by Li^+ extraction and electron redistribution. (b), Bader charge analysis of Ru and Co sites in RuO_2 , LiCoO_2 , $\text{RuO}_2/\text{LiCoO}_2$, and reconstructed $\text{RuO}_2/\text{Li}_{1-x}\text{CoO}_2$ models. (c), Schematic comparison of OER behavior over Ru/RuO_2 and RuO_2 catalysts. (d), Schematic illustration of the adsorbate evolution mechanism (AEM) and lattice oxygen mechanism (LOM) on Ru-based oxide surfaces. (e), Synthesis route of the Zr-Ru inter-doping heterostructure through MOF-confined adsorption and fused-salt treatment. (f), Zr K-edge FT-EXAFS spectra confirming the local coordination environment of Zr species. (g), Calculated OER free-energy diagrams for different Zr-O-Ru coordination configurations. (h), Charge-density distribution of the Zr-Ru heterointerface.

3.2 Oxygen Spillover and Oxygen Buffering: Redistributing Oxygen-Redox Stress

Beyond electronic regulation of catalytic centers, heterointerfaces can also govern the spatial transport and redistribution of reactive oxygen species [51]. Oxygen spillover refers to the migration of oxygen species across coupled domains, thereby enabling the spatial separation of oxygen activation, oxygen storage, oxygen transfer, and oxygen consumption. This interfacial transport process is particularly relevant to acidic OER, where the local accumulation of highly oxidizing oxygen species at vulnerable Ru- or Ir-based sites can accelerate metal overoxidation, oxygen-vacancy formation, and structural degradation. A properly designed heterointerface may therefore function as an oxygen buffering pathway that redistributes oxygen-redox stress away

from dissolution-prone active domains.

An atom-resolved mechanistic precedent for this concept was provided by Wang et al., who directly visualized interface-controlled bulk oxygen spillover in Ru/rutile-TiO₂ catalysts [52]. Although this study was performed under thermal oxidation conditions rather than electrochemical OER, it provides an important mechanistic basis for understanding how oxide heterointerfaces can direct oxygen transport. As illustrated in Fig. 3(a) and 3(b), in situ environmental TEM revealed that Ru oxidation did not proceed primarily through conventional surface diffusion. Instead, RuO₂ first nucleated at the buried Ru/rutile-TiO₂ interface and then propagated in a bottom-up manner along the interface. Combined isotope-labeling experiments, atom-resolved lattice-strain analysis, and DFT calculations demonstrated that oxygen was transported from the subsurface rutile-TiO₂ lattice to Ru particles through a vacancy-mediated pathway. During this process, the upper TiO₂ subsurface layers underwent reversible anisotropic lattice compression, providing dynamically adaptable channels for oxygen migration. Importantly, such bulk oxygen transport was activated only at the epitaxially compatible Ru/rutile-TiO₂ interface, whereas it was absent in Ru/anatase-TiO₂ and was suppressed after disruption of interfacial epitaxy. These results establish that oxygen spillover is governed not simply by support reducibility, but by the coupled effects of interfacial epitaxy, vacancy energetics, and lattice adaptability. This work highlights a general principle for functional oxygen-buffering heterointerfaces: an adjacent domain must not only possess oxygen storage or release capability, but also provide a structurally continuous and kinetically viable pathway for oxygen transport. In acidic OER, this principle implies that oxygen spillover can spatially redistribute reactive oxygen species and local oxidative stress, thereby preserve the reactivity of the primary catalytic phase while reduce its susceptibility to overoxidation and dissolution.

For oxygen spillover, isotope tracing or spatially resolved operando characterization provides the strongest support for oxygen spillover, whereas DFT-derived migration barriers mainly establish its energetic feasibility. In the absence of direct tracking, spillover is therefore treated here as a theory-supported mechanistic interpretation rather than a directly observed process.

A representative Ru-based acidic OER example was reported by Gou et al [19]. who constructed RuO₂/MoO₃ hetero-structured nanowires with abundant intimate interfaces. In this

system, RuO₂ acts as the primary site for *OH deprotonation and *O formation, whereas MoO₃ serves as an oxygen-accepting and redox-buffering domain. As illustrated in Fig. 3(c)-3(e), the stronger *O binding affinity and lower oxygen-vacancy formation energy of MoO₃ favor the interfacial migration of *O generated on RuO₂ toward the adjacent MoO₃ domain. The spilled-over *O subsequently couples with lattice oxygen from MoO₃ to form the *OO intermediate, while the resulting oxygen vacancies are generated and replenished predominantly within the MoO₃ phase rather than on RuO₂. This spatial redistribution preserves the kinetic benefit of lattice oxygen participation while preventing oxygen-vacancy accumulation and excessive oxidation of RuO₂. Operando Raman spectroscopy showed that the Ru-O vibration remained nearly unchanged during OER, whereas the Mo-O vibration exhibited a pronounced blueshift, indicating that the oxidative structural response was preferentially accommodated by MoO₃. Consistently, the Ru⁴⁺/Ru⁶⁺ redox feature was markedly weakened after MoO₃ incorporation, and isotope-labeled DEMS confirmed the persistence of a lattice-oxygen-mediated pathway. Consequently, RuO₂/MoO₃ achieved an overpotential of 167 mV at 10 mA cm⁻² and negligible performance decay over 300 h in 0.5 M H₂SO₄. This work demonstrates that oxygen spillover can convert a secondary oxide into an active oxygen acceptor and lattice-redox buffer, enabling RuO₂ to retain high OER reactivity while mitigating overoxidation-associated dissolution.

Although Ru-based heterojunctions provide the central basis for this review, the oxygen-spillover concept can also be extended to non-Ru systems. Fang et al. demonstrated a complementary oxygen-donor mode using porous tetragonal ZrO₂ supported IrO_x nanoclusters, denoted IrO_x/t-ZrO₂ [23]. In this heterostructure, t-ZrO₂ functions as an oxygen-donating interfacial partner rather than a passive support or oxygen acceptor. As illustrated in Fig. 3(f) and 3(g), conventional lattice-oxygen-mediated oxidation on IrO_x may generate oxygen vacancies and unstable high-valent Ir-oxo species, eventually leading to catalyst dissolution. In the IrO_x/t-ZrO₂ heterointerface, however, oxygen species generated on t-ZrO₂ can migrate to adjacent IrO_x clusters and compensate for lattice oxygen loss during OER. DFT calculations showed that t-ZrO₂ possesses a substantially lower water-dissociation barrier than monoclinic ZrO₂ and enables thermodynamically favorable oxygen migration toward IrO_x. Operando isotope-labeled DEMS, pH-dependent kinetics, and tetramethylammonium-ion probing further supported lattice oxygen

participation in the OER pathway. More importantly, operando XAFS revealed a dynamic and complementary structural evolution: Ir sites underwent initial oxidation and partial Ir-O coordination loss at lower potentials, whereas further anodic polarization did not induce continuous Ir overoxidation; meanwhile, the Zr *K*-edge shifted to lower energy and the Zr-O coordination weakened, consistent with support-derived oxygen migration toward IrO_x. Therefore, the t-ZrO₂ support acts as an interfacial oxygen reservoir that continuously replenishes oxygen-deficient IrO_x motifs, allowing the catalyst to retain the kinetic advantage of lattice oxygen redox while suppressing vacancy accumulation, Ir dissolution, and structural collapse. This oxygen-donor mode complements the oxygen-acceptor mode observed in RuO₂/MoO₃, expanding oxygen spillover from oxidative-stress removal to active lattice-oxygen replenishment.

Collectively, these studies indicate that oxygen spillover in acidic OER can be classified into two directionally distinct redox-buffering modes. In the oxygen-acceptor mode, exemplified by RuO₂/MoO₃, reactive oxygen species generated on the primary active phase migrate to an adjacent oxygen-affine buffer domain. The subsequent O-O coupling, vacancy formation, and oxygen-redox accommodation are thereby preferentially shifted from dissolution-prone RuO₂ to MoO₃, mitigating Ru overoxidation, oxygen-vacancy accumulation, and framework degradation. In the oxygen-donor mode, exemplified by IrO_x/t-ZrO₂, an oxygen-reservoir domain replenishes oxygen-deficient motifs in the active oxide, suppressing persistent vacancy accumulation and structural destabilization during lattice-oxygen-mediated OER. Although the latter is not Ru-based, it provides a valuable complementary model because clear oxygen-donor spillover remains less established in Ru-centered acidic OER heterojunctions. These two modes share the same essential objective: spatially redistributing oxygen-redox stress away from vulnerable active metal-oxygen frameworks. Their distinction lies in the direction of oxygen transfer and the corresponding stabilization requirement. Oxygen-acceptor interfaces require an auxiliary phase with sufficiently strong oxygen affinity, accessible vacancy formation, and rapid interfacial oxygen transport, whereas oxygen-donor interfaces require a reversibly redox-active oxygen reservoir capable of releasing oxygen without undergoing irreversible degradation. Thus, oxygen-spillover heterointerfaces should be designed not simply to maximize oxygen mobility, but to match the direction, extent, and reversibility of oxygen transfer with the dominant degradation pathway of

the active phase.

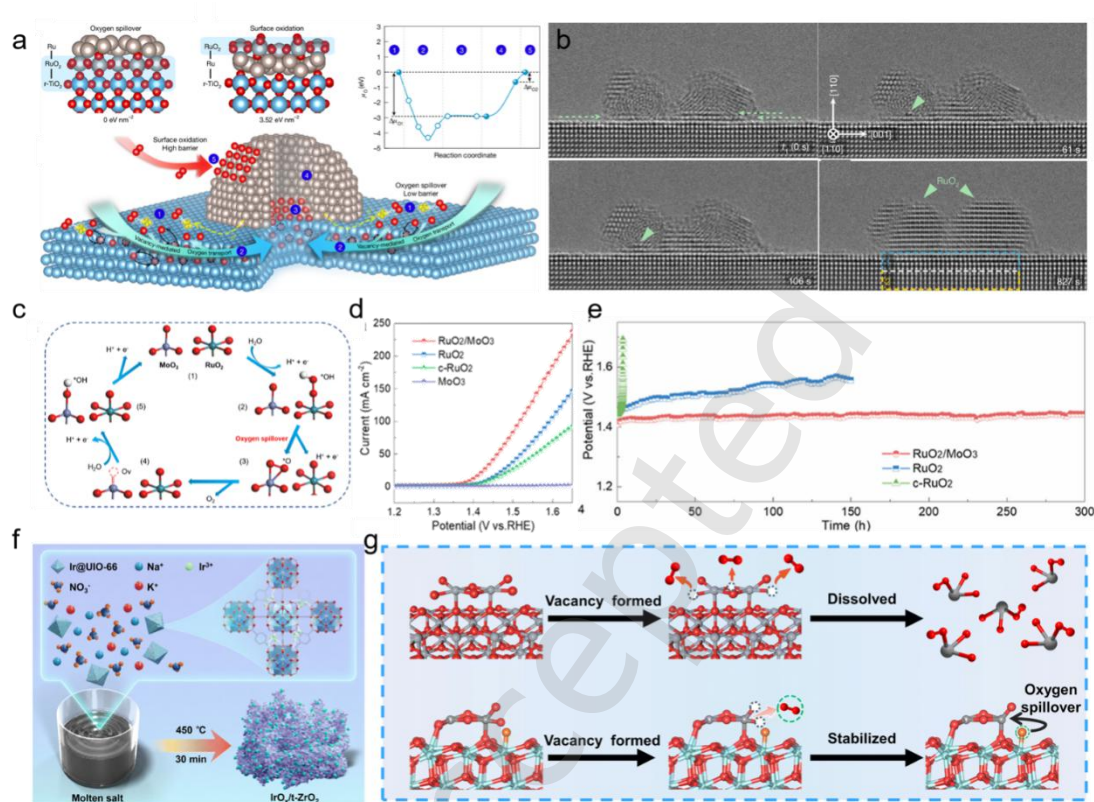


Figure 3 Oxygen Spillover as an Interfacial Reactor Function for Acidic OER Stabilization. (a), Schematic illustration and calculated energy profile of vacancy-mediated oxygen spillover at the Ru/rutile-TiO₂ interface. (b), Time-resolved atomic-resolution TEM images showing interfacial oxygen transport and bottom-up oxidation of Ru into RuO₂. (c), Proposed oxygen-spillover pathway in RuO₂/MoO₃ heterostructures. (d) and (e), OER polarization curves and chronopotentiometric stability tests of RuO₂/MoO₃ and reference catalysts in acidic electrolyte. (f), Molten-salt synthesis schematic of IrO_x/t-ZrO₂ heterostructures. (g), Proposed stabilization mechanism of IrO_x/t-ZrO₂, in which t-ZrO₂ replenishes oxygen-deficient IrO_x sites and suppresses catalyst dissolution.

3.3 Interfacial Water Regulation: Reconstructing Water Networks and Proton-Transfer Pathways

Beyond regulating the electronic structure of catalytic centers and the transport of oxygen species, functional heterointerfaces can actively reconstruct the interfacial water microenvironment [53]. In acidic OER, water molecules at the electrified catalyst-electrolyte interface are not merely passive reactants, but form dynamic hydrogen-bond networks that govern water activation, ^{*}OH deprotonation, proton-coupled electron transfer, and the stabilization of

oxygenated intermediates. When chemically distinct domains are coupled, interfacial charge polarization, local electric fields, Lewis acid-base interactions, and surface oxophilicity can collectively alter the orientation, coordination, and hydrogen-bond connectivity of interfacial water [54]. Such regulation facilitates proton transport and intermediate conversion while alleviating local proton accumulation and excessive oxidative stress. Therefore, heterointerfaces extend their role beyond solid-state electronic modulation and function as microenvironmental regulators at the catalyst-electrolyte boundary, where water organization and proton-transfer dynamics can be deliberately tuned to promote acidic OER activity and structural stability.

For this interfacial function, operando vibrational spectroscopy can directly track potential-dependent changes in interfacial water configurations, while kinetic isotope effects provide complementary evidence for proton-involved reaction kinetics. AIMD simulations, by contrast, mainly provide molecular-level interpretation of water orientation, hydrogen-bond connectivity, and possible proton-transfer pathway.

Deng et al [18]. demonstrated this concept using Lewis-acid-modified RuO₂ heterostructures, in which TiO₂, ZrO₂, and HfO₂ were introduced as interfacial water-regulating domains. Among them, ZrO₂-RuO₂ exhibited the most effective regulation of the water/proton microenvironment during acidic OER. As illustrated in Fig. 4(a) and 4(b), pristine RuO₂ suffers from insufficient interfacial water supply and proton accumulation under anodic polarization, which promotes lattice oxygen oxidation and the formation of soluble RuO₄ species. In contrast, the Lewis-acidic Zr sites in ZrO₂-RuO₂ can accept lone-pair electrons from water molecules, thereby trapping and enriching water near adjacent RuO₂ active sites while maintaining a connected hydrogen-bond network for proton transport. AIMD simulations revealed that the ZrO₂-RuO₂ interface establishes an optimized balance between water enrichment and hydrogen-bond connectivity. In situ ATR-SEIRAS and Raman spectroscopy further showed that ZrO₂ incorporation promotes the dynamic evolution of interfacial water from strongly hydrogen-bonded species toward more reactive free-water configurations under OER potentials, while preserving sufficient hydrogen-bond connectivity for proton transfer. This water-rich yet proton-conductive microenvironment continuously supplies reactant water to Ru sites and accelerates the deprotonation of oxygenated intermediates. Accordingly, *O-*OOH conversion is facilitated,

surface $^*\text{OH}$ coverage is reduced, and the reaction pathway shifts toward an AEM-dominated route with suppressed lattice oxygen participation. Therefore, the $\text{ZrO}_2\text{-RuO}_2$ heterointerface functions as an interfacial water reactor in which Lewis-acidic domains coordinate water trapping, hydrogen-bond reorganization, and proton transfer. By preventing local water deficiency and proton accumulation, this microenvironmental regulation mitigates Ru overoxidation and dissolution while maintaining rapid OER kinetics. As a result, the $\text{ZrO}_2\text{-RuO}_2$ catalyst achieved an overpotential of 170 mV at 10 mA cm^{-2} , stable operation for 1800 h at 10 mA cm^{-2} in $0.5 \text{ M H}_2\text{SO}_4$, and PEMWE operation at 2.0 A cm^{-2} for 100 h.

In addition to Lewis acid-mediated water enrichment, Ru-based heterointerfaces can also regulate interfacial water through built-in electric fields. A complementary mechanistic example was provided by Li et al [55] who constructed isolated-Gd-modified Ru/RuO_x heterostructures. Although this work was performed for alkaline hydrogen oxidation rather than acidic OER, it provides a useful mechanistic reference for understanding how Ru-based heterointerfaces can direct water orientation and proton-transfer pathways. In this system, the work-function mismatch between metallic Ru and oxidized RuO_x generated an intrinsic built-in electric field, which was further strengthened by atomically dispersed Gd. The reinforced interfacial field enhanced asymmetric charge redistribution and finely tuned the surface oxophilicity of the coupled Ru/RuO_x domains.

As illustrated in Fig. 4(c)-4(e), in situ SEIRAS revealed that the optimized interfacial electric field reoriented water molecules from a hydrogen-down configuration toward a preferential oxygen-down configuration. Compared with Ru/RuO_x, the Gd-modified heterostructure exhibited a substantially enhanced Stark tuning rate for oxygen-down water species, accompanied by a suppressed response from hydrogen-down water. This field-guided reorientation established a more favorable hydrogen-bond network and balanced hydroxyl coverage, thereby facilitating interfacial proton conduction without excessive site blocking. This study demonstrates that built-in electric fields can regulate interfacial water not only by altering water adsorption strength, but also by selectively stabilizing specific molecular orientations and hydrogen-bond configurations. Such a mechanism provides a transferable design principle for Ru-based acidic OER heterointerfaces, where appropriate interfacial electric fields may help balance water accessibility, hydrogen-bond

connectivity, and proton-transfer kinetics. Beyond direct regulation of water coordination and hydrogen-bond networks, modulation of the interfacial electric double layer provides another route to regulate the local proton microenvironment. High-density RuO₂ sub-nanoclusters were reported to induce an electric-double-layer overlapping effect, which modified the compact-layer potential and local H₃O⁺ distribution, thereby regulating intermediate coverage while simultaneously stabilizing Ru-O bonding and suppressing Ru dissolution [48].

Collectively, these Ru-based examples highlight interfacial water regulation as a critical route for improving acidic OER activity and stability. In Lewis-acidic ZrO₂-RuO₂ heterointerfaces, Zr sites enrich water molecules near Ru active centers and reconstruct the interfacial hydrogen-bond network, thereby sustaining water supply and accelerating proton transfer while alleviating local proton accumulation. This water-rich yet dynamically connected microenvironment promotes oxygenated-intermediate deprotonation and suppresses local water deficiency, which can otherwise favor excessive lattice-oxygen activation, Ru-O framework destabilization, and Ru dissolution. Complementarily, Ru/RuO_x-Gd heterointerfaces demonstrate that built-in electric fields can further regulate water orientation and hydrogen-bond organization through local charge polarization. Together, these findings suggest that rational control of water availability, molecular orientation, and proton-transfer dynamics can shift Ru-based catalysts away from destructive oxygen-redox regimes, providing a microenvironmental strategy to mitigate lattice oxygen loss and improve long-term acidic OER stability.

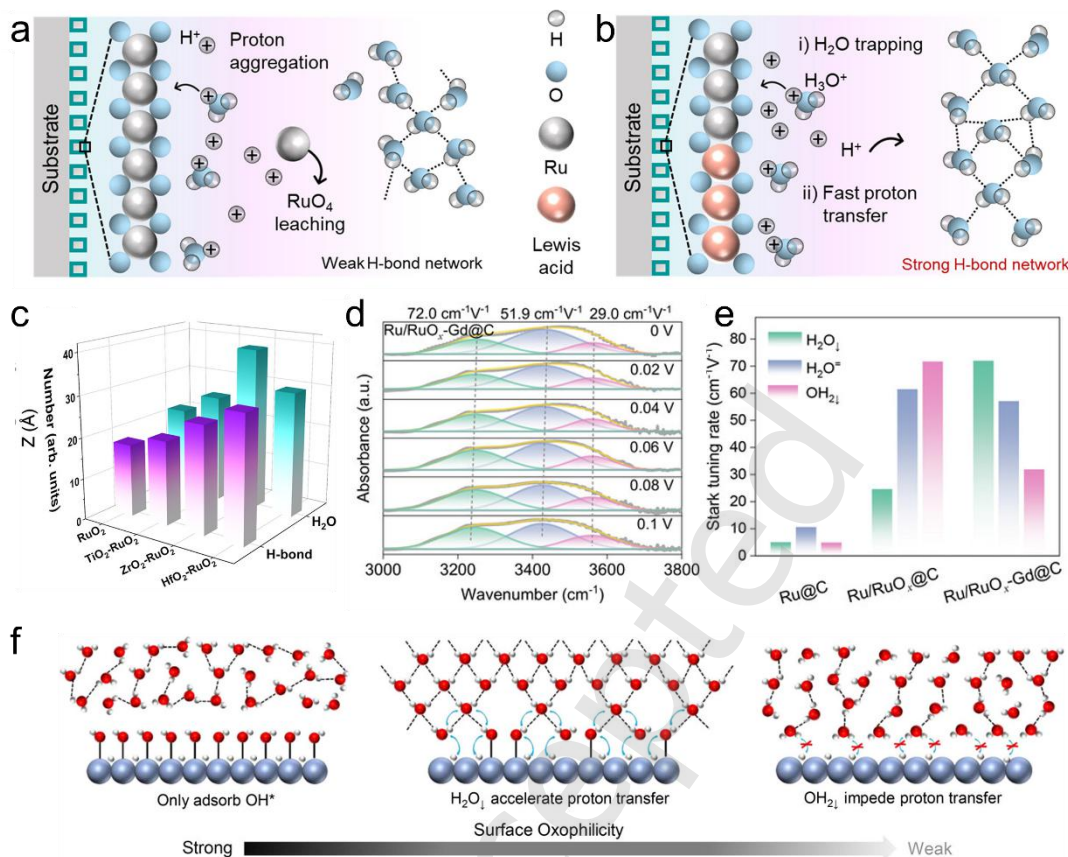


Figure 4 Heterointerface-mediated regulation of interfacial water and proton-transfer microenvironments in acidic OER. (a), Schematic illustration of proton aggregation, weak hydrogen-bond networks, and RuO_4 leaching on conventional Ru-based surfaces. (b), Lewis-acid-modified Ru-based interface for H_2O trapping, strengthened hydrogen-bond networks, and accelerated proton transfer. (c), Quantitative comparison of interfacial O and hydrogen-bond numbers on RuO_2 and oxide-RuO₂ heterointerfaces. (d), Potential-dependent infrared spectra of interfacial water on $\text{Ru/RuO}_x\text{-Gd@C}$. (e), Stark tuning rates of different interfacial water species on Ru@C , $\text{Ru/RuO}_x\text{@C}$, and $\text{Ru/RuO}_x\text{-Gd@C}$. (f), Schematic relationship between surface oxophilicity, interfacial water configuration, and proton-transfer behavior, showing that moderately oxophilic surfaces favor H_2O -mediated proton transport whereas weakly oxophilic surfaces hinder proton transfer.

3.4 Dual-Site Synergy: Spatially Organizing Cooperative OER Pathways

Heterointerface can create spatially adjacent yet chemically differentiated active sites that cooperatively mediate distinct elementary steps of acidic OER. Unlike single-component catalysts, in which one metal-oxygen motif must simultaneously activate water, stabilize oxygenated intermediates, promote O-O bond formation, and resist oxidative degradation, heterointerfaces distribute these functions across electronically coupled sites with complementary adsorption and redox properties [10, 30]. One site may favor H_2O activation or $^*\text{OH}/^*\text{O}$ stabilization, whereas the

neighboring site facilitates $^*\text{OOH}$ formation, lattice-oxygen regulation, or O-O coupling. This interfacial division of labor can reduce the energetic burden of individual steps, alleviate excessive oxidation of a single active motif, and enable cooperative pathways inaccessible to isolated sites, thereby improving both OER kinetics and structural durability.

From an evidentiary standpoint, dual-site cooperation can be supported experimentally by operando identification of intersite O-O intermediates and isotope-sensitive analysis of oxygen coupling, while DFT calculations can provide complementary mechanistic evidence by revealing cooperative transition states and reduced O-O coupling barriers involving adjacent sites.

Before discussing dual-site cooperation at heterointerfaces, Ru/MnO₂ provides an instructive mechanistic prototype for spatially organized OER catalysis [10]. Although this system is not a classical biphasic heterojunction, it clearly illustrates how support-directed atomic arrangement can create neighboring active centers and redirect the oxygen evolution pathway. As shown in Fig. 5(a), the oxide-path mechanism (OPM) enables two adjacent Ru-bound $^*\text{O}$ species to directly couple into an O-O intermediate, thereby bypassing the energetically demanding $^*\text{OOH}$ formation step involved in the conventional adsorbate evolution mechanism. In Ru/MnO₂, cation exchange and operando reconstruction generate ordered Ru atom arrays on α -MnO₂. The Ru-Ru distance is approximately 2.9 Å, shorter than that in rutile RuO₂ (~3.1 Å), providing a favorable geometric configuration for direct coupling between neighboring $^*\text{O}$ intermediates (Fig. 5(b)). Operando FT-IR identified O-O bridge-related and superoxol like intermediates, while no obvious $^*\text{OOH}$ signal was detected. Isotope-labeled DEMS further supported the direct coupling of adjacent oxygen adsorbates. This study demonstrates that dual-site OER catalysis can be enabled by precise geometric organization, even between chemically similar metal centers. For functional heterointerfaces, it highlights that intersite distance, coordination environment, and electronic communication are critical parameters for constructing cooperative reaction ensembles capable of promoting O-O coupling and overcoming the $^*\text{OOH}$ -related scaling limitation.

A metal/oxide heterojunction example of cooperative O-O coupling was reported by Song et al [56]. using sub-4 nm Ru/RuO₂ Schottky nanojunctions. In this system, the Ru (100)/RuO₂ (110) interface introduces lattice strain and interfacial charge redistribution, generating electronically coupled Ru-O ensembles that favor the cooperative coupling of adjacent oxygenated species.

Rather than proceeding through the conventional *OOH-mediated AEM pathway, the Ru/RuO₂ interface promotes an oxide-path mechanism (OPM), in which neighboring oxygen adsorbates directly form an O-O bond. As shown in Fig. 5(c)-5(e), operando isotope-labelled DEMS detected predominantly ³⁶O₂ in H₂¹⁸O electrolyte, with no detectable ³²O₂ signal, excluding substantial lattice oxygen participation in O-O bond formation. In situ ATR-IR further revealed a potential-dependent band at approximately 1050 cm⁻¹, assigned to a Ru-O-O-Ru intermediate, providing spectroscopic evidence for intersite oxygen coupling. DFT calculations showed that the Ru/RuO₂ heterointerface lowers the free-energy barrier for O₂ formation to 1.77 eV, while increasing the barrier for the competing RuO₄ forming pathway. Therefore, the Schottky heterointerface not only enables cooperative O-O coupling between adjacent Ru-O motifs, but also directs the reaction away from destructive Ru overoxidation. This case illustrates how metal/oxide heterointerface can create interfacial reaction ensembles that couple dual-site OER kinetics with enhanced resistance to oxidative dissolution [29].

A representative heterojunction example of spatially organized dual-site catalysis was reported by Song et al [20], using a lattice-matched RuO₂-CeO₂ heterostructure. The intimate RuO₂-CeO₂ interface contains Ru-O-Ce bridge motifs that establish interfacial charge transfer and local lattice distortion, thereby generating two spatially differentiated Ru-site populations. As illustrated in Fig. 5(f), Ru sites located at the RuO₂-CeO₂ interface preferentially follow a dual-site oxide-path mechanism (OPM), whereas Ru sites located away from the interface operate through an enhanced adsorbate evolution mechanism (AEM-plus). At the interfacial Ru sites, the Ru-O-Ce bridge provides strong electronic coupling and differentiated *OH adsorption behavior, enabling adjacent oxygenated intermediates to undergo direct O-O coupling through the OPM pathway without forming the energetically demanding *OOH intermediate. In contrast, lattice matching induces tensile distortion within the non-interfacial RuO₂ domain, where adjacent oxygen atoms become more effective proton acceptors and facilitate *OOH formation through the AEM-plus pathway. Operando ATR-SEIRAS detected the simultaneous emergence of *O-O and *OOH species, while isotope-labelled DEMS excluded substantial lattice oxygen participation, supporting the coexistence of interfacial OPM and non-interfacial AEM-plus pathways. This system demonstrates that heterojunctions-enabled dual-site synergy need not rely solely on two

dissimilar metal centers directly sharing one elementary step. Instead, a functional heterointerface can spatially organize distinct yet cooperative reaction environments: interfacial sites bypass the $^*\text{OOH}$ -associated scaling limitation through direct O-O coupling, while nearby strained RuO_2 sites accelerate the conventional AEM sequence. Through this site-specialized pathway differentiation, the RuO_2 - CeO_2 heterostructure achieved an overpotential of 180 mV at 10 mA cm^{-2} and stable acidic OER operation for over 1000 h. This work highlights that heterointerface can enhance acidic OER not only by tuning individual site energetics, but also by orchestrating multiple complementary reaction pathways across spatially differentiated catalytic sites.

A complementary mechanistic example is provided by Pei et al [57], who demonstrated that RuO_x -cluster/ CeO_x interfaces can act as spatially and electronically coupled dual-site ensembles for acidic OER. By incorporating Ru species into CeO_x as single atoms, sub-nanoclusters, or RuO_x domains, they constructed distinct Ce-Ce-Ce-Ru, Ce-Ru-Ru-Ce, and Ce-Ce-Ru-Ru interfacial motifs. The sub-nanocluster $\text{RuO}_x/\text{CeO}_x$ interface exhibited the most favorable configuration, in which Ru-O-Ce orbital hybridization enhanced the π -orbital contribution and promoted electron delocalization between interfacial metal sites and adsorbed $^*\text{O}$ intermediates. This electronic delocalization increased $^*\text{O}$ coverage and weakened $^*\text{O}$ - $^*\text{O}$ repulsion, thereby facilitating direct O-O coupling through the OPM pathway. In situ ATR-SEIRAS identified bridge-type O-O intermediates at dual active sites, and isotope-labeled DEMS further verified that O_2 was generated through direct coupling of two surface-adsorbed oxygen intermediates. DFT calculations showed that the RuSnCO_x - CeO_x interface shortened the O^*-O^* distance to 2.89 Å and reduced the OPM energy barrier to approximately 1.371 eV. In addition, the delocalized interfacial electronic structure suppressed Ru overoxidation and accelerated water dissociation and $^*\text{OH}/^*\text{O}$ replenishment. This study highlights that effective dual-site cooperation at heterointerfaces requires not only neighboring active centers, but also suitable intersite distance, coordination geometry, and orbital communication. Such a principle is highly relevant for acidic OER heterostructures, where cooperative O-O coupling can bypass the $^*\text{OOH}$ -related scaling limitation while maintaining the stability of Ru-based active sites.

Collectively, Ru-based interfacial architectures demonstrate that dual-site synergy can spatially reorganize OER pathways and relieve the oxidative burden otherwise concentrated on

isolated Ru-O motifs. In MnO₂-templated Ru arrays, geometric confinement shortens the Ru-Ru distance and enables direct coupling of adjacent *O species through an OPM pathway. In RuO₂-CeO₂ heterostructures, interfacial Ru sites preferentially promote OPM, whereas strained RuO₂ regions away from the interface facilitate an AEM-type pathway, illustrating the coexistence of spatially differentiated reaction channels. Similarly, Ru/RuO₂ Schottky junctions generate electronically coupled Ru-O ensembles that favor intersite O-O coupling while suppressing competing Ru overoxidation pathways. The central advantage of these dual-site configurations is therefore not simply an increased density of active centers, but the ability to bypass, or reduce the energetic penalty associated with, the *OOH intermediate and to distribute O-O bond formation across adjacent sites. Such pathway reorganization lowers the kinetic and oxidative stress imposed on individual Ru centers, thereby helping to retain high OER activity while mitigating lattice destabilization and Ru dissolution. A critical challenge, however, is that auxiliary oxides such as MoO₃ and CeO₂, despite serving as oxygen-redox buffers or pathway-regulating domains, may themselves undergo dissolution, redox-driven reconstruction, or loss of interfacial integrity under prolonged acidic anodic operation. Their initial catalytic benefit should therefore not be equated with long-term interfacial stability. Future dual-site and oxygen-buffering heterointerface should incorporate acid-resistant buffer-phase design, including lattice anchoring, compositionally stabilized oxides, strongly bonded or coherent interfaces, and transport-accessible protective architectures. Equally important, the persistence of the buffer phase and its interfacial function should be verified through quantitative dissolution analysis and post-/operando structural characterization under PEMWE relevant conditions.

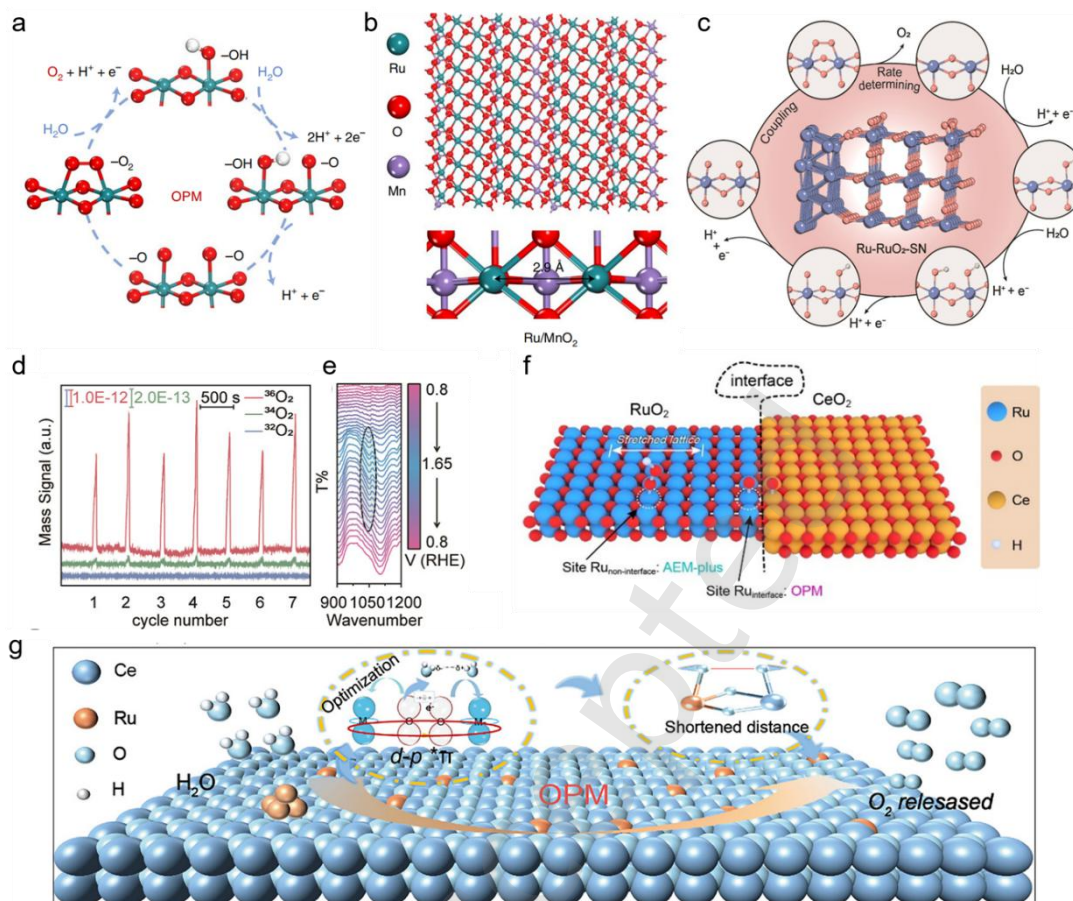


Figure 5 Dual-Site Cooperative Interfacial Functional Reactors. (a), Schematic illustration of the oxide-pair mechanism (OPM) involving direct coupling of adjacent oxygen species. (b), Atomic model of the Ru/MnO₂ heterointerface and the optimized Ru-Mn intersite distance for O-O coupling. (c), Proposed OPM pathway on Ru-RuO₂-SN, where neighboring Ru-O motifs participate in the rate-determining O₂ formation step. (d), Isotopic labelling mass spectrometry and potential-dependent vibrational spectra used to identify lattice-oxygen participation during OER. (e), Schematic of the RuO₂/CeO₂ interface, showing OPM at interfacial Ru sites and AEM-plus at non-interfacial Ru sites. (f), Proposed Ce-Ru dual-site pathway, in which optimized orbital coupling and shortened intersite distance promote OPM-type O₂ evolution. (g), Schematic illustration of Ce-mediated regulation of the OPM pathway, where optimized *d-p* orbital interaction and shortened intersite distance facilitate O-O coupling and O₂ evolution.

3.5 Balanced Lattice Oxygen Redox: Retaining Reactivity While Preventing Irreversible Oxygen Loss

Lattice oxygen redox is intrinsically double-edged in acidic OER. Moderate oxygen-lattice activity can facilitate oxygenated-intermediate conversion and O-O bond formation, whereas excessive lattice oxygen oxidation induces irreversible oxygen loss, oxygen-vacancy accumulation, metal overoxidation, and ultimately catalyst dissolution. Therefore, the objective is not to completely eliminate lattice oxygen reactivity, but to confine it within a reversible and structurally

tolerable regime that preserves the integrity of the active metal–oxygen framework [16].

For lattice-oxygen redox, isotope-labeled DEMS provides the most direct evidence for lattice-oxygen contribution to evolved O_2 , while operando Raman or XAS can track the accompanying structural and coordination evolution under OER conditions. By contrast, DFT-derived vacancy-formation energetics, Ru-O covalency, and LOM/AEM energy landscapes, primarily provide microscopic explanations for the experimentally observed changes in lattice-oxygen activity.

A useful mechanistic benchmark was provided by Ping et al. through interstitial Si-stabilized RuO_2 . Although this material is not a heterojunction, it clearly demonstrates how lattice oxygen can be stabilized by local structural anchoring. As illustrated in Fig. 6(a), interstitial Si forms robust Si-O linkages within the RuO_2 lattice, weakens Ru-O covalency, and suppresses the lattice oxygen mechanism that otherwise generates oxygen vacancies and soluble RuO_4 species. The catalyst consequently shifts toward an AEM-dominated pathway while retaining favorable *OOH conversion kinetics. Isotope-labelled DEMS showed that lattice oxygen participation was suppressed by approximately 95% relative to commercial RuO_2 , accompanied by markedly reduced Ru dissolution and stable operation for 800 h in acidic electrolyte. This result establishes a central principle for functional heterojunction design: catalytic stability can be achieved by regulating, rather than simply maximizing or eliminating, lattice oxygen redox [5], thereby preserving sufficient oxygen reactivity for fast OER while preventing irreversible oxygen loss from the active framework.

Building on this principle, heterointerface engineering offers an alternative route to stabilize lattice oxygen through localized interfacial coupling. Guan et al.[58]. constructed atomically coupled W-O-Ru interfacial units on RuO_2 , where the incorporation of W_1O_3 -like motifs increased the formation energies of both Ru and O vacancies, while the O $2p$ band center shifted to lower energy, indicating suppressed lattice-oxygen reactivity and enhanced resistance to vacancy formation. In situ Raman and ^{18}O isotope-labeled DEMS further showed that the W-O-Ru interface suppresses lattice distortion and lattice-oxygen participation, while ATR-SEIRAS supports a shift toward a more reversible AEM-dominated pathway (Fig. 6(b)-6(d)). This stabilization was accompanied by markedly reduced Ru dissolution and preservation of the Ru-O

coordination framework under OER conditions. These results demonstrate that the W-O-Ru heterointerface suppresses lattice-oxygen activation through the coordinated regulation of vacancy thermodynamics, Ru-O electronic structure, and interfacial strain, thereby mitigating vacancy accumulation, Ru overoxidation, and dissolution while preserving favorable OER kinetics.

In another representative example, Duan et al[59]. reported a lattice-matched $\text{RuO}_2\text{-TiO}_x$ heterointerface (Fig. 6(e)-6(g)). Interfacial tensile strain and charge redistribution elongate the Ru-O bonds and reduce Ru 4d-O 2p hybridization, thereby weakening Ru-O covalency and suppressing lattice-oxygen participation. ^{18}O isotope-labeled DEMS confirms a markedly reduced contribution of lattice oxygen to O_2 evolution, while operando spectroscopy reveals suppressed Ru overoxidation and local structural reconstruction. Consequently, the heterointerface stabilizes the Ru-O framework and limits irreversible oxygen loss and Ru dissolution, demonstrating how strain-mediated interfacial coupling can effectively suppress excessive lattice-oxygen activation during acidic OER.

Overall, these examples highlight stabilized lattice-oxygen as a critical function of functional heterointerfaces. By regulating local coordination, Ru-O covalency, vacancy formation, and interfacial strain, heterointerfaces can convert destructive lattice-oxygen oxidation into a more controllable and reversible oxygen-redox process. Such regulation does not simply suppress lattice-oxygen participation, but balances lattice-oxygen activity with framework stability, thereby retaining the kinetic advantages of oxygen redox while preventing lattice oxygen loss, Ru overoxidation, and metal dissolution. This balance is essential for designing RuO_2 -based acidic OER heterojunctions that simultaneously deliver high activity and durable operation.

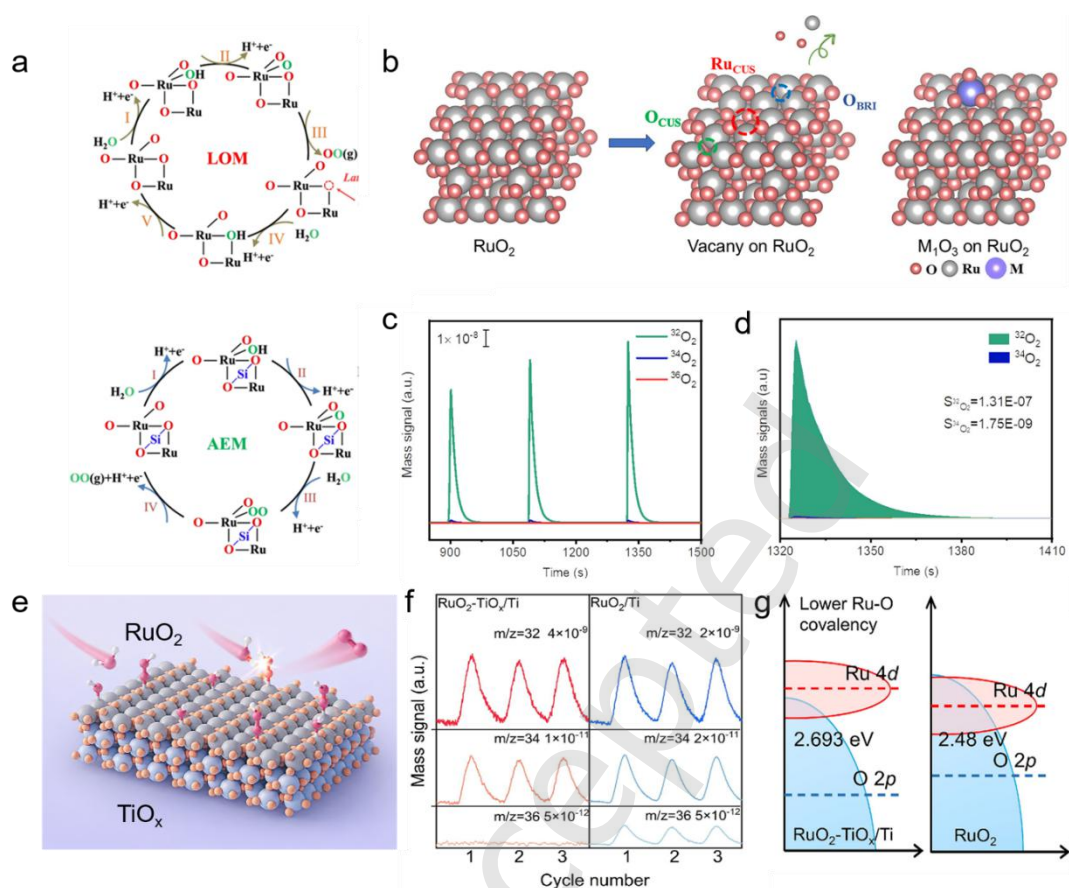


Figure 6 Regulation of lattice-oxygen redox by functional heterointerfaces in RuO₂-based acidic OER catalysts. (a), Schematic comparison of LOM and AEM pathways. (b), Vacancy formation on RuO₂ and interfacial stabilization by M₁O₃. (c) and (d), Isotope-labeled DEMS analysis of lattice-oxygen participation during OER. (e), Schematic representation of a lattice-matched RuO₂-TiO_x heterointerface. (f), Isotope-labeled mass spectrometry comparing lattice-oxygen participation in RuO₂-TiO_x/Ti and RuO₂/Ti. (g), Electronic-structure modulation of the RuO₂-TiO_x heterointerface, showing reduced Ru-O covalency. The heterointerface suppresses excessive lattice-oxygen activation through coordinated structural and electronic regulation, thereby mitigating lattice degradation under acidic OER conditions.

Having discussed the five major interfacial functions mainly from Ru-based heterojunctions catalysts, it is necessary to compare whether these mechanistic advantages can be reflected in practical stability metrics. Table 1 summarizes representative acidic OER heterojunctions catalysts, including Ru-centered systems and selected non-Ru analogues, with emphasis on electrolyte, catalyst composition, catalyst loading, current density, stability duration, testing configuration, operating temperature, degradation metrics. This comparison shows that the concept of functional interfacial reactors is not limited to a single Ru-based material family, but can be extended to low-noble-metal and non-noble-metal OER systems through interface-regulated stabilization.

Table 1 Stability comparison of representative heterojunctions catalysts for acidic OER.

Category	Catalysts	Electrolyte	Activity(η_{10})	Stability(h)	Current density (mA cm ⁻²)	loading (mg cm ⁻²)	Temperature	Degradation metric	System	Ref
Ru-based	RuO ₂ /LiCoO ₂	0.5 M H ₂ SO ₄	150 ±2 mV	2300	10	NR	NR	NR	Two electrode	[17]
		Water		2000	1000	4	80 °C	NR	PEMWE	
	Ru/RuO ₂	0.5 M H ₂ SO ₄	182 mV	270	100	5	NR	0.43 mg after 96 h	Two electrode	[21]
		0.5 M H ₂ SO ₄		1100	100	6	NR	22.8 μV h ⁻¹ ; Ru dissolution: 0.58 ppb; S-number: 6.7 × 10 ⁶	Two electrode	
	Ru-RuO ₂ -SN	Water	165 mV	1100	100	2	60 °C	56.4 μV h ⁻¹	PEMWE	[56]
		Water		100	500	2	60 °C	NR	PEMWE	
	ZrO ₂ -5.5RuO ₂	0.5 M H ₂ SO ₄	137 mV	655 h	10	5	NR	NR	Two electrode	[50]
	RuO ₂ /MoO ₃	0.5 M H ₂ SO ₄	167 mV	300	10	4	NR	16 ppb (20 h)	Two electrode	[19]
	ZrO ₂ -RuO ₂	0.5 M H ₂ SO ₄	170 mV	1800	10	0.51	NR	0.014 mV h ⁻¹	Two electrode	[18]
		Water		100	1000	2.5	80 °C	0.5 mV h ⁻¹	PEMWE	
	RuO ₂ /CeO ₂ @C	0.5 M H ₂ SO ₄	170 mV	100	10	NR	NR	3 ppm	Two electrode	[60]

RuO ₂ -CeO ₂	0.5 M H ₂ SO ₄	180mV	1000	10	NR	NR	NR	Two electrode	[20]
RuO ₂ /MnO ₂ -γ	0.5 M H ₂ SO ₄	220mV	80	10	5	NR	NR	Two electrode	[61]
RuO ₂ /WO ₃ IOs	0.5 M H ₂ SO ₄	180 mV	100	10	NR	NR	Ru loss ≈ 2% after 10,000 CV cycles	Two electrode	[62]
Ru/RuO ₂ /NC	0.5 M H ₂ SO ₄	211 mV	100	10	5	NR	Ru loss ≈ 0.1 ppm 4,000 CV cycles	Two electrode	[63]
Ru-RuO ₂ /Mn ₃ O ₄ /C P	0.5 M H ₂ SO ₄	182 mV	400	10	5	Room temperature	NR	Two electrode	[64]
MnO ₂ /RuO ₂	0.5 M H ₂ SO ₄	181 mV	140	10	5	NR	0.85% Loss Ru after 1000 CVs	Two electrode	[65]
Mn-RuO ₂ /CeO ₂	0.1 M HClO ₄	227 mV	300	10	NR	NR	Δη ₁₀ ≈ 5 mV after 5000 CV cycles	Two electrode	[66]
	Water		100	100	NR	80 °C	Negligible voltage increases over 100 h	PEMWE	
Ru/RuO _{2-x}	0.5 M H ₂ SO ₄	164 mV	200	100	0.5	NR	NR	Two electrode	[67]
	Water		100	500	5	NR	NR	PEMWE	
RuO ₂ /V ₂ O ₅	0.5 M H ₂ SO ₄	216 mV	100	10	NR	NR	Δη ₁₀ ≈ 5 mV after 1000 CV cycles	Two electrode	[68]
	0.5 M H ₂ SO ₄		200	10	5	NR	NR	Two electrode	
RuO ₂ /TiO ₂		152 mV							[69]
	Water		35	1000	2.5	80 °C	10.8 mV h ⁻¹	PEMWE	

Non-Ru	Pr ₂ O ₃ /RuO ₂	0.5 M H ₂ SO ₄	162 mV	100	10	NR	NR	NR	Two electrode	[70]
	IrO _x /CeO ₂	0.5 M H ₂ SO ₄	220 mV	300	10	0.56	NR	NR	Two electrode	[71]
	IrO _x /TiN	0.1 M HClO ₄	293 mV	250	10	3.92	NR	0.116 mV h ⁻¹	Two electrode	[22]
	Ir/MnO _x	0.1 M HClO ₄	200 mV	200	10	2	NR	NR	Two electrode	[72]
		Water		300	1000	0.2	80 °C	0.02 mV h ⁻¹	PEMWE	
	Ce/IrO ₂	0.5 M H ₂ SO ₄	194 mV	90	10	2	NR	NR	Two electrode	[39]
		Water		400	900		80 °C	NR	PEMWE	
	Co ₃ O ₄ /MnO ₂	0.5 M H ₂ SO ₄	319 mV	100	200	5	NR	NR	Two electrode	[73]
	IrO _x /t-ZrO ₂	0.1 M HClO ₄	287.5 mV	1000	10	2.5	NR	0.001 µg h ⁻¹	Two electrode	[23]
		Water		1600	1000	0.5	80 °C	0.00625 mV h ⁻¹	PEMWE	

3.6 Toward Rational Design of RuO₂-Based Functional Heterointerfaces

To move beyond a case-by-case summary of representative heterojunction systems, we have introduced a design roadmap (Fig 7) that connects interfacial structure, dominant interfacial function, mechanistic descriptors, quantitative stability indicators, and PEMWE-relevant performance metrics. Within this framework, structural features such as interfacial bonding, lattice strain, coupled domains, adjacent active sites, and local coordination environments are related to the five dominant interfacial functions discussed in this Review. Each function is further associated with experimentally accessible or theoretically supported descriptors, which can then be considered together with catalyst degradation metrics and device-level PEMWE parameters. The roadmap is also presented in a bidirectional manner, allowing both forward design from atomic-scale interfacial engineering toward device performance and reverse consideration from PEMWE requirements toward suitable stability targets, functions, and structural motifs.

The framework further highlights possible descriptors for evaluating each interfacial function. Electronic coupling may be examined through Ru valence, interfacial charge redistribution, and Ru–O covalency; oxygen spillover and redox buffering through oxygen migration and vacancy-formation energetics; interfacial water/proton regulation through hydrogen-bond structure, proton-transfer barriers, and kinetic isotope effects; dual-site cooperation through site distance, intermediate distribution, and O–O coupling; and lattice-oxygen involvement through isotope labeling and oxygen-vacancy energetics. These descriptors can be further linked with stability indicators such as Ru dissolution, S-number, structural reconstruction, and voltage degradation, and finally considered alongside PEMWE-relevant parameters including noble-metal loading, current density, cell voltage, temperature, and long-term durability. This framework may therefore provide a useful route toward more function-oriented and application-relevant heterointerface design.

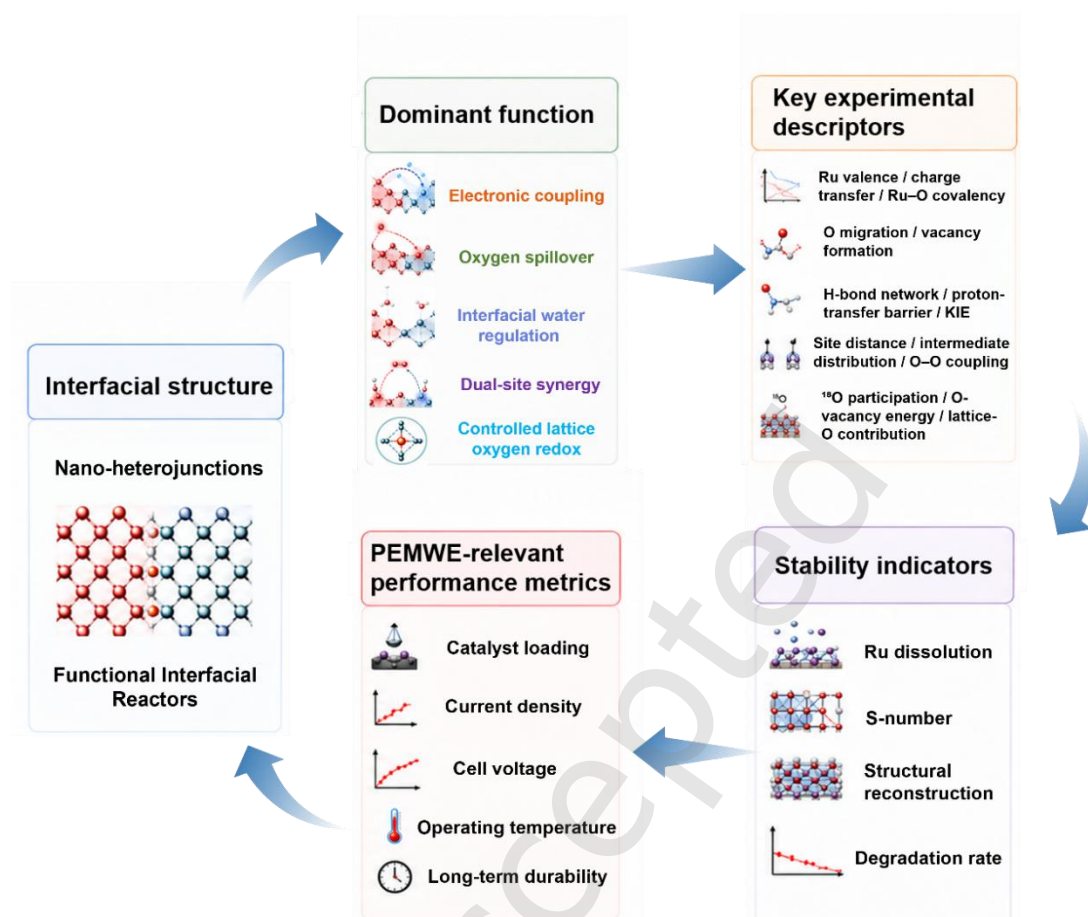


Figure 7 Design roadmap linking interfacial structure, dominant function, and mechanistic descriptors for RuO₂-based functional heterointerfaces toward acidic OER and PEM water electrolysis. Interfacial structural motifs are linked to five dominant functions, including electronic coupling, oxygen spillover, interfacial water/proton regulation, dual-site cooperation, and controlled lattice-oxygen redox. Representative mechanistic descriptors are further correlated with quantitative stability indicators and PEMWE-relevant performance metrics. The closed-loop framework illustrates both forward design from atomic-scale interfacial engineering to device-level performance and reverse design from PEMWE requirements to targeted interfacial structures.

4. Conclusion and Outlook

Toward Optimized Interfacial Functions in RuO₂ Catalysts for Acidic OER

RuO₂-based heterojunctions should be understood as functional interfacial reactors rather than simple multicomponent composites. Through electronic coupling, oxygen spillover and redox buffering, interfacial water/proton regulation, dual-site cooperation, and balanced lattice-oxygen redox, these interfaces simultaneously optimize OER kinetics and redistribute localized oxidative stress. Their fundamental value therefore lies in maintaining Ru sites in a highly active yet dynamically stable state, thereby alleviating the intrinsic activity-stability trade-off of Ru-based

acidic OER catalysts.

Based on these insights, we propose a unified Ru-centered interfacial reactivity–corrosion buffering strategy. The key is to construct chemically coupled secondary domains adjacent to RuO₂ that regulate charge transfer, oxygen-species migration, proton transport, and cooperative O-O bond formation, thereby directing Ru-centered redox processes toward productive OER turnover rather than Ru overoxidation, irreversible lattice-oxygen loss, and dissolution. Future design should focus on atomically defined Ru-O-M bridges, coherent oxide/oxide interfaces, metal/oxide junctions, and dynamically stable core-shell or supported RuO₂ architectures.

From the perspective of practical translation, evaluating functional heterointerfaces under more standardized and PEMWE-relevant operating conditions would facilitate a more meaningful comparison of their practical performance. A comprehensive assessment of catalyst stability may consider catalyst and noble-metal loading, operating current density, temperature, and cell configuration. Future studies may also benefit from reporting catalyst and Ru/Ir loadings and examining promising interfaces in membrane-electrode assemblies under A cm⁻²-level current densities and elevated temperatures. Long-term stability measurements could be complemented by quantitative degradation metrics, including Ru/Ir and secondary-component dissolution, S-number, structural reconstruction, and voltage degradation rate. Operando characterization may further help clarify whether the designed interface remains structurally and functionally intact under working conditions. Additional attention to long-term MEA operation and scalable synthesis would also be valuable. Establishing such condition-resolved and mechanism-informed evaluation protocols could help bridge atomic-scale interfacial regulation with durable device-level PEMWE performance.

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