



# Polyoxometalates for Oxygen Evolution Electrocatalysis: From Molecular Active Motifs to Interfacial Regulators and Practical Electrolyzers

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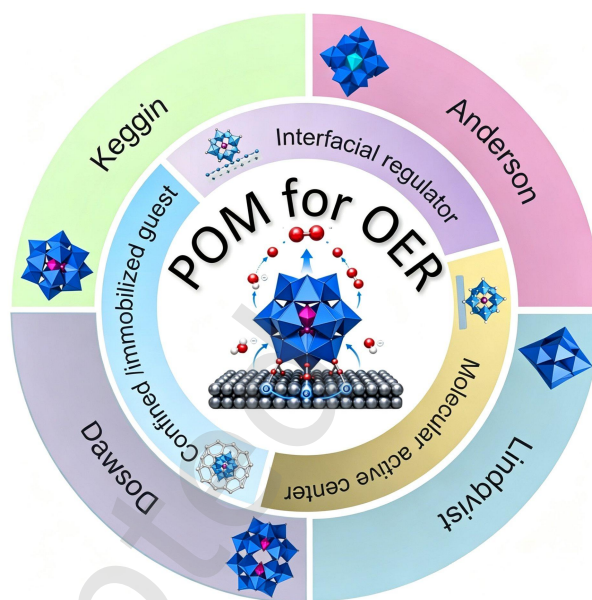
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Evolving roles of polyoxometalates in OER electrocatalysis are illustrated as molecular active centers, confined guests, interfacial regulators and stabilization modules. Correlations between POM structures, interfacial interactions, active- phase reconstruction and device performance are established to deliver design principles for efficient and durable water electrolysis under practical conditions.



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## ABSTRACT

The oxygen evolution reaction (OER) remains the principal kinetic bottleneck in water electrolysis because its multistep proton-electron transfer is coupled with dynamic structural evolution under anodic bias. Beyond the intrinsic four-electron barrier, practical operation is constrained by metal dissolution, phase reconstruction, interfacial instability, and catalyst-layer degradation at high current densities. Polyoxometalates (POMs), featuring structurally programmable metal-oxygen clusters, reversible multielectron redox chemistry, oxygen-rich surfaces, and versatile coordination sites, offer a distinctive platform for addressing these challenges. This review analyzes the evolution of POMs from discrete molecular catalysts to confined guests, interfacial electronic regulators, reconstruction-directing units, and stabilization modules in OER electrocatalysts. Particular emphasis is placed on how POM structure and interfacial bonding modify metal valence, orbital hybridization, charge transfer, d-band characteristics, and intermediate adsorption energetics, and how these effects govern activity and durability. The discussion further extends to high-current-density electrolysis, saline media, membrane-electrode assemblies, and device-level validation. Key unresolved issues include identification of the true active phase, definition of pH-potential-time stability windows, conductivity and loading limitations, and POM leaching. A six-pathway framework is finally proposed to connect representative POM states with the elementary OER steps and guide mechanism-informed catalyst design. This framework highlights priorities for scalable, durable, and predictable electrolyzer implementation.

## KEYWORDS

Polyoxometalates; Oxygen evolution reaction; Interfacial electronic regulation; Active-phase reconstruction; High-current-density electrolysis

## 1 Introduction

### 1.1 The Core Bottleneck of OER

Water electrolysis is considered a key technological pathway for linking renewable electricity with green hydrogen[1-6]. The oxygen evolution reaction (OER) at the anode has always been a critical bottleneck determining overall energy efficiency and device lifespan, due to its four-electron-coupled proton transfer

mechanism, numerous reaction intermediates, and complex potential landscape. Compared to hydrogen evolution at the cathode, OER requires a higher driving potential and is often accompanied by significant ohmic polarization, interfacial concentration polarization, and dynamic evolution of the active phase at industrially relevant current densities[7]. For commercial alkaline electrolytic systems, the real challenge lies not merely in achieving lower overpotentials at 10 mA cm<sup>-2</sup>, but in simultaneously achieving high activity, low decay, and structural durability at current densities of hundreds of

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milliamperes or even amperes[8, 9].

In recent years, nickel-iron layered double hydroxide (NiFe-LDH), CoFe oxyhydroxide, and their derivatives have shown great promise as non-precious metal anode catalysts[10-12]. However, at high potentials, these systems still commonly face issues such as the dissolution of active metal sites, local phase separation, continuous surface restructuring, and mechanical degradation of the catalytic layer. Particularly under conditions of long-term operation, complex electrolytes, and device integration, the active phase often undergoes a continuous transition from surface rearrangement to deep-layer structural evolution, thereby blurring the boundaries between the “initial pre-catalyst-true active phase-deactivated phase”. Consequently, the development of functional units capable of providing efficient electron transport while simultaneously stabilizing key metal sites and regulating the reconstruction pathways has become a central scientific challenge in the design of OER catalytic systems[8, 13, 14].

It is against this backdrop that Polyoxometalates (POMs) has come to the forefront of OER research. Unlike traditional metal oxide or simple salt precursors, POM possesses both a tunable cluster structure and the ability to undergo reversible multi-electron transfer[15-17]. It possesses an oxygen-rich surface and multi-site coordination characteristics, and is capable of forming stable and tunable composite interfaces with metal-organic frameworks (MOFs), LDHs, carbon materials, and metal (oxy)hydroxides[18]. These characteristics mean that POM can not only participate in reactions as an active center at the molecular level, but also serve as an electron reservoir, an interface regulator, a restructuring inducer, and a stabilizing module within broader composite systems.

Recent studies further indicate that POM-related OER research should be considered within the broader transition from conventional alkaline water splitting toward complex-media, desalination-coupled, and device-level electrolysis. A chloride-repelling NiFeP/amorphous NiFe-LDH electrocatalyst demonstrated that efficient alkaline seawater electrolysis requires the simultaneous regulation of lattice-oxygen-mediated activity, chloride resistance, and device-level durability, delivering cell voltages of 2.03 and 2.10 V at 500 mA cm<sup>-2</sup> in 1 M KOH and alkaline seawater, respectively. A recent review further summarized the major challenges associated with seawater electrolysis, including competing chlorine chemistry, impurity-induced active-site blocking, catalyst corrosion, ion-transport limitations, and electrolyzer configuration[19, 20]. From a water-sustainability perspective, advances in desalination technologies also suggest that hydrogen production should be evaluated together with membrane processes,

brine management, energy consumption, and sustainable freshwater supply[21]. These studies provide an application-oriented basis for assessing whether POM-based interfacial regulators can maintain OER selectivity, structural integrity, and long-term stability under practical saline-water and desalination-related conditions.

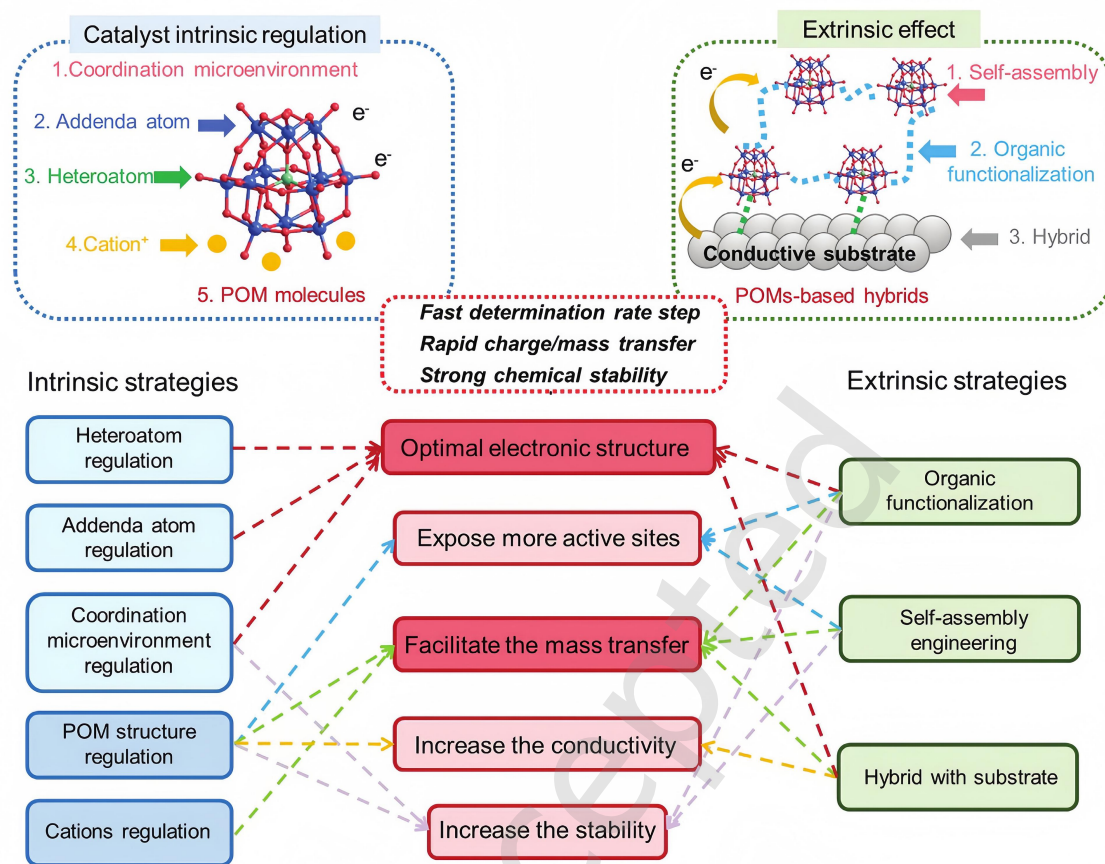
## 1.2 The Unique Chemical Advantages of POM

Compared to traditional metal oxide, metal salt precursors, or single transition metal complexes, the appeal of POM in OER catalytic systems stems not merely from its considerable catalytic activity, but from its combination of structural designability, electronic tunability, surface coordination diversity, and excellent heteroassembly capabilities. For this reason, POM can not only function as a molecular-scale active unit but can also be developed into an electron-regulating unit, an interface-stabilizing unit, and a restructuring-inducing unit within composite electrodes, thereby demonstrating unique and systematic advantages in OER catalyst design[22, 23].

First, POM possesses a tunable metal-oxygen cluster framework. Its discrete inorganic clusters, composed of high-valent early-transition metals and oxygen atoms, allow for multi-level structural regulation by altering the heteroatom center, the type of metal added, the number of vacancy sites, and the substitution pattern of the transition metals. Consequently, POM is more suitable as a model platform for studying the structure-activity relationship in OER than amorphous oxides, whose compositions are often ambiguous. Second, POM possesses significant multi-electron redox capabilities, enabling rapid and reversible transitions between various oxidation states and mediating proton-coupled electron transfer processes. This makes it naturally suited to the four-electron reaction mechanism of OER[24].

Furthermore, POM possesses an oxygen-rich surface and the ability to form multi-site coordination. The abundant terminal oxygen atoms, bridging oxygen atoms, and various types of M-O-M bonding sites distributed across its surface not only facilitate hydrogen bonding, substrate molecule accumulation, and intermediate stabilization, but also create conditions for directed coordination with active sites such as Fe, Co, and Ni, as well as for interfacial electron coupling[25, 26].

Finally, POM is easily integrated into composite interfaces with MOFs[27], LDHs, carbon materials, and metal (oxy)hydroxides. Whether through pore confinement, interlayer insertion, surface grafting, or site-directed docking, POM can be effectively incorporated into continuous charge and mass transport networks, thereby truly translating the structural advantages at the molecular scale into activity, stability, and sustainable performance in actual electrodes.



**Figure 1** Conceptual framework for POM-based OER electrocatalysts, illustrating how molecular structural design, interfacial coupling, active-state reconstruction, and device-oriented stabilization are connected across different length scales. Reproduced with permission from Ref. [28], under the CC BY-NC-ND 4.0 license.

Overall, the regulation of POM-based OER catalysts should be understood as the combined result of intrinsic cluster design and extrinsic interfacial engineering. Intrinsic regulation involves the heteroatom center, addenda metals, vacancy state, transition-metal substitution, counter-cations, and local coordination environment of the cluster. Extrinsic regulation involves organic functionalization, self-assembly, interlayer intercalation, surface anchoring, conductive-substrate coupling, and heterojunction construction. These two levels are not independent: the molecular structure determines the available redox and coordination sites, whereas the interface determines whether these sites can be translated into charge transport, controlled reconstruction, and long-term stability under OER conditions (Fig. 1).

At the current stage of POM-OER research, the transition from molecular active centers to interfacial regulators should also be understood as a shift in the descriptors used to evaluate catalytic performance. In transition-metal-containing POM composites, the catalytic response is often governed by how the POM unit perturbs adjacent Ni, Fe, or Co centers through interfacial coordination and charge transfer. Such perturbations may alter the metal valence distribution, d-band position and

occupancy, metal-oxygen covalency, local charge density, and frontier-orbital coupling, thereby changing the interaction between active sites and oxygen-containing intermediates. For example, electron withdrawal from neighboring metal centers can facilitate the formation of high-valent NiOOH/CoOOH species and accelerate surface deprotonation, whereas excessive oxidation may strengthen  $^*O$  adsorption and impede subsequent  $^*OOH$  formation or  $O_2$  release. Conversely, electron donation or charge buffering by redox-active POM clusters can stabilize highly oxidized intermediates, reduce local charge accumulation, and maintain reversible redox cycling under sustained anodic polarization. These electronic effects are ultimately reflected in measurable material properties, including the onset potential for surface reconstruction, overpotential, Tafel slope, charge-transfer resistance, turnover frequency, and stability at high current density. In addition, stronger M-O-POM interfacial bonding and enhanced metal-oxygen covalency may suppress metal dissolution and preserve electronically active interfaces during long-term electrolysis. Therefore, the most meaningful structure-performance relationship is not a simple comparison of POM skeletons, but a continuous correlation of POM structure and interfacial bonding  $\rightarrow$  electronic-state perturbation  $\rightarrow$  intermediate adsorption

and reconstruction kinetics  $\rightarrow$  catalytic activity and durability. Quantitative descriptors such as XPS/XANES valence shifts, Bader charge, projected density of states, d-band parameters, and  $\Delta G$  values of  $^*OH$ ,  $^*O$ , and  $^*OOH$  should therefore be correlated with electrochemical metrics to establish a more convincing mechanistic interpretation[29, 30].

Existing reviews of POM-based OER catalysts have generally treated cluster structure, synthesis, and catalytic performance as separate topics, leaving the evolution of POMs from molecular species to interfacial regulators and device-level stabilizers insufficiently resolved[31-33]. This review therefore considers POMs as functional units whose catalytic roles are governed by cluster topology, immobilization mode, reconstruction behavior, and operating conditions[31, 32].

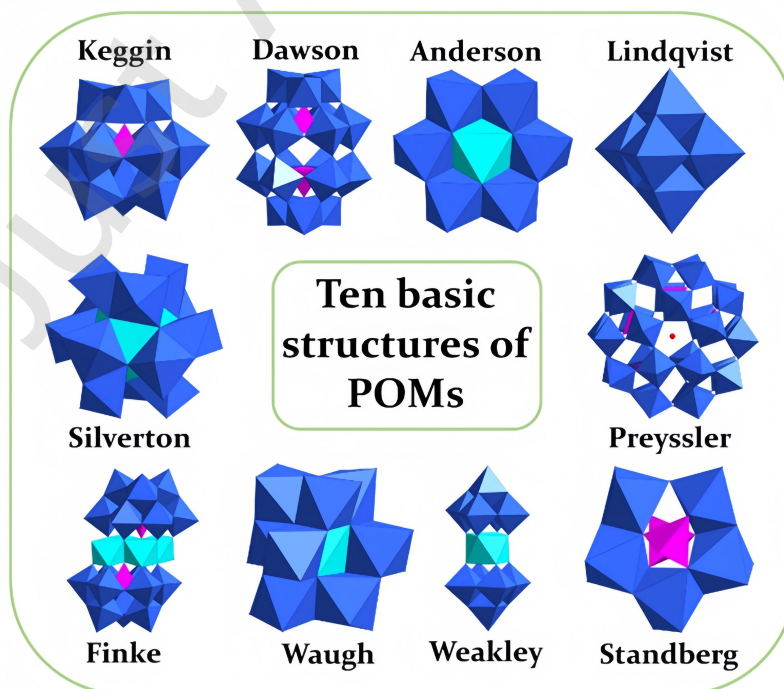
A multiscale framework linking POM molecular structure, interfacial coupling, active-phase reconstruction, and electrolyzer implementation is established[34, 35]. Within this framework, Keggin, Dawson, lacunary, Anderson, Lindqvist, and transition-metal-substituted POMs are compared in terms of proton-electron transfer, interfacial charge regulation, intermediate adsorption, oxyhydroxide formation, metal-leaching suppression, and compatibility with membrane-electrode operation[34-36]. Six POM-mediated OER pathways are further correlated with  $^*OH$ ,  $^*O$ , and  $^*OOH$  formation and  $O_2$  evolution[34]. The analysis emphasizes three criteria: matching POM stability windows with electrolyte and potential conditions; ensuring robust immobilization under

high-current-density or saline operation; and optimizing POM loading together with conductivity, mass transport, ionomer compatibility, and electrode adhesion[36, 37].

## 2 The Structural Foundation and Operational Models of POM for OER

### 2.1 Structural Types of POM and Related Features of OER

From an OER perspective, the structural classification of POMs is not merely a matter of nomenclature, because cluster topology directly affects electronic structure, coordination reactivity, interfacial assembly, and catalytic function. Representative architectures include Keggin[38], Dawson[39], Anderson[40], Silverton[41], Lindqvist[42] and Waugh[43], as summarized in Fig. 2. Among them, Keggin-type POMs are frequently used in OER-related systems because of their robust and well-defined frameworks, reversible multielectron redox behavior, and versatile coordination properties[28, 44]. These features facilitate their incorporation into LDHs, MOFs, conductive supports, and metal (oxy)hydroxides as redox-active units, interfacial regulators, or structural stabilizers. Nevertheless, their actual catalytic role depends on immobilization, interfacial coupling, reconstruction behavior, and operating conditions [45]. Table 1 summarizes the classification criteria, general formulas, and OER-relevant structural features of representative POM categories, providing a basis for linking cluster topology with potential catalytic functions.



**Figure 2** Classical POMs structures. Reprinted with permission from Ref. [46], © 2024 Elsevier B.V.

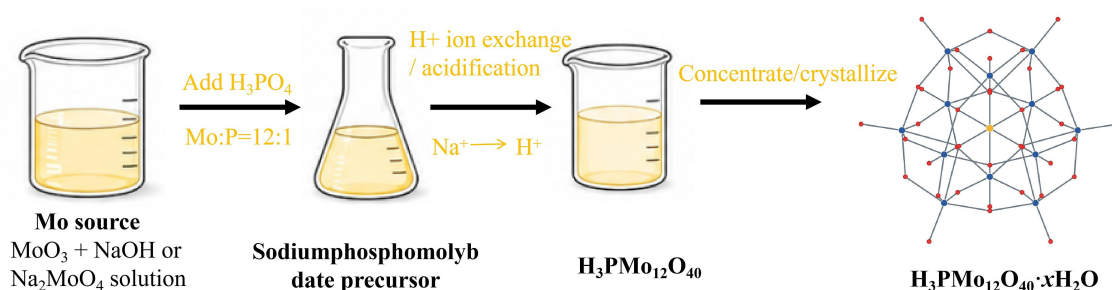
**Table 1** Classification criteria, general formulas, and distinguishing structural features of representative POM categories.

| POM category                     | Main classification criterion                                                        | Typical/general formula                                                         | Structural features relevant to OER                                                                                             | Ref.     |
|----------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------|----------|
| Keggin                           | Saturated heteropolyanion with one central heteroatom and twelve addenda atoms       | $[XM_{12}O_{40}]^{n-}$ ; e.g., $[PMo_{12}O_{40}]^{3-}$ , $[PW_{12}O_{40}]^{3-}$ | Stable, reproducible framework; suitable for intercalation, confinement, and interface anchoring                                | [47, 48] |
| Dawson                           | Two fused lacunary/Keggin-derived fragments with expanded topology                   | $[X_2M_{18}O_{62}]^{n-}$ ; e.g., $[P_2W_{18}O_{62}]^{6-}$                       | Larger framework and higher functionalization freedom; favorable for multimetal coupling and heterojunction construction        | [49, 50] |
| Anderson                         | Planar or disk-like six-addenda framework around a central heteroatom                | $[XM_6O_{24}]^{n-}$ or protonated derivatives                                   | Exposed oxygen-rich surface and accessible functionalization sites; useful for anchoring and organic modification               | [51, 52] |
| Lindqvist                        | Iso-/heteropolyanion composed of six edge-sharing $MO_6$ octahedra                   | $[M_6O_{19}]^{n-}$                                                              | Compact and highly symmetric cluster; often used as a small redox-active or structure-directing unit                            | [53, 54] |
| Lacunary POM                     | Vacancy generated by removing one or more $MO_6$ units from a saturated framework    | $[XM_{11}O_{39}]^{n-}$ , $[XM_9O_{34}]^{n-}$ , etc.                             | Vacant sites provide strong metal-capturing ability; useful for metal anchoring, bridge formation, and reconstruction induction | [55, 56] |
| Transition-metal-substituted POM | Partial replacement or grafting of addenda/vacancy sites by Co, Fe, Ni, Mn, Ru, etc. | $[Tn(XM_9O_{34})_2]^{m-}$ , $[TM_xM_{12-x}O_{40}]^n$ ; etc.                     | Introduces traceable redox-active centers and clearer molecular active-site models for OER mechanism analysis                   | [57, 58] |

Note: X represents the central heteroatom (e.g., P, Si, As, or Ge), whereas M denotes the addenda metal (e.g., W, Mo, V, Nb, or Ta).

### 2.1.1 Keggin-type POM: A highly stable platform for microenvironment-sensitive ligands

Keggin-type POM is the most common and easiest-to-synthesize type of structure in OER-related research[16, 59-61]. As illustrated in Fig. 3, Keggin-type phosphomolybdic acid ( $H_3PMo_{12}O_{40} \cdot xH_2O$ ) is generally prepared through the acid-assisted assembly of molybdate species around a central phosphate unit, followed by protonation, crystallization, and purification. This classical synthetic route yields the structurally well-defined  $[PMo_{12}O_{40}]^{3-}$  cluster and highlights the synthetic reproducibility and structural robustness of the Keggin framework[62]. Their common features include a stable framework, well-defined composition, reproducible synthesis, and clear pathways for subsequent modification, making them highly suitable as foundational platforms for the further construction of MOFs, LDHs, and other host-guest systems. It should be emphasized that the core advantage of Keggin-type POMs lies primarily in their property as a “stable molecular platform,” which stems from their “electron sponge” nature. Here, “electron sponge” is used only as shorthand for reversible multielectron redox buffering by the POM framework, rather than as direct proof of interfacial charge transfer. This role should be assigned only when spectroscopic or theoretical descriptors correlate with catalytic kinetics[60, 63]. On the other hand, after intercalating Keggin-type phosphotungstic acid (PTA) into NiFe-LDH, host-guest interactions can be utilized to modulate the electronic structure of the Ni and Fe active sites, widen the interlayer spacing, and suppress metal leaching, thereby simultaneously enhancing both activity and stability under high current densities[64]. The catalyst requires only  $342 \pm 9$  mV at  $1000 \text{ mA cm}^{-2}$ , and can operate stably for 500 h. An AEMWE assembled with this catalyst requires only 1.93 V to reach  $1000 \text{ mA cm}^{-2}$  at  $60^\circ\text{C}$ . Furthermore, within the MOF@POM superstructure, POM also serves as a coupling unit in the construction of the interfacial electron transport network, leveraging the synergistic effects of multiple metals-including W, Ni, Co, and Fe-to enhance charge transport efficiency and stabilize the active phase[65]. A low overpotential of 178 mV at  $10 \text{ mA cm}^{-2}$  was achieved under alkaline conditions. It is evident that the true value of Keggin-type POMs lies in their ability to leverage the characteristics of a well-defined, localizable, intercalable, and couplable molecular platform to achieve the directed generation of active phases, interfacial electronic-state perturbation, and structural stabilization. This transforms the originally limited-activity polymetallic oxygen clusters into highly efficient and durable OER structural units.

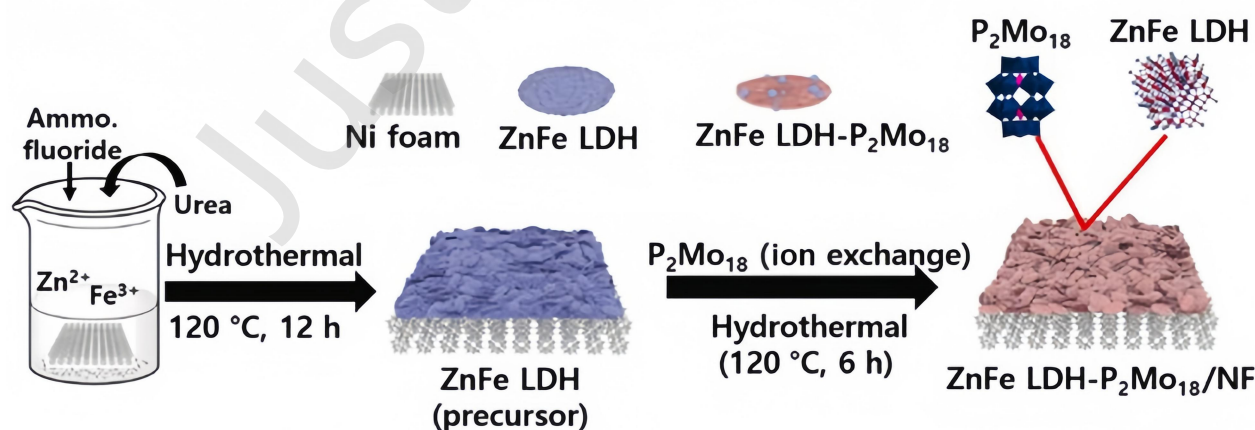


**Figure 3** The classic synthesis route for Keggin-type phosphomolybdic acid ( $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ ). Created by the authors based on Ref. [62].

### 2.1.2 Dawson-type POM: Greater design flexibility and expanded structural potential

Compared to Keggin, the significance of Wells-Dawson-type POMs in OER research lies more in their role as “functionalizable frameworks” and “scalable structural units”: their topological structure is more adaptable, offering greater scope for post-modification and multi-level regulation, making them particularly suitable for introducing new electronic regulation pathways through vacancy formation, metal substitution, and organic/inorganic assembly. Specifically, the open Dawson framework  $[\text{Si}_2\text{W}_{18}\text{O}_{66}]^{16-}$  can accommodate multiple Co sites and has been employed for electrocatalytic water oxidation under neutral conditions, demonstrating its ability to facilitate the incorporation of active metal sites and the regulation of localized coordination environments at the molecular scale[66]. Furthermore, the Wells-Dawson sandwich-type multi-metal POM can also be composited with N-doped carbon nanotubes, where  $\text{Fe}_2\text{Ni}_2@\text{MWCNT-N}_6$  exhibits a

$\eta_{10}$  of 0.36 V and a Tafel slope of  $45 \text{ mV dec}^{-1}$  in OER, indicating that the Dawson framework facilitates the coupling of multi-metal synergy with the conductive support; For example, Gautam et al. prepared  $\text{ZnFe-LDH}/\text{P}_2\text{Mo}_{18}$  heterojunctions on nanofiltration membranes using a two-step hydrothermal method (Fig. 4). When Dawson-type  $\text{P}_2\text{Mo}_{18}$  forms a hierarchical heterojunction with  $\text{ZnFe-LDH}$ , the OER overpotential at 20 and  $50 \text{ mA cm}^{-2}$  can be reduced to 275 and 330 mV, respectively, with an overall water splitting voltage of only 1.54 V. This further demonstrates that such structures are more suitable for use as interface-modulating and framework-expanding units embedded in complex systems such as LDHs and MOFs[66]. It is evident that the advantage of Wells-Dawson-type POMs does not lie in the direct reactivity of the individual backbone alone, but rather in their greater design flexibility, which allows them to function simultaneously at three levels: molecular site construction, conductive network coupling, and heterojunction assembly.



**Figure 4** Schematic diagram of the synthesized  $\text{ZnFe LDH-P}_2\text{Mo}_{18}/\text{NF}$  hybrid compound. Reproduced with permission from Ref. [66], © 2023 Elsevier B.V.

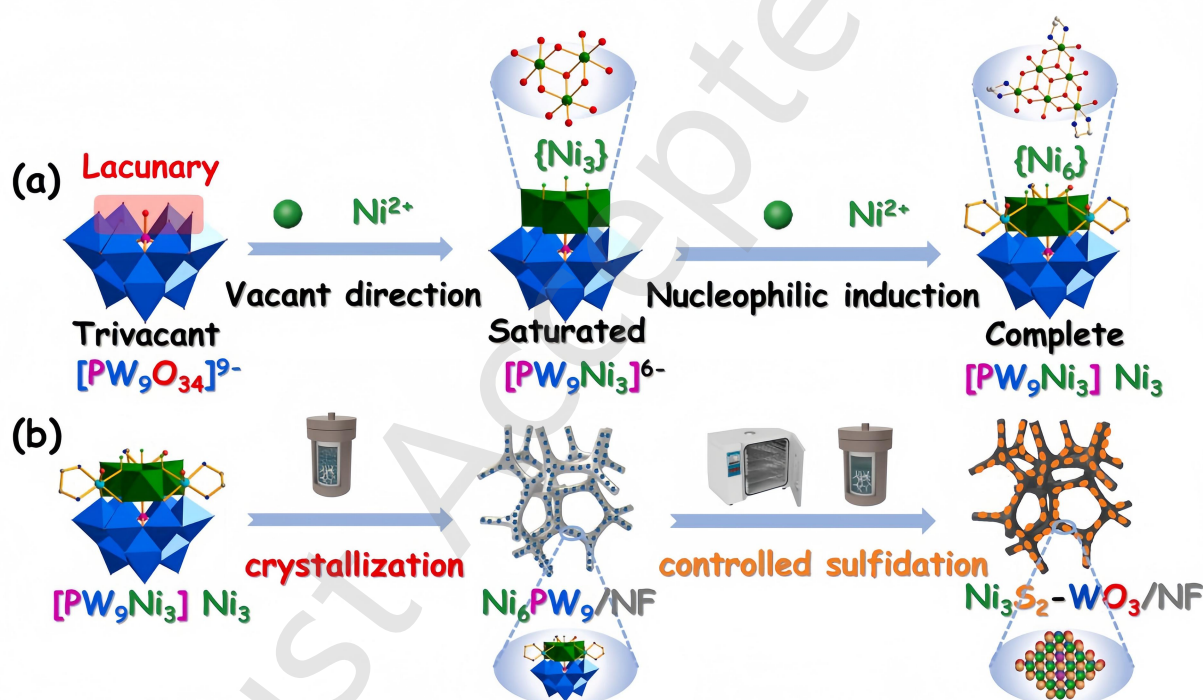
### 2.1.3 Lacunary POM: From a Lacunar Structure to a Reactive Platform

While the primary advantage of Keggin-type POMs lies in their skeletal stability and that of Dawson-type POMs in

their greater functionalization flexibility, the core significance of lacunary POMs lies in the coordination reactivity resulting from their lacunae. Due to the absence of certain metal-oxygen octahedra, lacunary POM exposes more reactive vacant sites and exhibits stronger

metal-capturing capabilities. Consequently, it is better suited than saturated frameworks as a pre-functionalized platform for metal anchoring, interfacial bridging, and multicomponent coupling. For example, X-ray diffraction (XRD) and infrared (IR) spectroscopy analyses confirmed the successful synthesis of  $\text{Ni}_6\text{PW}_9$  (Fig. 5a,b). Benefiting from the molecular-level anchoring effect of the lacunary  $[\text{PW}_9\text{O}_{34}]^{9-}$  framework, Ni species can be preorganized in the precursor and subsequently transformed into  $\text{WO}_3$ -confined, highly dispersed  $\text{Ni}_3\text{S}_2$  during controlled sulfidation. The resulting catalyst delivers low overpotentials of 86 and 107 mV at 10 and 20  $\text{mA cm}^{-2}$ , respectively, and 370 mV at 200  $\text{mA cm}^{-2}$ , highlighting that lacunary POMs can not only stabilize metal sites in the precursor state, but also direct the evolution of the active phase and promote catalytic performance through

atomic-level dispersion and Ni-W synergy[67]; On the other hand, trilacunary  $\text{PW}_9$  can also form a grafted superstructure by reassembling with  $\text{CoFe-MOF}$  via Ni-O bridges, indicating that its vacancy sites not only facilitate metal grafting but also serve as connection nodes for constructing heterogeneous interfaces, thereby integrating different components into a unified electron transport network[68]. Therefore, the significance of lacunar POMs in the OER system typically lies not in their ability to catalyze the current flow on their own, but rather in their role as designable molecular precursors that, through vacancy-driven coordination chemistry, facilitate the subsequent formation of active phases, chemically bridged charge-transport pathways, and structural reorganization.



**Figure 5** Schematic diagram of the synthesis of  $\text{Ni}_3\text{S}_2\text{-WO}_3/\text{NF}$ -1 catalyst using  $\text{Ni}_6\text{PW}_9$  polyoxometalate as precursor. Reproduced with permission from Ref. [67], © 2023 Elsevier Inc.

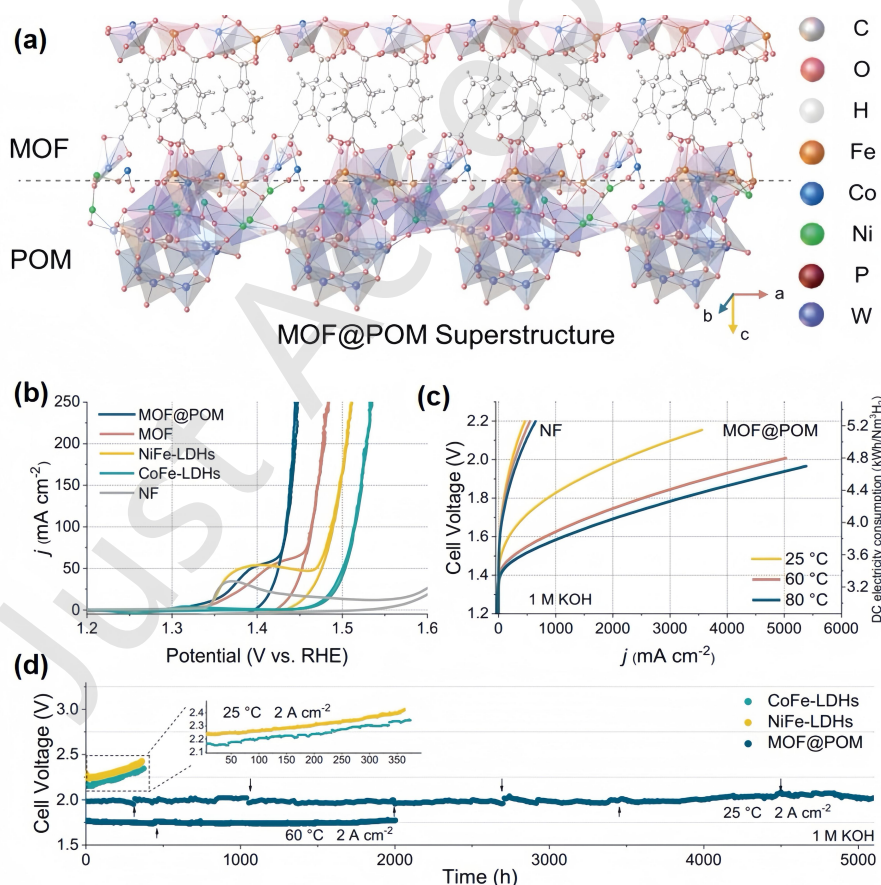
#### 2.1.4 Transition-Metal-Substituted POMs: Structural Units Closest to Intrinsic Molecular Active Centers

Compared to saturated Keggin or deficient platforms, transition metal-substituted POMs typically represent a “true molecular active site” in OER. This is because the introduction of transition metal sites such as Co, Fe, Ni, and Mn not only reshapes the overall electronic structure of the cluster but also often directly endows localized metal sites with the ability to participate in the key oxidation steps of OER. Consequently, such POMs are better suited as molecular catalytic models with well-defined structural boundaries and traceable electron transfer pathways, providing an ideal system for identifying the actual active species. Studies exemplified by Co-substituted POMs demonstrate that the significance

of these clusters lies not only in their ability to exhibit water oxidation activity but also in their clear molecular boundaries, which allow researchers to distinguish between “molecular-state catalysis” and “catalysis via in situ-generated oxides/hydroxides”[69]. Furthermore, in the site-selectively synthesized heterometallic substitution cluster  $[\text{Co}_2\text{Ni}_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ , the occupancy of Co and Ni sites can be precisely quantified, and its aqueous oxidation rate is approximately one order of magnitude higher than that of the isostructural  $[\text{Co}_4(\text{PW}_9\text{O}_{34})_2]^{10-}$ , indicating that the type and arrangement of adjacent transition metal sites can directly reshape the local electronic environment and regulate reaction kinetics[70]. Similarly, Fe-substituted cobalt-phosphate POM can reduce the overpotential of OER at 10  $\text{mA cm}^{-2}$  to 385 mV in an acidic medium, which

is 66 mV lower than that of the parent Co cluster, and shows no significant decline even after 24 hours of continuous operation. This further demonstrates that transition metal substitution not only enhances intrinsic activity but also simultaneously improves catalytic stability[71]. It is worth noting that the role of these POM structural units containing transition metals is not limited to isolated molecular clusters but can extend further to more complex interfacial coupling systems. As shown in the Fig.6, the tridentate PW9-based POM can be ordered into a MOF@POM superstructure through Ni-O bridging with layered CoFe-MOF, forming a system with well-defined interfacial connections; Under OER conditions, this precursor is further in situ converted into a CoFe oxyhydroxide active layer grafted onto the POM, indicating that POM units involving transition metals not only serve as structural building blocks at the molecular scale but also determine the precursor's reconstruction pathways, interfacial electron transport mechanisms, and the stability of the final active phase. Correspondingly, the electrochemical results shown in the figure also indicate

that this MOF@POM superstructure requires only a 178 mV overpotential at  $10 \text{ mA cm}^{-2}$  under alkaline conditions, achieves  $3 \text{ A cm}^{-2}$  at 1.78 V in an AEM water electrolysis cell at  $80^\circ\text{C}$ , and can operate stably for 5,140 hours at  $2 \text{ A cm}^{-2}$  under room temperature conditions, significantly outperforming the comparative CoFe-LDH and NiFe-LDH systems. This suggests that the value of transition metal substitution for POM in OER should no longer be understood merely in terms of “whether it provides a directly reactive molecular active site,” but should also include its ability to further define interfacial bonding modes, regulate electron transport pathways, suppress metal leaching, and maintain structural stability under operating conditions. In this sense, the core value of transition metal-substituted POM in OER lies in its ability to simultaneously integrate a “designable molecular framework” and “metal sites capable of direct reaction” within the same structural unit, thereby serving as a crucial bridge connecting molecular catalysis research with the elucidation of real electrochemical mechanisms.



**Figure 6** (a) Structural model of the MOF@POM superstructure, showing the ordered coupling of a trilacunary Keggin-type POM with layered CoFe-MOF through Ni-O bridging; (b) electrochemical polarization curves of MOF@POM, MOF, NiFe-LDHs, CoFe-LDHs, and Ni foam; (c) polarization curves of an AEM water electrolyzer using MOF@POM as the anode at 25, 60, and  $80^\circ\text{C}$ ; (d) long-term durability of different catalysts in 1 M KOH at  $2 \text{ A cm}^{-2}$ . Arrows indicate the replacement of fresh electrolyte during the test. Adapted with permission from Ref. [65], © 2025 American Association for the Advancement of Science.

## 2.2 Applications of Four Types of POM in OER

Based on current research, POMs in OER are better

classified according to their functional roles rather than simply by their structural names. First, as intrinsic molecular active centers, certain POMs with transition

metal substitutions or well-defined structural boundaries can serve directly as molecular-level water oxidation models to distinguish whether catalytic processes are dominated by molecular clusters or derived active phases. Studies represented by Co<sub>4</sub>-POM and Ru-POM have demonstrated that POMs not only serve as ideal models for structure-activity relationship analysis but also participate directly in OER as discrete metal-oxygen cluster units[72, 73]. Second, as a confined or immobilized guest, POM can be embedded within a host such as MOF. Through spatial confinement and host-guest interactions, this arrangement enhances dispersion, reduces loss, and improves charge transport, the POM@ZIF-67 system exemplifies this functional role[74]. Third, in composite catalysts, POM can act as an interfacial electronic regulator and reconstruction inducer. In the PW<sub>12</sub>-modified NiFe-LDH system, a positive Ni 2p shift and an increased Ni<sup>3+</sup>/Ni<sup>2+</sup> ratio accompany an approximately 68 mV decrease in overpotential relative to pristine NiFe-LDH, providing a measurable link between electronic-state perturbation and OER kinetics[75]. Fourth, under conditions of high current density and complex media,

POM can further function as a stabilizing module by confining and anchoring active components to prevent their loss, thereby ensuring the sustained operation of the electrode in alkaline water and seawater. This demonstrates that its role is no longer limited to that of an active additive, but rather that of a structural stabilizing unit under harsh operating conditions[76]. Therefore, understanding POMs in terms of their “functional roles” is more conducive to integrating seemingly disparate areas of research-such as molecular catalysis, localized immobilization, interfacial regulation, and stabilization under harsh conditions-into a unified analytical framework. These four broad functions are further resolved below into six mechanistic mediation pathways so that the structural motifs of POMs can be directly connected with the elementary PCET (Proton-Coupled Electron Transfer) events of OER. Table 2 summarizes the structure-dependent roles of representative POMs in OER, linking their structural features with functions such as confinement, interfacial regulation, structural construction, and molecular catalysis.

**Table 2** Typical functional orientations of different POM structural types in OER.

| Structural Type                   | Key structural features                                                                                     | More pronounced structural advantages                                                           | More typical roles in OER                                                     | Ref.     |
|-----------------------------------|-------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|----------|
| Keggin                            | The scaffold is mature and stable, sensitive to its microenvironment, and easily localized and intercalated | Stabilization of the platform, multiple electron transfers, and subsequent interfacial coupling | Confined objects, interlayer units, interface stabilization modules           | [77]     |
| Dawson                            | Greater freedom in topology and functionalization, facilitating expansion into complex structures           | Potential for Deep Functionalization and Multiscale Material Construction                       | Multi-component composite precursors, expanded framework structural units     | [28, 78] |
| Iacunary POM                      | Exposed vacant sites, high reactivity in coordination reactions                                             | Metal Anchoring, Interface Bridging, and Reconstruction Induction                               | Heterogeneous interface construction units, reconstruction-oriented platforms | [79, 80] |
| Transition-metal-substituted POMs | By introducing directly redox-active metal sites, the active center becomes more clearly defined            | Intrinsic molecular active sites and traceable electron transfer pathways                       | Molecular active sites, mechanistic models                                    | [81, 82] |

### 2.3 Mechanistic Mapping between POM Structures and OER Four-Step Proton-Electron Transfer

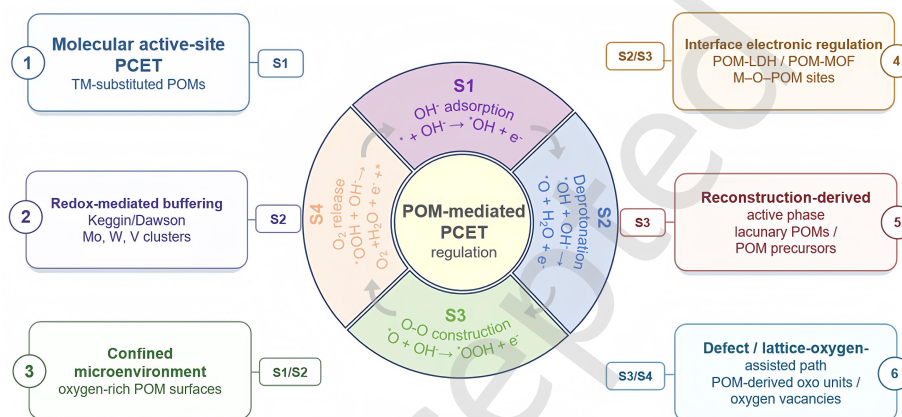
To establish a structure-mechanism correlation framework for POM-based OER electrocatalysts, six representative POM-mediated reaction pathways are proposed based on their distinct structural characteristics and regulatory functions within composite catalytic systems. These pathways do not represent six

independent OER mechanisms, but rather describe different modes by which POM units participate in, regulate, or redirect the elementary reaction processes under electrochemical operating conditions. Considering the intrinsic complexity and dynamic nature of OER mechanisms, including the coexistence and interconversion among adsorbate evolution mechanism (AEM), lattice oxygen mechanism (LOM), oxide path mechanism (OPM), oxo-coupling mechanism (OCM), and

intramolecular oxygen coupling mechanism (IMOC), the POM-mediated pathways are correlated with the four-step alkaline proton-coupled electron transfer (PCET) sequence: (1)  $\cdot\text{O} + \text{OH}^- \rightarrow \cdot\text{OH} + \text{e}^-$ , (2)  $\cdot\text{OH} + \text{OH}^- \rightarrow \cdot\text{O} + \text{H}_2\text{O} + \text{e}^-$ , (3)  $\cdot\text{O} + \text{OH}^- \rightarrow \cdot\text{OOH} + \text{e}^-$ , and (4)  $\cdot\text{OOH} + \text{OH}^- \rightarrow \text{O}_2 + \text{H}_2\text{O} + \text{e}^- + \cdot$ . As summarized in Fig. 7, transition-metal-substituted POMs, Keggin/Dawson-type redox-active clusters, oxygen-enriched POM interfaces, POM-LDH/POM-MOF heterointerfaces, lacunary POM precursors, and POM-derived defect or lattice-oxygen-containing species regulate distinct elementary steps associated with the formation,

transformation, and removal of key oxygen intermediates, including  $\cdot\text{OH}$ ,  $\cdot\text{O}$ ,  $\cdot\text{OOH}$ , and  $\text{O}_2$ [83, 84].

The proposed framework highlights that the catalytic contribution of POMs is intrinsically dependent on their structural configuration, immobilization environment, electrolyte conditions, applied potential, and reconstruction pathway. Therefore, the role of POMs in OER catalysis should be interpreted beyond conventional structural classification and instead evaluated through the dynamic coupling between POM motifs, interfacial electronic structures, and potential-dependent elementary reaction steps.

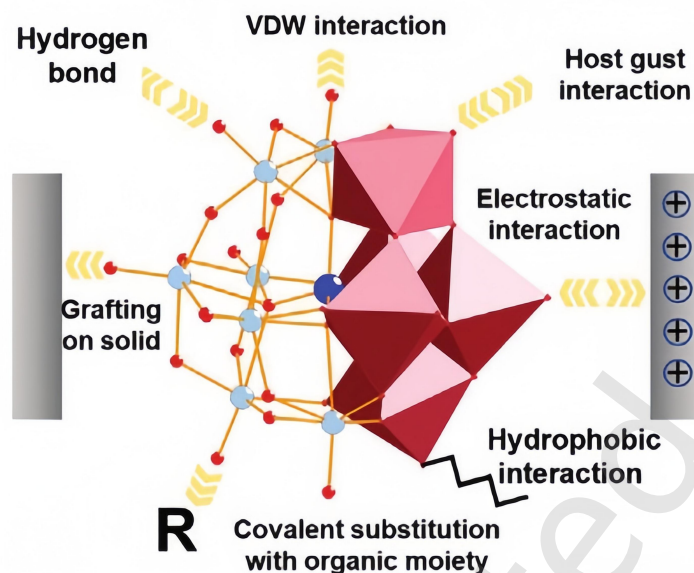


**Figure 7** POM-mediated OER pathways mapped onto the four-step alkaline PCET sequence. Created by the authors based on Refs. [85-87].

### 3 Intrinsic POM as an OER Active Center: From Molecular Catalysis to the Identification of Actual Active Species

#### 3.1 The Starting Point and Academic Value of Research on Molecular POM-OER Catalysts

The unique significance of molecular POMs in OER research lies primarily in their well-defined metal-oxygen cluster frameworks, tunable composition and substitution sites, and reversible multi-electron redox behavior. As a result, they are more suitable than amorphous metal oxides—which have ambiguous compositions and undergo continuous restructuring during operation—as model systems for studying electron transfer, proton coupling processes, and structure-property relationships[88, 89]. Recent studies have further demonstrated that the academic value of molecular POMs extends beyond the fact that “molecular clusters can also catalyze water oxidation”, rather, it lies in their position at a critical transition zone between homogeneous molecular catalysis and heterogeneous electrode catalysis: on the one hand, they retain structural discernibility at the molecular scale; on the other hand, they can enter a working state closer to that of a real electrode environment through insolubilization, immobilization, or interfacial coupling. As illustrated in Fig. 8, POM-based nanostructures can be constructed through diverse host-guest and interfacial interaction modes, which facilitate cluster immobilization, electronic communication with the supporting matrix, and structural stabilization under catalytic conditions. These interactions provide an important structural basis for integrating molecularly defined POMs into electrode-compatible catalytic architectures[90]. This is particularly evident in recent mechanistic studies. For example, in the Co-POM/TiO<sub>2</sub> system, interfacial hole injection, charge accumulation within the clusters, and subsequent oxidation steps can be resolved step-by-step, demonstrating that the significance of molecular POMs lies not only in their role as active centers but also in the fact that their reaction pathways are “traceable”[91]. At the same time, operando X-ray absorption spectroscopy (XAS) studies of cobalt-substituted POM indicate that, even though some systems undergo destabilization or evolution under OER conditions, the initial molecular structure provides a clear reference for determining whether the actual activity stems from molecular clusters or derived oxides/hydroxides[92]. Therefore, the enduring academic value of early research on Co-POMs, Weakley sandwich-type multinuclear clusters, and their derivatives stems not only from their demonstrated water oxidation activity, but also from the fact that these structurally well-defined molecular clusters enable the establishment of analyzable causal relationships between localized metal sites, site synergy, and coordination environment regulation; this research tradition continues to be upheld in recent high-core-sandwich-type Co-POM electrocatalysts[93].

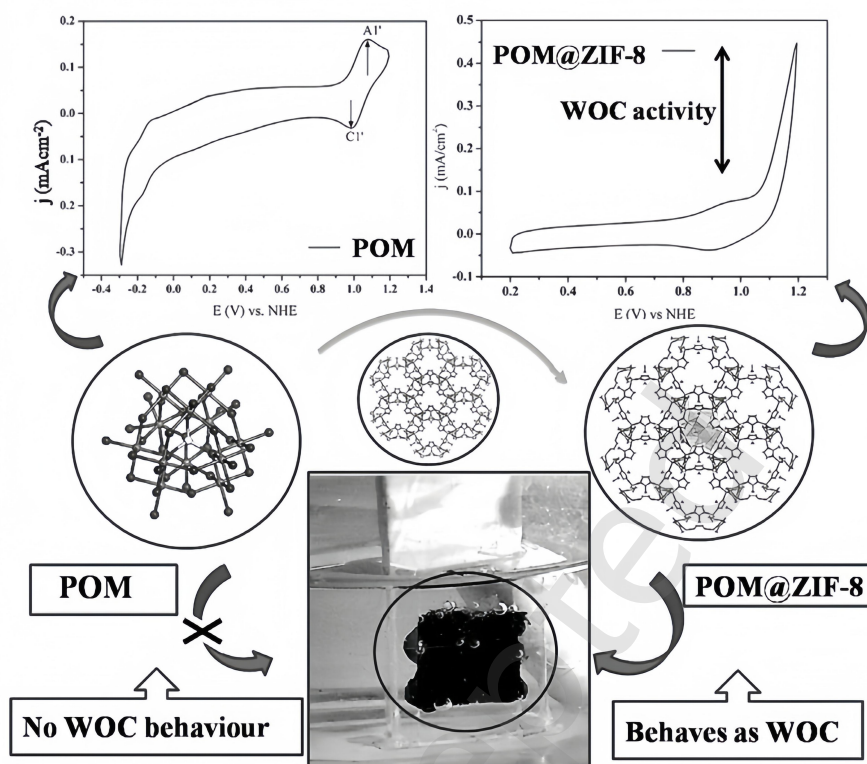


**Figure 8** Various interaction modes in POM-based nanostructures. Reproduced with permission from Ref. [90], © 2024 Wiley-VCH GmbH.

### 3.2 Limitations of Keggin-type POM and Microenvironment Activation

If molecular transition metal-substituted POMs represent a molecular catalytic approach centered on well-defined metal sites, then Keggin-type POMs better illustrate another equally important research direction: For such structurally saturated, framework-stable clusters, the bottleneck often lies not in whether they possess reversible redox capabilities, but rather in the fact that bare molecules typically lack sufficiently accessible reaction sites, while also facing issues such as dissolution and loss, insufficient interfacial electron transport, and weak electrode coupling. Therefore, in the context of OER, the value of Keggin-type POMs is often not manifested as “directly high activity of bare clusters,” but rather as a molecular platform that can be reactivated through confinement, immobilization, and interfacial engineering. Recent reviews and interfacial studies have also generally pointed out that the key obstacles to the practical application of POMs in electrocatalysis primarily include high solubility, low conductivity, and insufficient interfacial interactions, while adsorption-driven electrode-POM interactions, host-guest confinement, and structural immobilization are effective pathways for improving their charge transfer and operational stability[28, 94].

From this perspective, the significance of early work represented by POM@ZIF-8 lies not in the fact that it demonstrated the “unexpected activity” of a particular saturated Keggin cluster, but rather in its suggestion of a more general principle: Keggin units, which originally lacked sufficiently open reaction sites and ideal interfacial transport, can be transformed into effective OER components through the remodeling of their external microenvironment. As illustrated in Fig. 9, the pristine POM exhibits no discernible water oxidation catalysis (WOC) behavior, whereas encapsulation within ZIF-8 gives rise to a pronounced catalytic oxidation current. This contrast highlights the decisive role of the ZIF-8-confined microenvironment in activating an otherwise poorly accessible molecular POM toward water oxidation[95]. Recent studies have further extended this principle from MOF confinement to broader scenarios such as sol-gel immobilization, MOF embedding, and LDH intercalation. For example, Singh et al. embedded  $K_6[CoW_{12}O_{40}]$  into a tetramethyl orthosilicate (TMOS)-derived sol-gel network, achieving stable OER under acidic conditions with electrode reusability exceeding 90 days. This demonstrates that heterogeneous confinement not only suppresses cluster loss but also significantly enhances electrochemical operational stability[96]. Li et al. point out that Ni-containing Keggin POMs are inherently prone to hydrolytic decomposition; however, by incorporating positively charged MIL-101(Cr), uncontrolled hydrolysis can be prevented and recyclable electrochemical water oxidation can be achieved[97]. More recent work has also shown that when the Keggin-type  $H_5PMo_{10}V_2O_{40}$  is intercalated into MgAl-LDH, it exhibits an OER overpotential of 411 mV at 10 mA cm<sup>-2</sup> and a current retention rate of approximately 97 % over 12 hours in 1.0 M KOH, further demonstrating that spatial confinement and interlayer immobilization help reduce POM leaching and improve interfacial catalytic performance[98]. Therefore, the “limitations” of Keggin-type POM do not imply that it lacks catalytic potential, rather, they indicate that its performance is highly dependent on whether the microenvironment can provide suitable anchoring, localized electronic regulation, and charge transport pathways. True breakthroughs typically arise from the activation of the microenvironment through the combined effects of confinement, immobilization, and interfacial coupling.



**Figure 9** Activation of POM for water oxidation by encapsulation in ZIF-8. Reproduced with permission from Ref. [95], © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

### 3.3 Identification of the Actual Active Species: Molecular POM or Derived Oxides/Hydroxides

The identification of the true active species in POM-based OER systems should be formulated as a four-dimensional, operation-resolved problem rather than as a binary comparison between an intact molecular cluster and a reconstructed oxide/oxyhydroxide. The relevant variables are: (i) electrolyte pH and composition, which govern cluster protonation, hydrolysis, and solution/surface speciation. (ii) applied potential or current density, which determines the oxidation-state trajectory and the driving force for reconstruction. (iii) immobilization mode and interfacial bond strength, which control cluster retention and the spatial extent of reconstruction, and (iv) operation time, because activation, steady-state catalysis, and long-term aging may correspond to chemically distinct working states. On this basis, POM-based catalysts can be classified into three operational states: a molecular-POM-dominant state, a hybrid POM/oxyhydroxide state, and a POM-derived oxide/oxyhydroxide-dominant state.

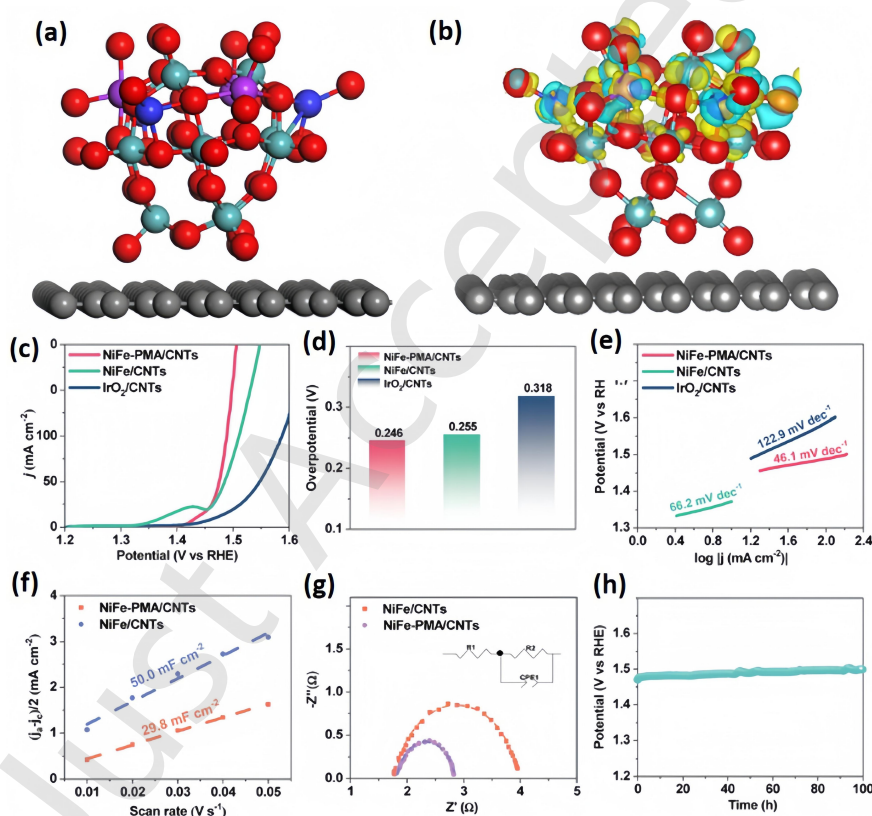
In the molecular-POM-dominant state, cluster-specific spectroscopic fingerprints persist under bias, dissolution of W/Mo/V/P is negligible, and catalytic changes correlate with the molecular redox state. In the hybrid state, the host metal centers reconstruct into MOOH/oxide motifs while the POM framework or M-O-POM linkage remains detectable and continues to regulate interfacial charge, coordination, or mass transport. In the

derived-phase-dominant state, the original molecular fingerprint disappears, POM elements are redistributed or leached, and the catalytic response converges toward that of newly formed oxides/oxyhydroxides. Accordingly, active-species assignment should follow the sequence of pH-dependent speciation analysis, potential-resolved operando characterization, immobilization/retention assessment, and time-resolved testing from initial activation to prolonged electrolysis. A defensible conclusion requires mutually consistent evidence from at least two independent structural probes, quantitative dissolution analysis, and electrochemical evolution; coexistence of molecular and reconstructed signatures should be reported explicitly as a hybrid working state rather than forced into either endpoint[99] [90, 100].

From this perspective, the retention of molecular POM primarily depends on its stability threshold in the working medium. Recent studies, represented by the Weakley sandwich-type Co<sub>4</sub>-POM, indicate that such clusters are relatively stable in neutral aqueous solutions, while their degradation becomes significantly more likely in alkaline media, and their stability also tends to decrease under acidic conditions. This implies that under mild potentials, neutral media, and conditions of strong confinement, the intrinsic contribution of molecular POM is more likely to be preserved. However, once exposed to strong alkaline environments, high potentials, and prolonged operation, the risk of cluster dissociation, rearrangement, and even transformation into a heterogeneous active phase increases significantly[101].

More notably, recent evidence from numerous POM composite systems points to a more established understanding: POM often does not function by having “intact molecular clusters directly carry the main catalytic current”, but rather by regulating the local electronic structure and deprotonation processes to promote the formation of the truly active oxyhydroxide phase. For example, Qiao et al. showed that the in situ incorporation of phosphomolybdic acid (PMA,  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ) into NiFe oxyhydroxide primarily induces interfacial electronic coupling among Ni, Fe, and Mo sites. The optimized structure and differential charge-density analysis (Fig. 10 a,b) provide a spatially resolved theoretical signature of interfacial electron transfer at the POM/NiFe interface, while the electrochemical results (Fig. 10 c-h) show reduced overpotential, accelerated reaction kinetics, lower

interfacial charge-transfer resistance, and excellent long-term stability. Importantly, the activity enhancement is achieved despite a lower  $C_{dl}$  than that of NiFe/CNTs, indicating that PMA mainly improves the intrinsic reactivity of interfacial sites through electronic regulation rather than by simply increasing the number of exposed active sites[102]; Furthermore, Zhang et al. (2026) confirmed via potential-dependent Raman spectroscopy that  $\text{PW}_{12}$ -intercalated NiFe-LDH promotes an early phase transition from hydroxide to oxyhydroxide, facilitating the formation of the  $\gamma\text{-NiOOH}$  active phase. For such systems, a more reasonable explanation for the observed high OER activity is typically the “formation of an oxyhydroxide active phase under the regulation of POM”, rather than the complete retention of the original molecular-state clusters[102, 103].



**Figure 10** (a) Optimized structures of the NiFe-PMA/CNT catalyst. The spheres in gray, red, pink, blue, violet, and cyan represent C, O, P, Ni, Fe, and Mo atoms, respectively. (b) The 3D differential charge density of the NiFe-PMA/CNT catalyst. The green symbols indicate a decrease in charge density, while the yellow symbols indicate an increase in charge density. (c) LSV curve. (d) Overpotential bar chart. (e) Tafel curve. (f) Double-layer capacitance. (g) Nyquist plot. (h) CP stability. Reproduced with permission from Ref. [102], under the CC BY-NC 3.0 license.

On the other hand, the contribution from a molecular or partially retained POM state does not necessarily disappear under OER conditions. For the NiW-POM/NF system, in situ Raman spectroscopy and in situ Fourier-transform infrared (FTIR) spectroscopy indicates that stable Ni-O-W bridge bonds can suppress extensive reconstruction during OER, suggesting that robust interfacial bonding may preserve a POM-involved catalytic pathway[104]. Molecular retention and derived

oxyhydroxide formation should therefore be regarded as two ends of a continuum rather than as mutually exclusive explanations. For each material, the dominant active species should be assigned only after considering pH, applied potential/current density, immobilization strength, operation time, dissolution behavior, and operando structural evidence. Table 3 provides a practical framework for distinguishing molecular POM, hybrid POM-host, and POM-derived oxide/oxyhydroxide states

based on pH, applied potential, immobilization strength, and current-density/time stress.

**Table 3** Quantitative screening framework for distinguishing molecular POM, hybrid POM-host, and POM-derived oxide/oxyhydroxide working states under OER conditions.

| Discriminator / quantitative window                                                                                                                                                                                                                                               | Default working-state assignment                                                                                       | Molecular-POM indicators                                                                                                   | Derived-phase indicators                                                                                               | Required test / representative references                                                                                                                                                       |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| pH 6-7 (near-neutral); pH 8-9 (transition); pH 13-14 (0.1-1 M KOH)                                                                                                                                                                                                                | pH 6-7: molecular/hybrid plausible; pH 8-9: case-dependent; pH 13-14: hybrid/oxide-dominant unless retention is proven | POM Raman/IR/XAS fingerprints retained; W/Mo/P and substituted-metal loss within analytical uncertainty ( $\leq 5\%$ )     | Lacunary/decomposition products, CoII/III oxide or MOOH formation; marked elemental loss or redistribution ( $>10\%$ ) | pH-resolved characterization at 6, 7, 8, 9, 13, and 14, with ICP mass balance and rinse controls[99, 101, 105].                                                                                 |
| $\leq 1.40$ - $1.45$ V vs RHE (pre-OER); $1.45$ - $1.60$ V (activation); $\geq 1.60$ V or $\eta \geq 0.37$ V (stress)                                                                                                                                                             | Below onset: molecular state plausible; activation region: hybrid; stress region: derived phase increasingly likely    | Reversible edge/valence changes; POM bands recover after returning to OCV                                                  | Persistent $\text{CoO}_x/\gamma\text{-NiOOH}/\text{FeOOH}$ signals and spectral hysteresis after potential release     | Operando Raman/XAS in $0.05$ - $0.10$ V steps ( $2$ - $10$ min $\text{step}^{-1}$ ), plus quasi-in situ XPS. $\text{Co}_4\text{-POM}$ was unstable at pH 6, $1.60$ V for $1200$ s[92, 99, 103]. |
| Weak adsorption/soluble POM versus interlayer, covalent, or M-O-POM anchoring; test $30$ - $60$ min at $1.50$ - $1.60$ V $100$ - $500$ mA $\text{cm}^{-2}$ for $\geq 100$ h; $1$ A $\text{cm}^{-2}$ for $\geq 1000$ h; sample at $0/1/10/100/1000$ h; include saline or MEA tests | Weak binding: leaching/redeposition likely; strong anchoring: molecular or hybrid interface possible                   | $\geq 90\%$ POM retained; M-O-W/M-O-Mo coordination persists; activity decreases after selective POM removal               | Activity survives POM removal; W/Mo redistribution and an oxide-rich surface layer appear                              | Electrode/electrolyte mass balance, rinse-transfer/selective-removal controls, EXAFS, and cross-sectional STEM-EDS [105, 106].                                                                  |
|                                                                                                                                                                                                                                                                                   | Assign activation, steady-state, and aged states separately                                                            | Stable operando POM fingerprints; cumulative dissolution/migration $\leq 5\%$ ; no W/Mo/P accumulation in membrane/ionomer | Time-dependent POM loss, MOOH/oxide growth, host-metal leaching, delamination, or membrane contamination               | Chronopotentiometry with time-resolved effluent ICP and post-mortem depth/cross-sectional mapping [64, 105, 106].                                                                               |

Note: These numerical ranges are merely recommended screening intervals, not universal thresholds. All potentials are referenced to RHE.

#### 4 POM as an Interface Modifier: Electronic Structure Modulation, Structural Rearrangement, and Activity Enhancement

While Chapter 3 focused primarily on whether POM can directly serve as the active center for OER in its molecular form, this chapter places greater emphasis on another, more representative line of research: In an increasing number of high-performance composite catalytic systems, the primary value of POM no longer lies in its role as an independent molecular unit directly bearing the main catalytic current, but rather in its systematic regulation of the electronic structure, local coordination environment, pre-catalyst restructuring pathways, and long-term stability of adjacent transition metal sites[107]. Recent studies have shown that the role of POM in OER systems has evolved beyond the traditional concepts of “substrate loading” or “reactive supplementatio”, gradually

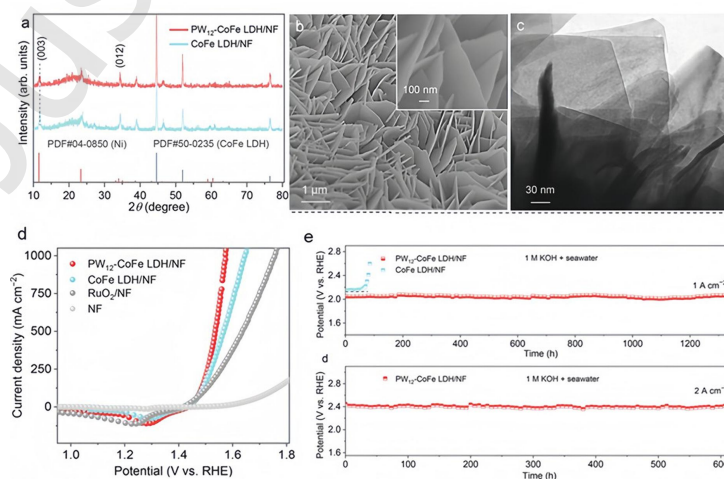
transforming into a regulatory unit capable of actively shaping the reaction microenvironment through interfacial coupling[108]. For example, in a POM-induced NiFe-LDH restructuring system, the introduction of POM is accompanied by vacancy formation, interlayer insertion, and changes in the local electronic environment, demonstrating its multiscale synergistic regulation of morphology, composition, and interfaces; In an Anderson-type POM-anchored Ni-MOF system, electrons at the interface are directed from the metal centers toward the POM, further altering the transformation process of key oxygen-containing intermediates, indicating that POM can act as a site-specific electronic state regulator to participate in the optimization of OER kinetics[109]. In POM-MOF-derived sulfides and heterosystems such as POM/MIL-101(Fe), POM further serves functions such as interfacial organization, the introduction of heteroatoms, and the enhancement of electronic coupling, thereby translating structural regulation into a simultaneous

improvement in both activity and stability[110, 111]. Therefore, in current OER research, the true significance of POMs no longer lies primarily in “whether they are sufficiently active,” but rather in their ability to actively define how adjacent active sites ultimately form, function, and remain stable through the reorganization of surface electrons, the reshaping of local structures, and the guidance of reconstruction pathways.

#### 4.1 POM is no longer just an “object,” but a “controller”

In early POM-OER research, POM was often understood as a molecular cluster with a defined structure, and its primary value was generally summarized as “providing additional active sites” or “serving as an immobilized active component.” However, with the development of composite systems combining POM with layered hydroxides, metal hydroxides, and conductive frameworks, this understanding is being significantly revised. A growing body of research indicates that in high-performance composite electrocatalysts, POM is often not the primary direct active phase on the surface. Instead, it actively modulates the electronic states and local coordination environments of adjacent transition metal sites, as well as the evolution of the precursor catalyst into the actual active phase, through mechanisms such as assembly induction, interlayer intercalation, interfacial anchoring, and electronic buffering[112]. For example,  $\text{PW}_{12}$  acts as a building block to induce the formation of ordered nanosheets of  $\text{Ni}(\text{OH})_2$  on  $\text{Co}/\text{NF}$ , indicating that POM is no longer merely a passively “loaded” guest but is capable of participating in the construction of the host structure[64, 113]. More notably, recent studies on the selective anchoring of  $\text{PW}_{12}$  at Fe sites within  $\text{CoFe}$  hydroxide indicate that POM does not function simply as an independent active cluster in seawater OER. Instead, it acts through site-specific interfacial coordination to reshape the local electronic

structure of the host hydroxide. As shown in Fig. 11a-c, the introduction of  $\text{PW}_{12}$  does not alter the LDH interlayer spacing or destroy the ultrathin nanosheet architecture, but leads to surface docking on  $\text{CoFe}$  LDH with preserved sheet-like morphology. Electrochemical results further reveal that such interfacial anchoring substantially enhances catalytic performance under alkaline seawater conditions (Fig. 11d-f). In particular,  $\text{PW}_{12}\text{-CoFe LDH}/\text{NF}$  shows improved activity relative to  $\text{CoFe LDH}/\text{NF}$  and maintains stable operation for over 1300 h at  $1 \text{ A cm}^{-2}$  and over 600 h at  $2 \text{ A cm}^{-2}$ . Combined with spectroscopic and theoretical analyses, this behavior has been attributed to the preferential coordination of  $\text{PW}_{12}\text{-POM}$  at Fe sites, which stabilizes Fe against leaching, produces spectroscopically and theoretically supported electronic-state changes at adjacent Co sites, and synergistically regulates the competitive adsorption of  $\text{OH}^-$  and  $\text{Cl}^-$ , thereby suppressing chloride corrosion while preserving selective oxygen evolution. In this sense, the role of POM in such systems is no longer adequately described as that of an isolated molecular catalyst; rather, it should be understood as an interfacial electronic and structural regulator that stabilizes host-metal active sites under harsh operating conditions. Similarly, in POM electrocatalytic systems assembled via CNTs under acidic conditions, as well as in Keggin-type POM systems supported on the interface of porous Mn oxides, the primary contribution of POM is more evident in amplifying overall catalytic performance by stabilizing interfacial contact, improving electron transport, and maintaining the availability of redox units, rather than simply relying on isolated clusters to generate catalytic current on their own[113-116]. Therefore, in current research on OER composite catalysts, POM is no longer best characterized as a “source of additional activity,” but rather as an interface regulator capable of reshaping the reactivity of adjacent metal sites.



**Figure 11** Structural characterization and alkaline-seawater OER performance of  $\text{PW}_{12}\text{-CoFe LDH}/\text{NF}$ : (a) XRD patterns of  $\text{CoFe LDH}/\text{NF}$  and  $\text{PW}_{12}\text{-CoFe LDH}/\text{NF}$ ; (b, c) scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of  $\text{PW}_{12}\text{-CoFe LDH}$ ; (d) polarization curves of  $\text{PW}_{12}\text{-CoFe LDH}/\text{NF}$ ,  $\text{CoFe LDH}/\text{NF}$ ,  $\text{RuO}_2/\text{NF}$ , and NF; and (e, f) chronopotentiometric stability in 1 M KOH + seawater at 1 and  $2 \text{ A cm}^{-2}$ , respectively. Reproduced with permission from Ref. [117], under the CC BY 4.0 license.

#### 4.2 POM-LDH System: Intercalation, Etching, and Local Structure Control

In current research on the role of POM in regulating OER interfaces, the POM-LDH system is representative not merely because POM can intercalate into the LDH layers, but because it couples several previously separate processes—interlayer confinement, electronic structure modulation, and pre-catalyst restructuring—within a single material system. Recent studies on LDHs have consistently shown that layered hydroxides such as NiFe-LDH do not act as static catalytic surfaces during the OER process, but rather undergo significant structural rearrangement and a dynamic evolution from hydroxide to oxyhydroxide. Consequently, any anionic guest capable of altering the interlayer chemical environment, localized electronic states, and deprotonation behavior will further influence the formation mechanism and reaction kinetics of the actual active phase[118]. From this perspective, the role of POM in LDH cannot be simply understood as “layer expansion” or “loss prevention”, but rather as a multi-variable synergistic regulation strategy: on the one hand, the highly charged, oxygen-rich, and well-defined POM anions act as interlayer pillars and electron buffering units, altering the hydrogen-bond network, interlayer spacing, and the local charge distribution around Ni/Fe sites; on the other hand, the strong electrostatic and coordination interactions between POM and the positive layers of LDH further influence the surface deprotonation and restructuring initiation processes, thereby altering the timing and pathway of the transition from the precursor catalyst to the true oxyhydroxide active phase[119, 120]. More importantly, recent research on POM-intercalated LDH nanocomposites has clearly demonstrated that such systems do not exhibit “universal stability” outside of a specific medium: When reaction conditions fall within the window that the POM framework can maintain, the synergistic effect between the intercalated POM and LDH is preserved; however, once conditions exceed the pH stability limits, one must be wary of POM dissociation, cluster distortion, and the resulting misidentification of reactive species[121]. Therefore, the true significance of the POM-LDH system should not be reduced merely to “improved performance after intercalation”, but should be understood as a multiscale mechanism platform capable of simultaneously linking interlayer confinement, localized electronic regulation, deprotonation kinetics, and pre-catalyst restructuring. In terms of specific performance, in systems represented by PTA-intercalated NiFe-LDH, Keggin-type POMs not only enable the formation of a more uniform, ultra-thin nanosheet structure within the LDH upon intercalation, but also significantly reduce metal leaching through strong host-guest interactions, achieving stable operation for 500 hours at 1000 mA cm<sup>-2</sup>. When assembled into an AEM electrolyzer, it can deliver 1000 mA cm<sup>-2</sup> at just 1.93 V at 60 °C, indicating that its advantage lies not merely in layer

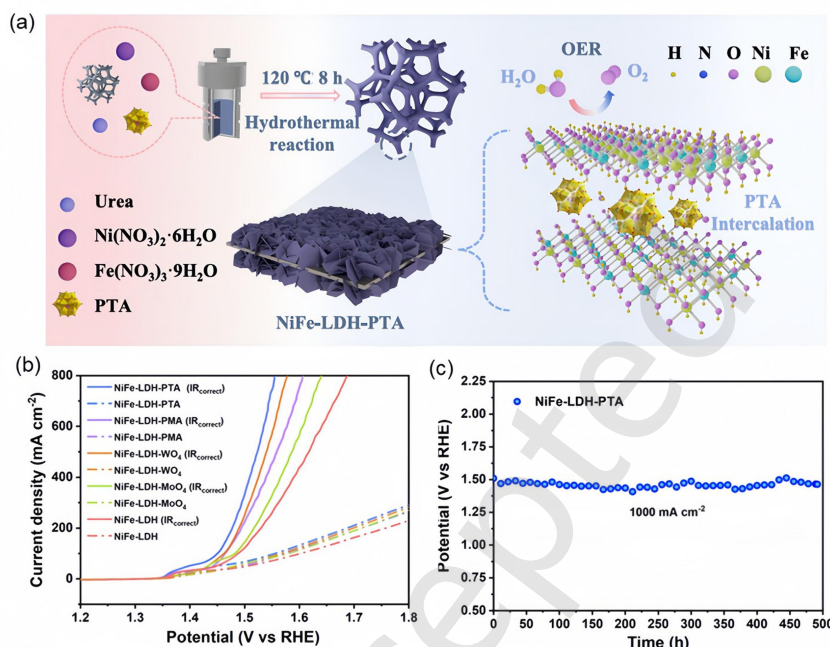
expansion itself, but in the simultaneous maintenance of active phase formation and structural stability under high-current conditions[122]. Furthermore, research by Zhang et al. on a PTA-intercalated NiFe-LDH system indicates that large, highly charged Keggin-type POM anions do not merely reside in the interlayer space as passive guests. Instead, PTA intercalation expands the LDH interlayer and induces strong host-guest electronic interactions, leading to higher-valence Ni and Fe species and promoting the formation of active oxyhydroxide species at lower anodic potentials. As shown in Fig. 12, this intercalation strategy enables NiFe-LDH-PTA to deliver superior OER activity over a wide current range, requiring only  $220 \pm 3$  mV at 100 mA cm<sup>-2</sup> and  $342 \pm 9$  mV at 1000 mA cm<sup>-2</sup>, while maintaining stable operation for about 500 h at 1000 mA cm<sup>-2</sup> in 1 M KOH. More importantly, PTA significantly suppresses Ni/Fe dissolution during operation, indicating that the role of POM in this system is not limited to interlayer occupation, but extends to regulating the electronic structure, activation pathway, and structural stability of the LDH host under ampere-scale conditions[103]. Meanwhile, research by Soriano-López et al. on POM-intercalated LDH nanocomposites indicates that such synergistic effects are not universally applicable under non-aqueous conditions: Their performance advantages are primarily manifested in higher water oxidation efficiency and better stability compared to Cs-Co<sub>4</sub>-POM and commercial Co<sub>3</sub>O<sub>4</sub> in near-neutral media; however, once the pH exceeds the stability limit of the POM framework, the clusters may undergo hydrolysis and destabilization, transforming into interlayer mixed-valent Co(II/III) oxides[105]. Therefore, discussions regarding their source of activity and stability must always be conducted in conjunction with the medium conditions.

#### 4.3 POM-MOF/Metal Hydroxide Interfaces: Electronic Coupling and Heterogeneous Synergy

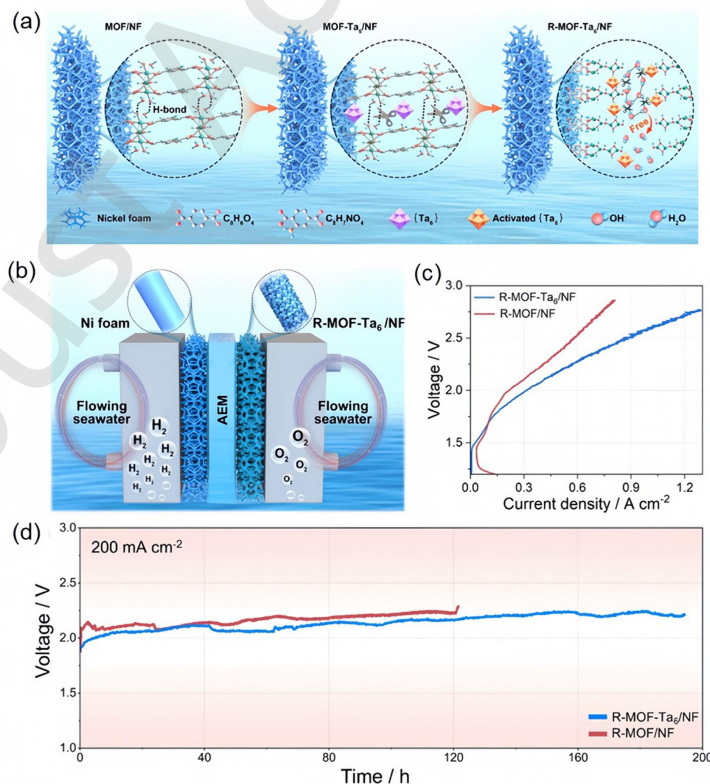
While the POM-LDH system primarily demonstrates POM's multivariate synergistic regulation of layered hosts, the POM-MOF and metal hydroxide interfaces further reveal that POM's core function in heterostructures is not merely to “adhere” to the host surface, but rather to integrate dispersed metal sites into a synergistically functioning reactive interface through bridging, surface anchoring, and localized charge rearrangement. Recent studies indicate that this type of interface regulation can proceed along two pathways: One representative pathway is [Ta<sub>6</sub>] mediated interfacial OH<sup>-</sup> supply in layered MOFs: in a layered Ni-MOF, the incorporation of [Ta<sub>6</sub>O<sub>19</sub>]<sup>8-</sup> reconstructs the H-bond networks both within the interlayers and at the catalyst-electrolyte interface, enabling more free OH<sup>-</sup> to penetrate the inner Helmholtz plane, deepening the activation-induced reconstruction of the MOF, and modulating the electronic structure of Ni sites through Ni-to-Ta charge transfer. Consequently, the reconstructed R-MOF-Ta<sub>6</sub>/NF achieves an overpotential of 235 mV at 10 mA cm<sup>-2</sup> in alkaline seawater; when integrated into an AEM seawater electrolyzer, it delivers

500 mA cm<sup>-2</sup> at 2.18 V and remains stable for 195 h at 200 mA cm<sup>-2</sup> (Fig. 13), demonstrating that POM can enhance MOF interfacial reactivity not only by expanding the interlayer space, but more importantly by reconfiguring the local H-bond microenvironment and OH<sup>-</sup> supply

pathway at the working interface[124], demonstrating that POM can enhance MOF interfacial reactivity by restructuring the interlayer and interfacial hydrogen-bond networks, increasing the availability of OH<sup>-</sup>, and modulating the electronic states of Ni sites.



**Figure 12** (a) Schematic illustration of the fabrication process of NiFe-LDH-PTA on Ni foam. (b) Polarization curves recorded at a scan rate of 2 mV s<sup>-1</sup> with and without iR compensation. (c) Stability test of NiFe-LDH-PTA at 1000 mA cm<sup>-2</sup>. Adapted with permission from Ref. [123], © 2025 American Chemical Society.



**Figure 13** (a) Schematic illustration of the role of the (Ta<sub>6</sub>) cluster in modulating the hydrogen-bonding network and MOF structure. (b) Schematic representation of the alkaline seawater AEM electrolyzer. (c) Polarization curves of the electrolyzer using R-MOF-Ta<sub>6</sub>/NF as the anode catalyst. (d) Durability test of the alkaline seawater AEM electrolyzer. Adapted with permission from Ref. [124], © 2025 The Authors; published by Elsevier Inc.



The  $\eta_{10}$  values of the two POM@NH<sub>2</sub>-MIL-101(Fe) composites, Ni<sub>4</sub>Mo<sub>12</sub>@Fe and Ni<sub>4</sub>Mo<sub>12</sub>@Fe, in 1 M KOH are 332.64 and 352.64 mV, respectively, both outperforming their respective single components, indicating that host-guest synergy can effectively enhance the overall catalytic efficiency of MOF-based heterojunctions; In contrast, at the metal hydroxide interface, POM-modified Ni(OH)<sub>2</sub> reduces  $\eta_{10}$  to 215 mV, while the NiFe oxyhydroxide hybrid with in situ-introduced POM further delivers an overpotential of 203 mV at 10 mA cm<sup>-2</sup> and a turnover frequency (TOF) of 2.34 s<sup>-1</sup>, suggesting that POM's regulation of metal site electronic states and intermediate transformation kinetics can be directly translated into faster OER kinetics[102]. Another category involves surface electronic engineering based on metal hydroxides, for example, in a POM-modified Ni(OH)<sub>2</sub> system, POM is no longer merely an additional component, but rather, through the combined effects of directed charge traction and localized fields, it alters the oxidation state of Ni sites and the kinetics of intermediate transformations[125]. At the same time, studies on the reversible surface restructuring of MOFs during the OER process suggest that what truly matters at heterogeneous interfaces is not merely whether they are initially bonded, but whether these interfaces can sustain electronic coupling under operating conditions and guide the formation of more favorable oxyhydroxide active configurations[126]. Similar findings have been observed in Fe-doped POM-based organic-inorganic hybrid materials, where the environment surrounding metal sites and oxygen vacancies can be further reshaped, thereby simultaneously improving intermediate adsorption, conductivity, and stability; Taking Fe-POMOC as an example, Fe doping induces the formation of more oxygen vacancies and optimizes the distribution of active sites on the surface, enabling the system to achieve an overpotential of 244 mV at 10 mA cm<sup>-2</sup> and a Tafel slope of 45 mV dec<sup>-1</sup> in 1 M KOH, with activity already surpassing that of commercial RuO<sub>2</sub> (255 mV at 10 mA cm<sup>-2</sup>), indicating that the synergistic remodeling of adjacent metal sites and defect environments at the POM-based hybrid interface can effectively translate into improved OER kinetics and durability[127]. Therefore, the true value of POM at the interface of MOFs or metal hydroxides does not lie primarily in the amount of independent catalytic current it contributes, but rather in its ability to integrate different metal centers and support nodes into a single reactive electronic network through bridging, coordination, and electron buffering.

#### 4.4 POM-induced pre-catalyst-active phase transition

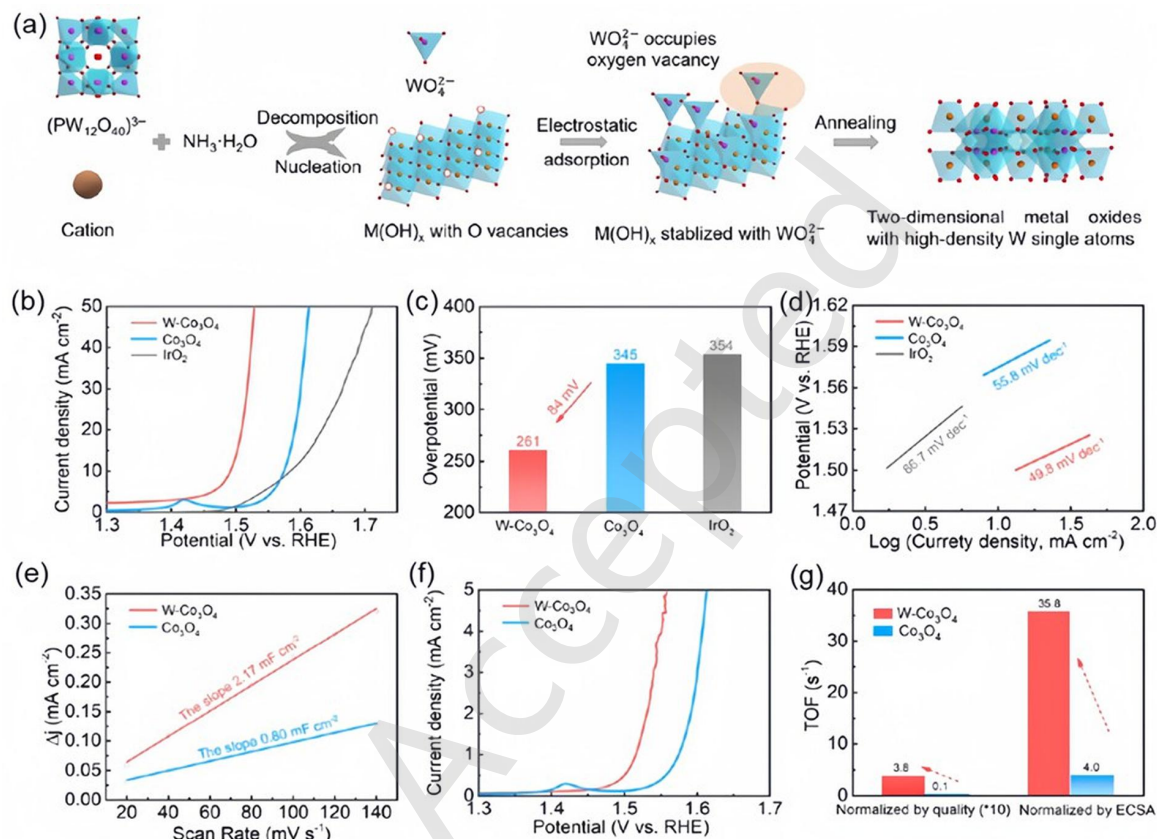
Building on the previous section's discussion of electronic coupling at heterogeneous interfaces, the deeper role of POM in many OER composite systems goes beyond merely altering the electronic state of the interface at a given moment, it further defines when the precursor catalyst begins to activate, the pathways along which it undergoes restructuring, and the final working state in which it stabilizes. Recent research has characterized this phenomenon as "progressivity" in OER electrocatalysis,

meaning that the continuous improvement in catalytic performance is often closely linked to surface oxidation, localized deprotonation, and the gradual generation of active sites[128]. This dynamic evolution is particularly characteristic of POM systems, as POM can serve both as a multi-electron buffer unit to stabilize highly reactive intermediate structures and as a pre-organized metal-oxygen cluster precursor to participate in the formation of new active phases[129]. For example, pH-triggered decomposition of Keggin-type [PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> can generate WO<sub>4</sub><sup>2-</sup> species that are captured by oxygen vacancies in newly nucleated Co(OH)<sub>x</sub>, thereby producing a high-density W single-atom precursor and suppressing the collapse of the ultrathin hydroxide intermediate. After annealing, this precursor evolves into two-dimensional W-Co<sub>3</sub>O<sub>4</sub>, showing that POM-derived oxo-anion units are not merely deposited on the catalyst surface but can directly participate in precursor stabilization, structural preorganization, and the subsequent generation of the active oxide/oxyhydroxide interface. As shown in Fig. 14, the resulting W-Co<sub>3</sub>O<sub>4</sub> exhibits an  $\eta_{10}$  of 261 mV in alkaline electrolyte, 84 mV lower than that of pure Co<sub>3</sub>O<sub>4</sub>, together with a lower Tafel slope and markedly higher ECSA-normalized activity and TOF, indicating simultaneous enhancement of both apparent and intrinsic OER performance. Mechanistically, the anchored W species strengthen OH<sup>-</sup> adsorption and distort the local Co-O coordination environment, thereby facilitating the conversion of the spinel surface into a more active oxyhydroxide working state. The catalyst further maintains stable OER operation for over 290 h at 10 mA cm<sup>-2</sup>, underscoring that POM-derived units can function as genuine reconstruction triggers rather than passive additives[130]. Furthermore, by leveraging pH-triggered POM decomposition and an oxygen vacancy anchoring strategy, high-density tungsten single atoms can be incorporated into two-dimensional spinel oxides. This not only enhances OH<sup>-</sup> adsorption but also actively disrupts the surface structural integrity, ultimately transforming the material into a more active oxyhydroxide working phase. This suggests that POM derivatives can even serve directly as "restructuring triggers"[131]. In a relatively mild yet equally representative pathway, the wet etching of NiMoO<sub>4</sub>@NF with PTA/PMA not only introduced Ni/Mo vacancies and electronic restructuring but was also accompanied by significant Mo loss and an increase in Ni valence following OER, indicating that the role of POM extends beyond the pretreatment stage and further dictates the formation mechanism of subsequent NiOOH-type active phases. The resulting PTA&PMA/NiMoO<sub>4</sub>@NF achieves 10 mA cm<sup>-2</sup> in 1 M KOH at just 200 mV and 100 mA cm<sup>-2</sup> at only 230 mV, with a Tafel slope of 32.8 mV dec<sup>-1</sup>, and can operate stably at 10 mA cm<sup>-2</sup> for 24 hours. More importantly, characterization of the samples after OER revealed significant loss of Mo, which was nearly depleted, while the Ni 2p peak shifted and the Ni<sup>3+</sup>/Ni<sup>2+</sup> ratio increased to 4.5. The authors



concluded that this facilitates the formation of NiOOH during the OER process[131]. A similar precursor-to-working phase logic is also carried forward in the latest POM-derived self-supporting porous microcolumn electrodes: the pre-assembled POM metal-oxygen clusters no longer serve merely as synthesis templates but are directly transformed into

self-supporting reaction interfaces conducive to OER[132]. Therefore, for OER systems involving POM, the more appropriate question is no longer “Does POM accompany restructuring?”, but rather “How does POM determine the starting point, path, extent, and final stable active phase of restructuring”.



**Figure 14** (a) A pH-triggered decomposition strategy of Keggin clusters enables high-density W single-atom anchoring via oxygen vacancies in metal hydroxide nuclei. (b-d) iR-corrected polarization curves, overpotentials at 10 mA cm<sup>-2</sup>, and Tafel plots of W-Co<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>, and IrO<sub>2</sub>. (e) CV current density versus scan rate for W-Co<sub>3</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub> (slope equals twice C<sub>dl</sub>). (f) ECSA-normalized iR-corrected polarization curves. (g) Mass- and ECSA-normalized TOFs at 1.58 V. Adapted with permission from Ref. [130], © 2025 American Chemical Society.

#### 4.5 Structure–Electronic State–Dynamics Correlation

Simply citing “performance improvements after introducing POM” is rarely sufficient to explain its catalytic role. In POM-involved OER systems, a convincing interpretation should instead be built on a continuous chain linking structural evolution, electronic-state rearrangement, and kinetic response. As discussed above, POM first perturbs the local structural environment by altering interlayer spacing, anchoring modes, vacancy chemistry, or precursor reconstruction pathways, these changes then propagate into redistribution of metal valence states, local charge density, d-electron population, and M–O covalency, and are ultimately manifested as facilitated deprotonation, optimized intermediate adsorption, lower charge-transfer resistance, and improved durability. Recent operando studies have further shown that local coordination geometry is not a static

background but a decisive factor in OER kinetics, and that the actual role of evolving Fe sites in Ni(Fe) oxyhydroxides can only be reliably established when operando spectroscopy is combined with theoretical analysis[133, 134]. On this basis, the role of POM as an interface modifier should be evaluated not by the empirical observation that “activity improves after addition”, but by whether its introduction can be causally connected to a measurable change in the reactivity of neighboring active sites. Only when this relationship is clearly established can POM be regarded not simply as an effective additive, but as an interface-regulating unit that can be rationally understood and further engineered. For example, in the PW<sub>12</sub>-modified NiFe-LDH system, the layered LDH framework and nanosheet-assembled morphology are largely retained after modification, whereas PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> preferentially coordinates with exposed Fe sites and progressively tunes the adjacent Ni sites, as reflected by

the positive shift of Ni 2p binding energy and the increase in the  $\text{Ni}^{3+}/\text{Ni}^{2+}$  ratio with treatment time. This interfacial electronic regulation is directly translated into kinetic enhancement, with the optimized NiFe-LDH-PW<sub>12</sub>-12 h sample showing an overpotential lowered by about 68 mV relative to pristine NiFe-LDH, together with faster electron transfer, improved reaction kinetics, and stable operation over 40 h, demonstrating that POM here functions as a fine electronic regulator rather than a passive surface additive[75]. As illustrated in Fig. 15, PW<sub>12</sub> was introduced into the preformed NiFe-LDH through a post-treatment process, and the electrocatalytic performance varied systematically with the modification time. The optimized NiFe-LDH-PW<sub>12</sub>-12 h sample exhibited enhanced OER activity and maintained stable current output for 40 h, supporting the correlation between PW<sub>12</sub>-induced interfacial regulation and improved catalytic kinetics. Likewise, when Anderson-type FeMo<sub>6</sub> is anchored on a Ni-MOF surface, interface-directed electron transfer promotes the formation of high-valent Ni species and accelerates the conversion of \*OH into subsequent oxygen-containing intermediates, indicating that host-guest coupling can sustain electronically effective interfaces during operation rather than serving as a static structural assembly[109]. Similarly, in Fe<sub>2</sub>Mo-NiS/Ni<sub>9</sub>S<sub>8</sub>/NF derived from a POM-MOF precursor, the contribution of POM is not exhausted at the precursor stage, but extends to the construction of an interface-rich heterostructure with measurable interfacial electronic-state changes, so that structural reorganization, electronic regulation, and kinetic improvement remain tightly correlated within a single mechanistic framework[110]. Taken together, these examples show that the interface-regulating role of POM becomes truly interpretable only when structural perturbation, electronic modulation, and catalytic response are discussed within the same chain of evidence.

Accordingly, “electron sponge”, “interfacial electron coupling,” and “charge redistribution” are used here only as descriptive shorthand. A mechanistic assignment requires convergent evidence from X-ray photoelectron spectroscopy (XPS) and X-ray absorption near-edge structure (XANES) valence shifts, Bader or differential charge-density analysis, PDOS/frontier-orbital overlap, EXAFS-derived M-O-POM coordination, and changes in  $\Delta G_{\text{OH}^*}$ ,  $\Delta G_{\text{O}^*}$ , or  $\Delta G_{\text{OOH}^*}$  that correlate with kinetic metrics. Although these studies fall outside the scope of POM-OER research, they provide representative examples of how qualitative electronic-regulation concepts can be quantitatively substantiated. Asymmetrically coordinated dual-atom sites have been correlated with intermetallic electronic coupling, intermediate adsorption, and reaction barriers through in situ X-ray absorption spectroscopy and density functional theory calculations[135]. Likewise, defect-engineered single-atom interfaces have been used to establish a direct relationship between metal-support frontier-orbital interactions, orbital regulation, adsorption energetics, and catalytic performance[136]. For POM-OER systems, quantitative attribution remains difficult because potential-driven leaching/reconstruction, heterogeneous anchoring, and coexistence of intact clusters with derived oxyhydroxides obscure the location and magnitude of charge transfer. Table 4 therefore summarizes the minimum descriptor set required to evaluate POM-induced electronic regulation, covering electronic states, interfacial bonding, adsorption energetics, structural reconstruction, and device-level relevance. Table 5 further compiles representative DFT models and quantitative energetic descriptors for different POM-regulated OER systems. Because the reported active sites, working-state models, and computational protocols differ, direct comparison should be restricted to systems within the same model family.

**Table 4** Minimum descriptor set for comparing POM-induced electronic regulation.

| Descriptor level               | Recommended evidence                                                                                                                                            | Purpose                                                                                    | Ref.       |
|--------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|------------|
| Electronic state               | XPS/XANES shifts; metal valence ratios; d-band center/filling; PDOS; Bader charge differences                                                                   | Determines whether POM perturbs the intrinsic activity of adjacent metal sites.            | [137, 138] |
| Interfacial bonding            | M-O-POM bond lengths; EXAFS coordination numbers; Raman/FTIR bridge vibrations; differential charge density                                                     | Clarifies whether the cluster is physically mixed, weakly adsorbed, or chemically coupled. | [139]      |
| Adsorption/reaction energetics | $\Delta G_{\text{OH}^*}$ , $\Delta G_{\text{O}^*}$ , or $\Delta G_{\text{OOH}^*}$ ; potential-determining step; theoretical overpotential; kinetic isotope data | Links electronic perturbation to OER rate-limiting steps.                                  | [140, 141] |
| Reconstruct ion and retention  | Operando Raman/FTIR/XAS; ICP-MS/ICP-OES; post-test XPS depth profiling; TEM/SEM after durability                                                                | Distinguishes molecular retention, guided reconstruction, and leaching/deactivation.       | [139]      |
| Device relevance               | Mass loading; sheet/contact resistance; ionomer compatibility; voltage decay; Faradaic efficiency; gas crossover                                                | Tests whether molecular/interface advantages survive MEA or electrolyzer operation.        | [142]      |

**Table 5** Model-resolved DFT comparison of POM-regulated OER energetics and cross-subtype evidence boundaries.

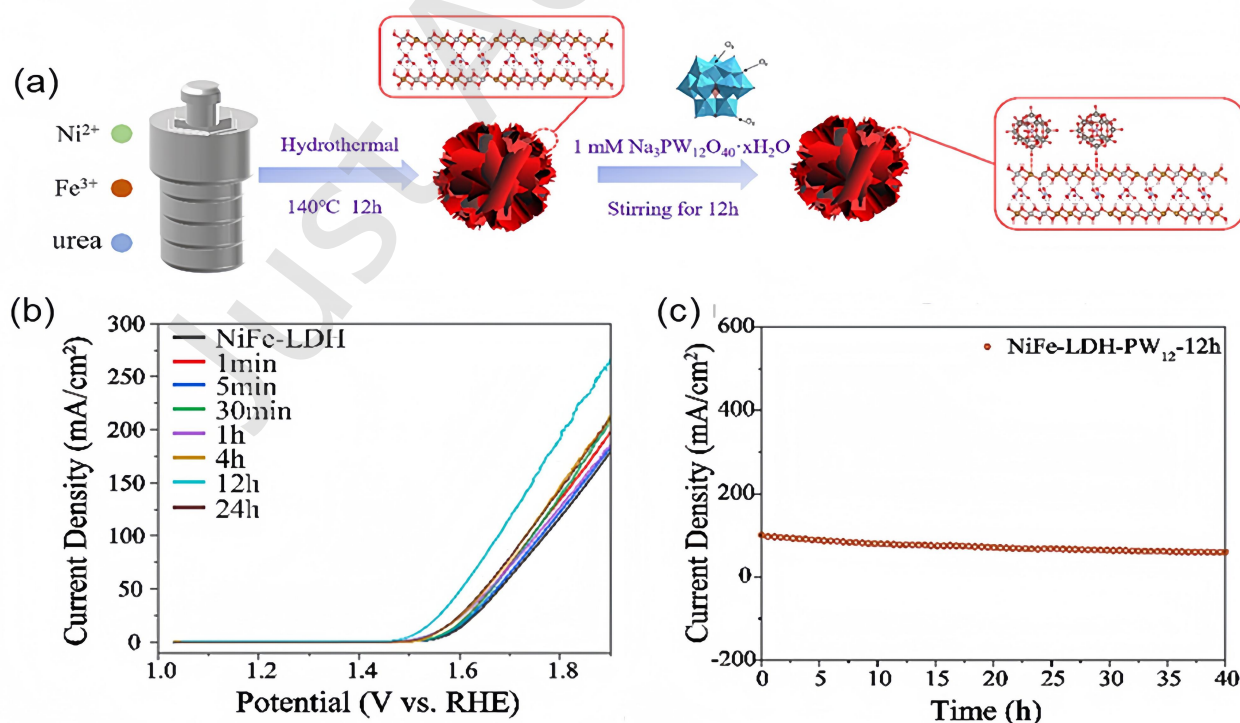
| POM subtype / representative model                                                                         | Model boundary and active site                                                                                                                                                            | OER energetics (eV)                                                                                                                    | Quantitative electronic descriptor / mechanistic implication                                                                                                                      | Ref.  |
|------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|
| No-POM reference: $\gamma$ -NiFeOOH-derived NiFe LDH                                                       | (001) surface; O bridge between Ni and Fe; same DFT+U protocol as the PMo <sub>12</sub> -derived model.                                                                                   | $\Delta G_1/\Delta G_2/\Delta G_3/\Delta G_4 = 0.80/2.02/1.37/0.73$ ; max = 2.02; $\eta_{\text{DFT}} = 0.79$ ; PDS: *OH → *O.          | d-band centers: Fe -2.97, Ni -3.05. Internal baseline for evaluating the PMo <sub>12</sub> -derived interface.                                                                    | [143] |
| Keggin-derived PMo <sub>12</sub> interface: NiFe LDH-PMo <sub>12</sub>                                     | Working-state model contains PMo <sub>12</sub> -derived MoO <sub>4</sub> <sup>2-</sup> plus an O vacancy on $\gamma$ -NiFeOOH, rather than an intact molecular PMo <sub>12</sub> cluster. | $\Delta G_1/\Delta G_2/\Delta G_3/\Delta G_4 = 0.39/1.45/1.57/1.51$ ; max = 1.57; $\eta_{\text{DFT}} = 0.34$ ; PDS: *O → *OOH.         | d-band centers: Fe -2.42, Ni -3.04. MoO <sub>4</sub> <sup>2-</sup> /V <sub>o</sub> cooperation balances *OH and *O binding and lowers the theoretical overpotential by 0.45 V.    | [143] |
| Saturated Keggin PTA intercalation: NiFe-LDH → NiFe-LDH-PTA                                                | NiFe-LDH host with interlayer H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> ; host active site retained in the calculation.                                                             | NiFe-LDH: 0.58/2.08/0.95/1.31; PTA: 0.42/1.42/1.67/1.41. max: 2.08 → 1.67; $\eta_{\text{DFT}}$ : 0.85 → 0.44.                          | The PDS shifts from *OH → *O to *O → *OOH, showing that PTA redistributes rather than uniformly weakens all intermediate binding.                                                 | [106] |
| Keggin PW <sub>12</sub> docked on CoFeOOH                                                                  | PW <sub>12</sub> preferentially docks at Fe; adjacent Co is used for OH <sup>-</sup> /Cl <sup>-</sup> competitive adsorption.                                                             | $\Delta G_{\text{OH}^*}$ : 1.087 → -0.836; *O → *OOH barrier: 2.487 → 2.425; $\Delta G_{\text{Cl}^*} = -0.226$ ; ClOR barrier = 2.917. | 0.88 e transfers from CoFeOOH to PW <sub>12</sub> ; Co d-band center -1.583 → -1.486. Quantitatively links charge transfer to OH <sup>-</sup> preference and chloride resistance. | [144] |
| Fe-substituted Keggin: Ni(OH) <sub>2</sub> -PMo <sub>11</sub> Fe vs Ni(OH) <sub>2</sub> -PMo <sub>12</sub> | Sub-1 nm Ni(OH) <sub>2</sub> nanowires templated by PMo <sub>11</sub> Fe or PMo <sub>12</sub> ; Ni remains the primary OER site.                                                          | Largest uphill step: 1.95 (PMo <sub>11</sub> Fe) vs 2.93 (PMo <sub>12</sub> ).                                                         | Differential charge density and PDOS show Fe-induced electronic modulation of Ni and stabilization of Ni-OOH-type intermediates.                                                  | [106] |
| V-substituted Keggin: PMo <sub>9</sub> V <sub>3</sub> -FNCO                                                | PMo <sub>9</sub> V <sub>3</sub> coupled to Fe <sub>0.2</sub> Ni <sub>0.8</sub> Co <sub>2</sub> O <sub>4</sub> ; surface-water adsorption models constructed for FNCO and POM-FNCO.        | H <sub>2</sub> O → *OH barrier = 1.74; overall OER $\Delta G = 1.00$ vs 4.64 for FNCO without POM.                                     | The substituted Keggin unit changes the first water-oxidation step and makes the overall pathway thermodynamically more favorable.                                                | [106] |

|                                                      |                                                                                                                                       |                                                                                                                                    |                                                                                                                                               |
|------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------|
| Monolacunary Keggin SiW <sub>11</sub> : NiFe LDH-POM | K <sub>8</sub> [SiW <sub>11</sub> O <sub>39</sub> ] incorporated in NiFe-LDH; W-containing interfacial model used for *OH adsorption. | Reported *OH <sup>-</sup> related barrier decreases from about 1.79 to about 1.30                                                  | Provides a quantitative single-intermediate result for a lacunary [16, interface, but cannot support a full topology ranking. 145]            |
| Dawson-type Ni/Cu sandwich polyoxotungstates         | Molecular Dawson sandwich models; DFT treats protonation, frontier orbitals and stepwise reduction, not an OER surface interface.     | LUMO: -2.73 (Ni-only) and ~-3.0 to -3.2 (Cu-containing); protonated 12H form: -4.48. E' <sub>red</sub> : -1.485 → -0.086 V vs SCE. | Quantifies proton-coupled electron acceptance and Cu-centered charge localization. No full interfacial *OH/*O/*OOH dataset was located. [146] |

Note:  $\Delta G_1$ - $\Delta G_4$  correspond to  $^* \rightarrow ^*\text{OH}$ ,  $^*\text{OH} \rightarrow ^*\text{O}$ ,  $^*\text{O} \rightarrow ^*\text{OOH}$ , and  $^*\text{OOH} \rightarrow \text{O}_2$ .  $\eta_{\text{DFT}} = \max(\Delta G_i)/e - 1.23 \text{ V}$ , ( $i = 1-4$ ). Rows with complete four-step sequences can be compared only within the same model family. Partial adsorption/barrier data and molecular-redox descriptors are retained because they are quantitative, but they are not used to rank POM skeletons.

Given that operando spectroscopic evidence is often discussed in a fragmented manner, the characteristic Raman, XAS, and ATR-IR signals are summarized here as a practical fingerprint matrix for evaluating POM-induced reconstruction in POM-LDH and POM-MOF electrocatalysts. This table is not intended to assign active species on the basis of an isolated vibrational band or a single absorption-edge shift. Instead, it provides a potential-resolved framework for correlating multiple

spectroscopic signatures, thereby distinguishing retained POM clusters, interfacial POM-derived residues, host-framework reconstruction, and the formation of oxyhydroxide-derived active phases[137, 147-152]. As summarized in Table 6, the combined evolution of POM-related bands, host-metal valence and coordination, ligand signals, and oxyhydroxide fingerprints provides a practical basis for assigning molecular, hybrid, or reconstructed working states.



**Figure 15** (a) Schematic illustration of the synthesis of NiFe-LDH-PW12-12 h. (b) Linear sweep voltammetry curves. (c) Chronoamperometric current density-time curve of NiFe-LDH-PW12-12 h over 40 h. Each measurement was repeated at least three times, and the corresponding error estimates are provided in the Supporting Information. Adapted with permission from Ref. [75], © 2023 Elsevier Inc.

**Table 6** Standardized in-situ spectral fingerprints of POM-induced restructuring in POM-LDH and POM-MOF catalysts

| System/potential window                   | Operando Raman                                                                                   | XAS/XANES/EXAFS                                                            | ATR-IR/FTIR                                                                        | Working-state interpretation                                                        |
|-------------------------------------------|--------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| POM-LDH, OCPlow bias                      | POM M=O/M-O-M bands retained; weak LDH M-O/M-OH[147, 153, 154].                                  | Ni/Co/Fe near initial hydroxide state; Mo/W/P shells retained[137, 155].   | POM M=O/M-O-M and OH/H <sub>2</sub> O bands retained.                              | Anchored POM remains; charge/microenvironment regulator[151, 153, 154, 156].        |
| POM-LDH, OER onset /moderate bias         | MOOH bands emerge (ca. 470-560 and 650-700 cm <sup>-1</sup> ); POM bands shift/weaken[150, 157]. | Ni/Co/Fe edges shift positive; shorter M-O and M-M scattering appear[158]. | M-OH/OH/H <sub>2</sub> O and possible *OOH increase; POM M-O weakens.              | Host oxidizes to MOOH; POM partly retained at interface[147, 150, 157, 159].        |
| POM-LDH, high potential/long OER          | MOOH/oxide bands dominate; residual Mo/W-O indicates retained POM[155].                          | High-valence host metals, Mo/W intensity/EXAFS tracks retention or loss.   | POM M-O retained or lost; OH/M-OH features dominate[148].                          | Hybrid active state or POM-derived precursor; verify by ICP and mapping.            |
| POM-MOF, low bias/pre-activation          | Ligand, metal-node and POM bands coexist; no strong MOOH.                                        | MOF/POM coordination largely retained.                                     | Ligand bands and POM M-O vibrations coexist.                                       | Intact confined molecular/interfacial precursor.                                    |
| POM-MOF, activation/reconstruction window | Ligand bands decay; Co/Ni/FeOOH bands grow; weak POM residues may remain[152].                   | Co/Ni/Fe oxidize; M-N/M-O-ligand converts to M-O/M-M.                      | Ligand C=N/C-O/C=O or carboxylate decreases; OH/M-OH increases.                    | MOF reconstructs; POM guides charge redistribution, stabilization and oxo bridges.  |
| General diagnostic rule                   | POM+MOOH coexis=hybrid active state; POM loss=precursor route.                                   | Combine valence, retention, M-O-POM distances.                             | Track POM M-O plus OH/H <sub>2</sub> O/*OH/*OOH at identical potentials[148, 154]. | Assign mechanisms only with Raman/XAS/IR, dissolution and stability agreement[160]. |

For POM-LDH systems, the central diagnostic criterion is whether characteristic POM-related vibrations and Mo/W/P signatures are retained while Ni-, Co-, or Fe-based oxyhydroxide features progressively emerge under OER-relevant potentials. In contrast, for POM-MOF systems, the key mechanistic issue is whether linker degradation and metal-node oxidation are accompanied by persistent POM-derived oxo species or M-O-POM interfacial motifs. Therefore, operando Raman, XAS, and ATR-IR results should be interpreted within the same potential or current-density window. Where feasible, these spectroscopic observations should also be correlated with ICP-based dissolution analysis, so as to avoid overestimating either the complete preservation of molecular POM units or their full conversion into reconstructed active phases.

## 5 The Role of POM in Demanding OER Applications: Stability, Selectivity, and Device

### Implementation

In contrast to the previous three chapters, which primarily focused on the sources of activity, interfacial regulation, and restructuring behavior, this chapter examines whether POM can still provide sustainable catalytic benefits under harsh operating conditions. For practical water electrolysis systems, the criteria for evaluating the performance of anode materials have long extended beyond overpotential values at low current densities. Instead, they depend on the material's ability to maintain critical active sites during high-current operation, resist corrosion and side-reaction interference in complex media, and sustain long-term stable output under membrane electrode assembly (MEA) and electrolyzer conditions[161-163]. This is particularly important for POM. Although POM systems possess a well-defined structure and tunable electronic properties at the molecular level, without sufficiently robust interfacial anchoring and structural support, these advantages may

not be maintained under conditions of continuous oxidation and engineered current[164]. Conversely, when POM can be stably incorporated into the working electrode through interfacial anchoring, local coordination regulation, and optimization of the mass transfer environment, its role is no longer limited to enhancing activity at the laboratory scale, but may further manifest in more application-relevant outcomes such as the preservation of active sites, adaptation to complex media, and extended device lifetime[124]. Therefore, the focus of this chapter is not on whether POM “can offer a slight performance boost”, but rather on whether it can truly translate the structural and electronic effects described earlier into advantages in terms of stability, selectivity, and device usability under conditions that more closely resemble real-world applications.

### 5.1 Resistance to leaching and stability of active sites

Under high-potential and high-current OER conditions, catalyst deactivation should be regarded as a coupled process involving host-metal dissolution, POM loss, phase reconstruction, and catalyst-layer relaxation rather than as a simple decay in current density. This issue is particularly critical for POM-based electrodes because many POM anions are intrinsically soluble, highly charged, and retained at interfaces through electrostatic interaction, host-guest confinement, or coordination bonding. At ampere-scale current densities, continuous oxygen bubbling, local pH gradients, electrolyte renewal, ionomer swelling, and mechanical scouring can weaken these interactions and promote the migration of W/Mo/V/P-containing POM units from the catalytic layer. Once POM leaching occurs, the apparent OER activity may no longer reflect the designed POM-regulated interface, but instead originate from reconstructed oxyhydroxide or oxide phases. Therefore, leaching should be evaluated as a mechanistic variable that determines the real working state of POM-OER electrodes, especially under industrially relevant electrolysis conditions[88, 165].

Accordingly, stability assessment should not rely solely on chronopotentiometry or post-test polarization curves. A more reliable protocol should combine electrolyte analysis by online or post-electrolysis ICP-MS/OES, time-dependent quantification of W/Mo/V/P and host-metal dissolution, post-mortem XPS depth profiling, cross-sectional SEM/TEM elemental mapping, and operando Raman/XAS/FTIR tracking of the retained POM fingerprint and reconstructed active phase. Recent studies on POM-intercalated LDH systems further show that the pH stability window of the POM framework must be explicitly considered; otherwise, activity enhancement observed in strong alkaline media may be incorrectly attributed to intact POM clusters while the actual active layer has evolved into confined cobalt or transition-metal oxyhydroxide/oxide species[141,142].

From a materials-design perspective, three stabilization strategies are especially relevant. First, covalent grafting

or strong coordination anchoring can convert labile electrostatic adsorption into more robust M-O-POM, C/N-linker-POM, or ligand-bridged interfaces, thereby improving resistance to bubble-induced detachment and electrolyte exchange. Second, interlayer confinement within LDH or layered MOF galleries can restrict lateral migration of POM clusters and simultaneously maintain local ion-transport channels, the ampere-scale performance of PTA-intercalated NiFe-LDH illustrates the importance of combining POM confinement with a conductive and reconstructable host framework. Third, carbon encapsulation, conductive polymer protection, or coupling with graphene/CNT-type networks can reduce direct POM exposure to the bulk electrolyte while compensating for the poor intrinsic conductivity of molecular clusters. However, such encapsulation should remain sufficiently permeable to OH<sup>-</sup> transport and O<sub>2</sub> release, because an overly dense shell may improve retention at the expense of mass transfer[88, 89, 166].

Thus, the mitigation of POM dissolution/leaching should be treated as a prerequisite for translating POM chemistry into practical OER electrodes. For alkaline LDH-based systems, interlayer confinement and strong M-O-POM bonding are generally more suitable; for saline or corrosive media, covalent/coordination anchoring and multi-defense interfacial layers are required, and for high-loading MEA-type catalytic layers, conductive carbon or polymer encapsulation should be optimized together with ionomer compatibility, porosity, and mechanical adhesion. Future POM-OER studies should therefore report both electrochemical durability and quantitative retention of POM-derived elements, enabling a clear distinction between retained-cluster regulation, controlled reconstruction, and uncontrolled leaching-driven deactivation.

### 5.2 Corrosion Resistance and Compatibility with Complex Media

Compared to three-electrode testing under conventional 1 M KOH conditions, OER in complex media provides a better test of whether a catalytic system possesses true robustness. In alkaline seawater, high-salt electrolytes, and unpurified natural water systems, the challenges faced by the catalytic layer extend beyond a mere decrease in reaction rate; they include interface instability resulting from the combined effects of Cl<sup>-</sup> competitive adsorption, active chlorine side reactions, and continuous corrosion. Therefore, the fundamental question this section seeks to address is not whether the catalyst “can function in seawater”, but whether it can minimize Cl<sup>-</sup> induced erosion of critical metal sites and interference with reaction selectivity while maintaining OER activity. Recent studies on direct seawater electrolysis have repeatedly demonstrated that stability in complex media does not depend solely on the corrosion resistance of the material itself, but rather on the interface’s ability to differentially regulate the transport, adsorption, and localized reaction

pathways of  $\text{OH}^-$  and  $\text{Cl}^-$  [167, 168]. In this regard, the POM systems discussed earlier are representative precisely because they do not achieve stability simply by repelling  $\text{Cl}^-$ , but rather by utilizing selective coordination, localized electronic rearrangement, and modulation of the interfacial microenvironment to make the active sites more inclined to maintain the  $\text{OH}^-$  reaction pathway required for OER. In other words, the role of POMs in complex media is not primarily passive isolation in the sense of a “protective layer”, but rather resembles an active reshaping of interfacial adsorption behavior and the local reaction environment. At the same time, recent work in the field of seawater electrolysis reminds us that there are no universal conclusions regarding adaptability to complex media that are independent of specific structures: even when they are equally capable of inhibiting chloride corrosion, the mechanisms relied upon by different systems may stem from ion screening, sacrificial interfacial reorganization, or the construction of multi-defense surfaces [169, 170]. Therefore, a more prudent assessment of POM would be that its effectiveness in complex media depends on whether the interfacial fixation is sufficiently robust, whether the local coordination environment favors the preferential reaction of  $\text{OH}^-$ , and whether the operating conditions remain within the stability window where the synergy between its structure and the interface can be maintained.

### 5.3 High Current Density and Device-Level Performance

High current density and device-level operation warrant separate discussion not merely because the test conditions are more “demanding”, but because they amplify many issues that are not yet significant at low currents. These include insufficient mechanical stability of the catalytic layer, localized mass transfer limitations, bubble coverage, imbalances in polymer wetting and interfacial adhesion, as well as synergistic mismatches between the electrode, membrane, and current collector within the membrane electrode assembly. Therefore, for POM systems, the evidence that is truly meaningful for practical applications is not a lower transient overpotential at a specific current point, but rather whether the advantages in interfacial stability and site retention established under three-electrode conditions can be sustained during ampere-scale output and long-term electrolyzer operation. Recent high-current OER and AEM water electrolysis research has clearly demonstrated that systems capable of advancing to device validation and maintaining long-term stability often require not only sufficiently high activity but also self-supporting or strongly coupled catalytic layer structures, interface bonding methods capable of withstanding continuous bubble scouring, and working interfaces that can maintain effective charge and ion transport within the membrane electrode environment. For example, the industrially scalable NiFe-LDH synthesis route has garnered significant attention not only because

of its high activity at the laboratory scale, but also because its preparation consistency and operational stability have already proven capable of supporting AEM electrolyzer validation [171]. Furthermore, the NiFe system based on functional anion re-intercalation demonstrates that high current stability often depends on the sustained maintenance of localized alkalinity at the electrode and the interfacial microenvironment, rather than simply on higher initial activity [172]. Similarly, recent research on alkaline electrolyzers and AEMWEs has generally emphasized that truly application-ready anode materials must simultaneously meet the requirements of industrial-scale current density, long-term stability, and scalable electrode fabrication routes; this is also where high-current OER research and device research are beginning to truly converge [171, 173-175]. In this sense, the incorporation of the POM system into device evaluation does not merely demonstrate that it “can also be incorporated into an electrolytic cell”, rather, it indicates that the interface regulation, site stabilization, and adaptability to complex media discussed earlier have begun to exert a measurable influence on the membrane electrode assembly and the overall system performance.

For AEM water electrolyzers, POM incorporation must be evaluated together with catalytic-layer architecture. Higher POM content may strengthen electron buffering, metal-site stabilization, and resistance to chloride attack, but it may also dilute the conductive network, increase tortuosity, increase ionomer demand, and weaken adhesion between the catalyst layer and porous transport layer. An optimal POM loading should therefore be identified by simultaneously reporting mass loading, electrochemically active area, sheet resistance, contact resistance, and bubble-removal behavior rather than only the initial overpotential [176-179].

Membrane compatibility is another decisive factor. Negatively charged POM units and POM-derived fragments may interact with cationic AEM ionomers, altering local water uptake,  $\text{OH}^-$  conductivity, and swelling behavior. If the POM is insufficiently immobilized, dissolved W/Mo/P species may migrate toward the membrane and affect ion conductivity or accelerate chemical degradation during long-cycle operation. MEA-level evaluation should therefore include membrane/ionomer compatibility, POM retention after operation, cross-sectional elemental mapping, Faradaic efficiency, and voltage-decay comparison at fixed current density [178-180].

For fair benchmarking, POM-based OER catalysts should be compared using a practical performance matrix rather than a single  $\eta_{10}$  value. At minimum, future reports should include current densities at 100, 500, and 1000  $\text{mA cm}^{-2}$ , cell voltage and decay rate in two-electrode AEMWE or MEA tests, catalyst loading, substrate, electrolyte, temperature, iR-correction method, and post-test evidence for POM retention, metal dissolution, and active-phase reconstruction [181, 182].

For fair benchmarking, POM-based OER systems should

be compared using a medium-resolved performance matrix rather than a single  $\eta_{10}$  value. Table 7 therefore consolidates the electrolyte and test configuration, overpotential at the stated current density, Tafel slope, long-term durability, and electrolyzer/MEA metrics for representative systems in neutral, alkaline,

natural-seawater, and alkaline-seawater media. Unreported values are identified rather than inferred, because direct ranking is meaningful only when current density, temperature, iR correction, catalyst loading, and device configuration are comparable.

**Table 7** Quantitative benchmarking of representative POM-based OER systems across neutral, alkaline, and seawater media.

| System                    | POM subtype/role                                                     | Medium and test configuration                           | Activity benchmark                                                                                            | Durability / device benchmark                                                        | Comparative significance                                                |       |
|---------------------------|----------------------------------------------------------------------|---------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|-------------------------------------------------------------------------|-------|
| POM@ZIF-8                 | Keggin Co-POM; confined molecular catalyst                           | Neutral aqueous electrolyte; three-electrode            | TOF=10.8 mol O <sub>2</sub> (mol Co) <sup>-1</sup> s <sup>-1</sup> ; $\eta_{10}$ and Tafel slope not reported | 1000 CV cycles                                                                       | Neutral-pH molecular benchmark; confinement limits cluster loss         | [183] |
| Sol-gel PTA microspheres  | Keggin PTA; insolubilized sol-gel network                            | pH 7 phosphate buffer; three-electrode on graphite felt | $\eta_{10}$ =397 mV (reported without a fixed j); Tafel=96 mV dec <sup>-1</sup>                               | 24 h at 0.4 V vs reversible hydrogen electrode (RHE); Faradaic efficiency >90%       | Adds conventional kinetic and lifetime metrics under neutral conditions | [184] |
| NiFe-LDH-PTA              | Keggin PTA; interlayer regulator and stabilizer                      | 1 M KOH; three-electrode and AEMWE                      | $\eta_{100}/\eta_{500}/\eta_{1000}$ =22 0 ± 3/291/342 ± 9 mV; Tafel=83.28 mV dec <sup>-1</sup>                | 500 h at 1 A cm <sup>-2</sup> ; AEMWE: 1.93 V at 1 A cm <sup>-2</sup> (60 °C), 170 h | Demonstrates ampere-scale OER and interlayer stabilization              | [64]  |
| MOF@POM                   | Trilacunar y Keggin PW <sub>9</sub> ; grafted MOF-POM superstructure | 1 M KOH; three-electrode and AEMWE                      | $\eta_{10}$ =178 mV; Tafel=27.7 mV dec <sup>-1</sup>                                                          | >5140 h at 2 A cm <sup>-2</sup> ; AEMWE: 1.78 V at 3 A cm <sup>-2</sup> (80 °C)      | Long-duration, high-current benchmark with stabilized Co/Fe sites       | [65]  |
| TFPQ@HO PG                | Preyssler P <sub>5</sub> W <sub>30</sub> ; confined woven thin film  | 1 M KOH; three-electrode                                | $\eta_{10}$ =130 mV; Tafel=35 mV dec <sup>-1</sup> ; TOF=8.55 s <sup>-1</sup>                                 | ≥1000 CV cycles; no detectable P5 leaching                                           | Molecular-cluster confinement combines rapid kinetics with retention    | [76]  |
| FeMoOS/NF                 | Anderson FeMo <sub>6</sub> -derived sulfide/oxide                    | 1 M KOH; self-supported Ni foam electrode               | $\eta_{50}$ =240 mV; Tafel=79 mV dec <sup>-1</sup>                                                            | 80 h at 50 mA cm <sup>-2</sup> ; 1000 CV cycles                                      | Quantifies POM-derived multicomponent reconstruction                    | [68]  |
| Ni-MOF-Fe Mo <sub>6</sub> | Anderson FeMo <sub>6</sub> ; surface electronic regulator            | 1 M KOH; three-electrode                                | $\eta_{10}$ =335 mV; Tafel=96.1 mV dec <sup>-1</sup>                                                          | ~94% current retained after 100 h; $\eta_{10}$ increase=33 mV                        | Links directional charge transfer with long-term surface stability      | [109] |
| Fe-POMOC                  | Fe-doped POM organic-inorganic hybrid                                | 1 M KOH; three-electrode                                | $\eta_{10}$ =244 mV; Tafel=45 mV dec <sup>-1</sup>                                                            | 25 h at 10 mA cm <sup>-2</sup> with negligible decay                                 | Defect and oxygen-vacancy regulation improves intrinsic kinetics        | [127] |

|                              |                                                                                                                       |                                                       |                                                                                                               |                                                                                                                 |                                                                           |       |
|------------------------------|-----------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|-------|
| PTA&PMA/<br>NMO@NF           | Keggin<br>PTA/PMA<br>etching;<br>defect-rich<br>NiMoO <sub>4</sub><br>interface                                       | 1 M KOH;<br>three-electrode;<br>iR-corrected          | $\eta_{10}/\eta_{100}=200/230$<br>mV; Tafel = 32.8 mV<br>dec <sup>-1</sup>                                    | 24 h at 10 mA<br>cm <sup>-2</sup> ; negligible<br>overpotential<br>change                                       | Shows activity<br>gains from<br>dual-POM etching<br>and<br>reconstruction | [185] |
| TFPQ@HO<br>PG                | Preyssler<br>P <sub>5</sub> W <sub>30</sub> ;<br>chloride-tol-<br>erant woven<br>thin film                            | Natural<br>seawater;<br>three-electrode               | $\eta_{10}=490$ mV;<br>Tafel=56 mV dec <sup>-1</sup>                                                          | ≥1000 CV cycles                                                                                                 | Direct<br>molecular-POM<br>benchmark in<br>untreated<br>seawater          | [76]  |
| PW <sub>12</sub> -CoFe       | Keggin<br>PW <sub>12</sub> ;<br>Fe-site-select<br>ive surface<br>docking                                              | 1 M<br>KOH+seawater;<br>three-electrode<br>and MEA    | $\eta_{100}/\eta_{500}/\eta_{1000}=26$<br>5/325/368 mV; Tafel<br>slope not reported in<br>the cited benchmark | >1300 h at 1 A<br>cm <sup>-2</sup> ; >600 h at 2 A<br>cm <sup>-2</sup> ; MEA >1000 h<br>at 1 A cm <sup>-2</sup> | High-current<br>chloride<br>resistance with<br>device-level<br>validation | [186] |
| R-MOF-Ta <sub>6</sub><br>/NF | Lindqvist<br>[Ta <sub>6</sub> O <sub>19</sub> ] <sup>8-</sup> ;<br>interfacial<br>OH <sup>-</sup> supply<br>regulator | Alkaline<br>seawater;<br>three-electrode<br>and AEMWE | $\eta_{10}=235$ mV;<br>Tafel=80.5 mV dec <sup>-1</sup>                                                        | AEMWE: 2.18 V at<br>500 mA cm <sup>-2</sup> ; 195 h<br>at 200 mA cm <sup>-2</sup>                               | Quantifies<br>H-bond-network<br>regulation and<br>seawater<br>durability  | [124] |

Note:  $\eta$  denotes the overpotential measured at  $j$  mA cm<sup>-2</sup>. Molecular neutral-pH systems may report TOF instead of  $\eta_{10}$ ; missing quantities are stated explicitly and were not estimated. Values should be compared only within the stated electrolyte, current density, temperature, catalyst loading, iR-correction protocol, and test configuration, CV-cycle stability and time-based durability are not directly interchangeable.

#### 5.4 From laboratory catalysts to practical electrodes

Taking the above results together, it is evident that the significance of POM in OER systems is undergoing a marked shift. Early research focused more on whether POM, as a molecular cluster, possessed significant activity, whereas in studies closer to practical applications, the value of POM is increasingly recognized for its role in supporting electrode interface stability, catalytic layer integrity, and device operational lifespan. For water electrolysis systems, this shift represents not merely a shift in research focus, but a change in the evaluation criteria themselves: as the scope of investigation expands from powdered catalysts to membrane electrodes and electrolyzers, the factors determining a material's true application potential are often no longer limited to its activity at a single current density, but rather include electrode construction methods, interfacial coupling strength, membrane-polymer compatibility, mass transfer pathways, and mechanical and chemical stability during continuous operation[143, 187]. Therefore, the significance of the intercalation, oriented docking, and interfacial grafting discussed earlier should not be understood merely as "improving catalytic performance", but rather as transforming the structural and electronic advantages of POM into more stable working interfaces to varying degrees. Recent research on water electrolysis membrane electrode design, the development of high-current electrodes, and the commercialization bottlenecks of AEMs all emphasize the same point: what truly determines whether a material can transition from

the laboratory to practical application is not the activity of a single catalytic site itself, but whether this activity can be embedded within a manufacturable, scalable, and long-lasting electrode-membrane system[188, 189]. In this sense, the most promising prospects for POM in OER are no longer limited to whether its activity can be further enhanced, but rather which POM structures are best suited to serve as stabilizers at the device level, which interfacial bonding methods are more conducive to long-term operation, and how these advantages can be further integrated with membrane-electrode assembly preparation, carrier engineering, and operating condition characterization.

#### 6 Summary of the Mechanism, Challenges, and Outlook

As discussed above, the function of POMs in OER can no longer be reduced to a single, static definition. In structurally well-defined molecular cluster systems, POMs may act directly as molecular-scale active units; in more complex heterogeneous catalysts, however, their contribution is more often reflected in interfacial electronic regulation, local structural reorganization, guidance of precatalyst-to-active-phase evolution, and stabilization of key metal sites during operation[28, 190]. More importantly, under high-current, complex-medium, and device-relevant conditions, the role of POMs extends beyond activity enhancement alone and increasingly concerns the maintenance of the active-state interface. By stabilizing local coordination environments, buffering charge accumulation, and modulating competitive

adsorption, POMs help preserve the structural and electronic features required for sustained OER. From this perspective, the value of POMs is best understood along a continuous framework of molecular structure design-interfacial coupling regulation-active-state stabilization, rather than as a collection of isolated functions. This broader understanding also helps define the key directions for future development of POM-based electrocatalysts. As summarized in Fig. 16, progress in this field now depends not only on the rational design of POM structures and composites, but also on deeper insight into POM-support interactions, improved durability and long-term stability, better control over selectivity and mass transport, and the use of advanced in situ/operando characterization to clarify structure-activity relationships under working conditions. Looking further ahead, data-driven approaches, integration into renewable-energy devices, and scale-up with cost and commercialization considerations will become increasingly important. Therefore, the significance of POM research lies not merely in identifying new active materials, but in establishing a representative chemical platform for understanding how activity originates, how

structures evolve under reaction conditions, and how catalyst design can be translated toward practical OER systems.

### 6.1 The Central Role of POM in OER

The contribution of POMs can be resolved at three connected levels. At the molecular level, their well-defined metal-oxygen frameworks provide traceable redox and coordination sites for analyzing electron transfer and elementary OER steps[191]. At the interface level, intercalation, grafting, confinement, and reconstruction couple POM units with Ni-, Fe-, or Co-based hosts, thereby modifying local valence states, deprotonation, intermediate adsorption, and charge transport[192]. At the operational level, robust POM-host bonding can suppress metal/POM loss, regulate competitive  $\text{OH}^-/\text{Cl}^-$  adsorption, and maintain active interfaces under high current density or saline conditions[193]. POMs should therefore be regarded as programmable chemical modules that connect molecular structure, interfacial regulation, active-phase evolution, and device durability, rather than as either isolated molecular catalysts or passive additives[194].



**Figure 16** Potential challenges and future outlook of POM-based electrocatalysts for electrochemical water splitting (EWS). Reproduced with permission from Ref. [28], under the CC BY-NC-ND 4.0 license.

### 6.2 Major Challenges and an Integrated Research Framework

Four issues currently limit the establishment of generalizable design principles. First, the true active state remains uncertain because intact clusters, partially retained POM–host interfaces, and derived oxides or oxyhydroxides may coexist or evolve sequentially during operation[195, 196]. Second, POM stability strongly depends on electrolyte composition, potential, current density, immobilization strength, and operating time; consequently, a structure that is stable at open circuit may hydrolyze, leach, or reconstruct under sustained OER bias. Third, molecular-level advantages do not automatically

persist in thick catalyst layers or membrane-electrode assemblies, where conductivity, mass transport, ionomer compatibility, adhesion, and gas removal become decisive[197, 198]. Fourth, the field still lacks a transferable structure-function relationship capable of identifying the appropriate POM–host combination for a specific operating window.

Addressing these limitations requires operation-resolved evidence rather than post-test inference. Active-state assignment should combine potential-dependent Raman, Fourier-transform infrared spectroscopy, and X-ray absorption spectroscopy with quantitative elemental mass balance, dissolution analysis, rinse-transfer or selective-removal controls, and matched

electrochemical kinetics. Electronic regulation should be supported by measurable descriptors, including valence shifts, M–O–POM coordination, Bader charge, orbital overlap, and adsorption free energies, with uncertainty explicitly reported [199, 200]. The central objective is to establish a causal relationship linking POM structure and interfacial bonding to working-state evolution, reaction kinetics, and long-term device stability.

To address these challenges and integrate data-driven analysis with mechanistic understanding, future studies should adopt a closed-loop workflow. Standardized datasets should connect POM topology and composition, host structure, interfacial bonding, synthesis parameters, operating conditions, operando descriptors, dissolution behavior, and device-level performance. Interpretable statistical or machine-learning models can then identify key descriptors and generate hypotheses regarding suitable POM–host combinations and operating windows. These predictions should be validated through parallel intercalation, grafting, and confinement synthesis, rapid electrochemical screening, accelerated durability testing, online inductively coupled plasma mass spectrometry or inductively coupled plasma optical emission spectrometry, operando spectroscopy, and evaluation at the membrane-electrode-assembly level. Traceable electronic laboratory notebook and laboratory information management system records, together with Findable, Accessible, Interoperable, and Reusable data practices, should return validated results to the model and close the design loop [201, 202]. Multi-objective optimization should balance activity with POM retention or controlled reconstruction, conductivity at practical loading, mass transport, long-term stability, and device compatibility.

### 6.3 Data-driven POM structural prediction and high-throughput experimental validation

The compositional and structural diversity of POMs makes conventional trial-and-error screening inefficient. Future datasets should encode POM-specific information, including topology, addenda and heteroatom identity, vacancy or substitution pattern, formal charge, counter-cations, immobilization mode, host matrix, and pH-potential stability, together with synthesis, performance, leaching, reconstruction, and device-level data [145, 203–205].

These inputs should be linked to physically meaningful targets such as adsorption energetics, interfacial binding, reconstructed active phase, conductivity, and membrane compatibility.

Descriptor-based models, graph neural networks, Bayesian optimization, SHapley Additive exPlanations (SHAP), and uncertainty quantification can then identify promising POM–host combinations without reducing selection to a black-box activity ranking. Model outputs should remain interpretable in terms of working-state descriptors and should be used to prioritize experiments rather than replace mechanistic validation.

Predictions should be tested through parallel intercalation, grafting, and confinement synthesis, rapid electrochemical screening, accelerated durability measurements, online inductively coupled plasma mass spectrometry or inductively coupled plasma optical emission spectrometry, operando spectroscopy, and membrane-electrode-assembly-level evaluation. Traceable electronic laboratory notebook and laboratory information management system records, together with Findable, Accessible, Interoperable, and Reusable data practices, are needed to return validated results to the model and close the design loop [206, 207]. Optimization should be multi-objective, balancing activity with POM retention or controlled reconstruction, high-loading conductivity, mass transport, long-term stability, and device compatibility.

### 6.4 Outlook for the Future

Near-term progress should focus on four concrete directions. First, establish pH-potential-time stability maps for representative POM families and report molecular, hybrid, and derived working states separately. Second, replace qualitative claims of charge redistribution with quantitative spectroscopic and theoretical descriptor chains. Third, develop standardized benchmarks at 100–1000 mA cm<sup>−2</sup> that report catalyst loading, iR correction, dissolution, Faradaic efficiency, voltage decay, and post-test reconstruction. Fourth, validate promising systems in high-loading electrodes, saline media, MEAs, and AEM water electrolyzers, while integrating data-driven selection with operando feedback [205]. These priorities shift the field from isolated performance gains toward predictable POM–host design within defined operating windows and, ultimately, durable and scalable anodes.

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### Declaration of conflicting interests

The authors declare no conflicting interests regarding the

content of this article.

## Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Supplementary Materials. Additional data related to this paper may be requested from the corresponding author upon request.

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