



## Recent progress of rare earth element electrocatalysts: The critical role of electronic configuration regulation

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*Nano Research Energy*, **Just Accepted Manuscript** • <https://doi.org/10.26599/NRE.2026.9120247>

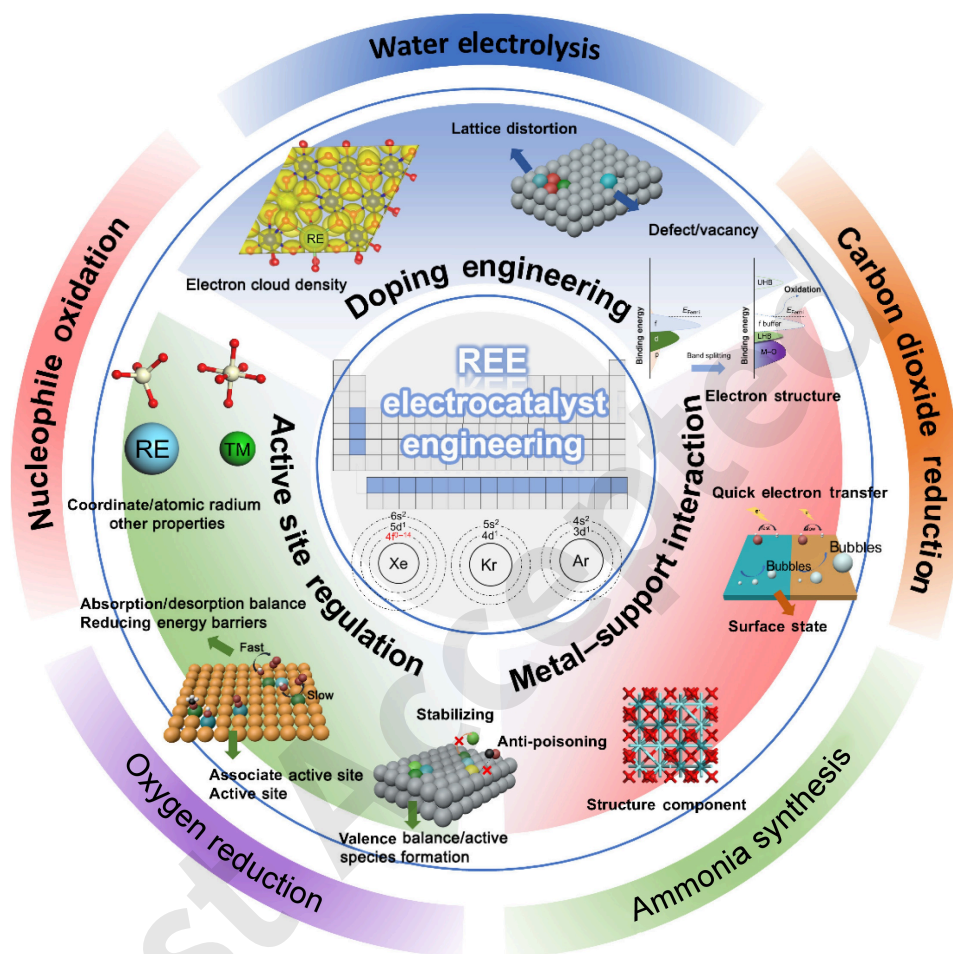
<https://www.sciopen.com/journal/2791-0091> on Aug. 25, 2026

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This review systematically summarizes recent advances in the development of rare-earth (RE)-based electrocatalysts, proposing forward-looking research directions, underscoring the role of emerging methodologies in guiding the application of rare earth catalysts in next-generation systems.



# Recent progress of rare earth element electrocatalysts: The critical role of electronic configuration regulation

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Received: 12 May 2026 / Revised: 18 June 2026 / Accepted: 27 June 2026

## ABSTRACT

The pursuit of high-performance electrocatalysts represents a central theme in the 21<sup>st</sup> century clean and sustainable chemical engineering and energy science. Among various electrocatalyst candidates, rare earth (RE)-based catalysts have garnered significant research interest due to their unique 4f electronic configurations that determine tunable electronic structure of the catalyst and the reactants' adsorption/desorption properties. These intrinsic characteristics endow RE materials with remarkable activity and selectivity in a wide range of electrocatalytic processes, positioning them as pivotal components toward the sustainable energy conversion technology deployment. Herein, we systematically summarize recent advances in the development of RE-based electrocatalysts, with emphasis placed on three key aspects: (1) the classification of metals and compounds spanning the mainstream rare elements series; (2) the structural design of RE-based catalysts; and (3) applications across diverse electrocatalysis types. By elucidating the fundamental impact of rare earth elements on catalytic properties and mechanisms, this review aims to guide the development of novel electrocatalysts. Finally, we propose forward-looking research directions, underscoring the role of emerging methodologies in guiding the application of rare earth catalysts in next-generation systems.

## KEYWORDS

rare earth, electrocatalyst, electronic configuration, 4f orbital, structure–activity relationship

## 1 Introduction

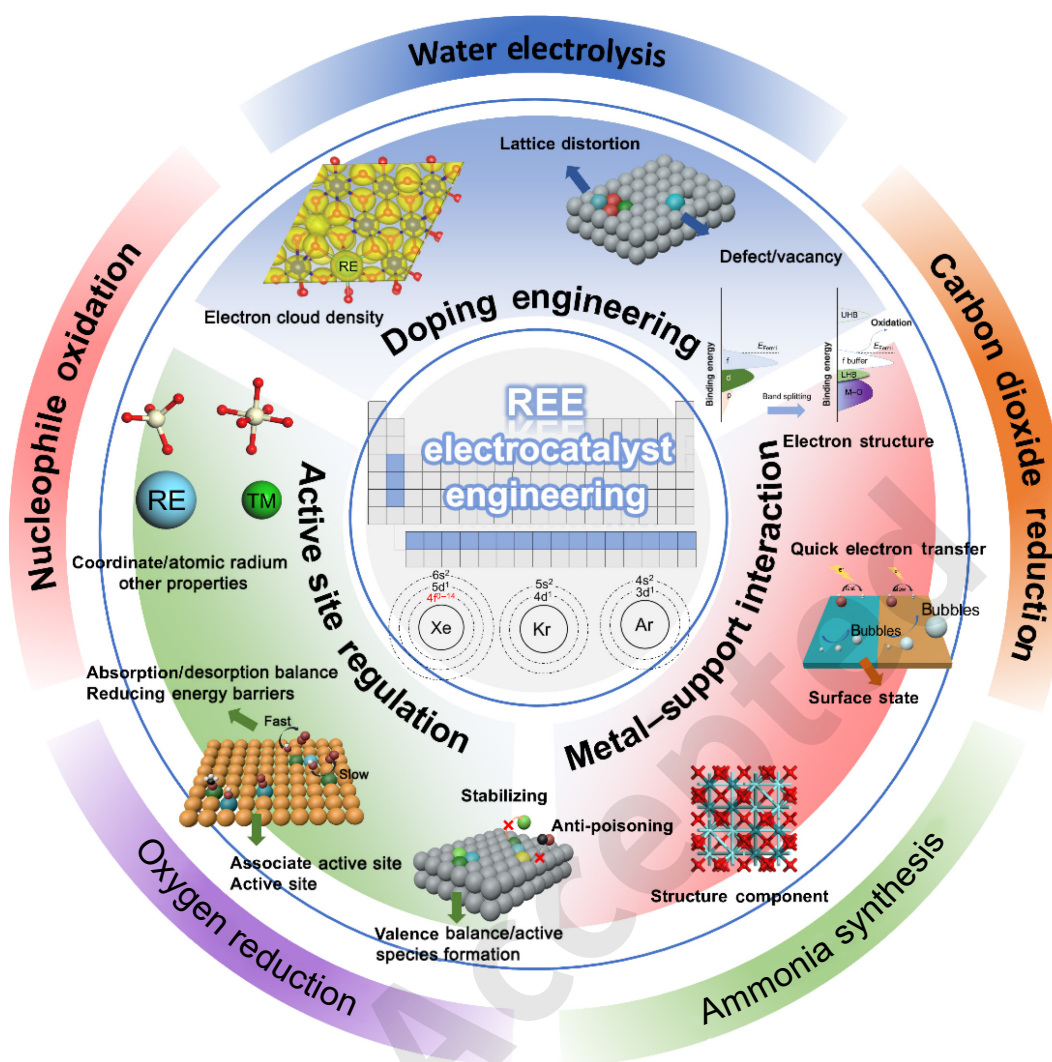
Rare earth (RE) elements (REEs) comprise a chemically homogeneous group of seventeen elements. Due to their excellent properties, they have been widely applied in various fields, including electrocatalysis (Fig. 1). The first discovered REE, yttrium (Y), was identified by the Finnish chemist Gadolin in 1794. Remarkably, the last discovered element in the series, promethium (Pm), was not isolated until 1947 by Marinsky and colleagues in the United States. When rare earth elements were first discovered, due to limitations in chemical analysis techniques, the so-called new elements were oxides of rare earth elements. Moreover, due to the limited development of exploration, mineral processing, and smelting [1–3], as well as insufficient understanding of the application value of rare earth elements, the yield of rare earth elements was very low. Hence, they were named “rare earth elements”. However, compared with some precious metals and even some more common elements, rare earth elements have an even higher content in the Earth's crust, reaching 0.016% [4].

REEs includes scandium (Sc, Group IIIB, Period 4), Y (Group IIIB, Period 5), and the fifteen lanthanides (Group IIIB, Period 6): lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), Pm, samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Conventionally classified based on physicochemical properties, REEs are often divided into light REEs (LREEs: La, Ce, Pr, Nd, Pm, Sm, and Eu, also termed the cerium group) and heavy REEs (HREEs: Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, and Sc, termed the yttrium group). A tripartite classification also exists: light (La, Ce, Pr, Nd, and Pm), medium (Sm, Eu, and Gd), and heavy (Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) REEs (Fig. 2).

Rare earth elements, with a large number of outer electrons, can form compounds with complex electronic structures, thus possessing unique optical [5, 6], electrical, and magnetic [7] properties. Due to their high chemical activity, they are widely used in the design and synthesis of functional materials [8], as well as in traditional industries (such as petrochemicals [9–11],

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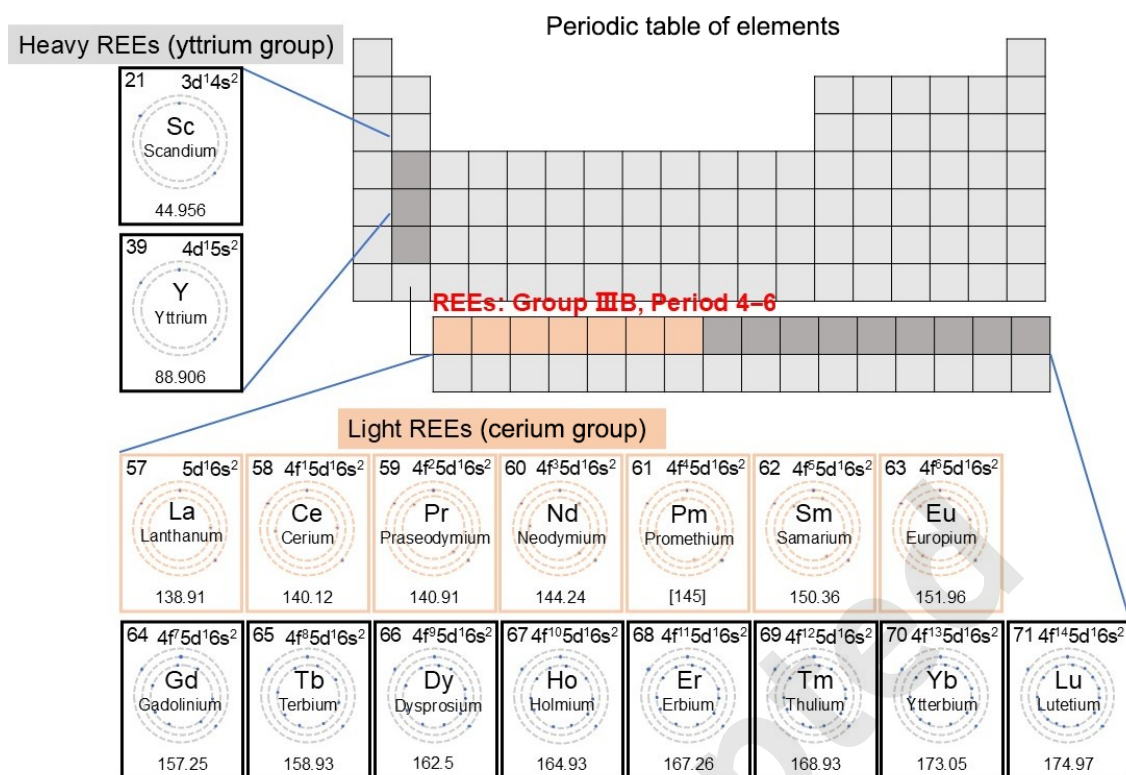
**Figure 1** Schematic diagram of REE electrocatalyst engineering.

metallurgy [12–14], glass [15,16], ceramics [17,18], textiles [19,20], and leather [21,22]), and critical fields (including electronics [23,24], communication [25,26], medicine [27,28], aviation [29,30], and national defense [31,32]), hence being hailed as the “vitamins of industry”. As an important strategic resource, rare earth elements have become increasingly important with the rapid development of industrialization, informatization, and globalization in the new century, gradually serving as a tool for international competition and influencing geopolitical fluctuations [33–35]. Although globally abundant in reserves, rare earth elements are unevenly distributed [36,37]. Moreover, most rare earth ores have low rare earth content and require complex processes to be converted into usable resources, resulting in their high scarcity [38–40]. Nevertheless, economic research shows that the global supply chain of rare earth elements is highly resilient. Given the vital role of rare earth elements in industrial production, factors, such as policies adopted by major rare earth-producing countries and advances in rare earth recycling technologies, may exert impacts on the overall rare earth supply chain, but will not bring about devastating disruptions [41,42]. From an environmental perspective, the extraction of heavy rare earth elements mainly relies on *in situ* leaching, and their extensive application may cause environmental damage. Light rare earth elements are primarily obtained through extraction and

separation, which tends to have a relatively minor environmental impact [43].

Electrocatalysis stands as a cornerstone technology for future energy storage and conversion systems. Within this field, REEs have demonstrated remarkable potential. The d-band center theory states that the valence electron structure has a direct impact on the adsorption and desorption behaviors of reactants and intermediates in the electrocatalytic process [44], thereby determining the reaction kinetics. The low binding energy of the valence electrons of REEs is conducive to regulating the electron cloud density of the catalyst and improving the charge transfer efficiency of the catalyst. Variable-valence rare earth elements (such as Ce, Pr, Sm, etc.) can effectively regulate the charge balance in electrocatalyst. They possess variable oxidation states (e.g.,  $\text{Ce}^{3+}/\text{Ce}^{4+}$ ), active 4f electrons, and a tendency to form oxygen vacancies ( $\text{O}_v$  or  $\text{V}_\text{O}$ ). The valence electrons that are easy to gain and lose endow REEs with valence-change characteristics. Acting as “electron buffers” in electrocatalysts, they dynamically compensate for local charge imbalance and reconstruct the electronic structure of active sites. REEs have incompletely filled 4f orbitals, which can interact with the d-orbital electrons of transition metals (TMs). Through reasonable catalyst design, the d-band center position of transition metals can be regulated, which can modify and activate the active sites. In addition, the unique





**Figure 2** The position of rare earth elements in the periodic table, the classification of rare earth elements, and the configuration of their valence electrons.

characteristics of the 4f orbital electrons of rare earth elements endow them with certain catalytic activity [45, 46]. In some electrocatalytic reactions, the 4f orbital electrons of rare earth elements can directly participate in the activation of reactants, break the chemical bonds of reactants through electron transfer, and reduce the reaction energy barrier. Furthermore, their versatile coordination chemistry characteristics allow for the formation of diverse complexes, enabling the rational design of high-performance electrocatalysts [47–49].

Recent years have witnessed significant progress in utilizing REEs for designing and engineering electrocatalysts for key reactions [50–55]. This benefits from the continuous advancement of first-principles calculations and catalyst engineering. Thanks to the unremitting efforts of researchers in theoretical chemistry, density functional theory (DFT) calculations can now provide strong guidance for analyzing the reaction mechanisms and synthesizing catalysts. For complex systems containing rare earth elements with 4f orbitals, DFT calculations can also deliver robust support to experimental researchers through comprehensive solutions and seamless integration with theoretical computing software [56, 57]. Therefore, the design of rare earth element catalysts based on theoretical research has become increasingly important.

Notably, Y, Ce, and La have been the focus of extensive advanced research. Encouraging results have also emerged for other REEs. This review comprehensively surveys representative works on REE-based electrocatalysts (excluding Pm and Ho, which currently lack significant reports in electrocatalysis). By classifying these works according to the roles of rare earth elements and the catalytic reactions involved, we summarize research strategies, catalyst performance metrics, characterization methodologies, and theoretical insights, aiming to provide a valuable reference for the burgeoning application of REEs in electrocatalysis.

## 2 Classification of rare earth element catalysts based on structural characteristics

Rare earth elements play versatile and critical roles in electrocatalysts, which stem from their unique electronic configurations, atomic radius, and chemical properties. By rationally regulating their local coordination, spatial distribution, and structural integration within electrocatalytic systems, rare earth species can be strategically engineered as dopants, supports, or host framework components, and active centers. Such structural engineering, including doping engineering, metal-support interaction engineering, and REE active site engineering, enables precise control over adsorption behaviors, charge transport, and reaction pathways.

### 2.1 Rare earth elements doping engineering

Rare earth elements doping engineering is a pivotal strategy for optimizing electrocatalysts, leveraging the unique electronic and structural features of REEs to precisely regulate catalytic performance. As promising dopants, REEs exert multiple regulatory effects on host catalysts. Firstly, their incompletely filled 4f orbitals interact with the 3d orbitals of transition metals, modulating the d-band center to tune the adsorption behavior of reaction intermediates. Secondly, the variable valence nature of REEs (e.g., Ce<sup>3+</sup>/Ce<sup>4+</sup>) enhances charge transfer efficiency between the catalyst and reactants, while preventing the excessive oxidation of metal sites and improving the activity and stability of the catalyst. Thirdly, the relatively large atomic diameter of REEs induces lattice distortion and oxygen vacancies in the host crystal structure, providing additional active sites for catalytic reactions. Besides, their intrinsic physicochemical properties, including electronegativity and hydrophilicity, can also be tailored via doping to improve catalyst–electrolyte interface contact and reduce mass transfer resistance. Additionally, REEs exhibit

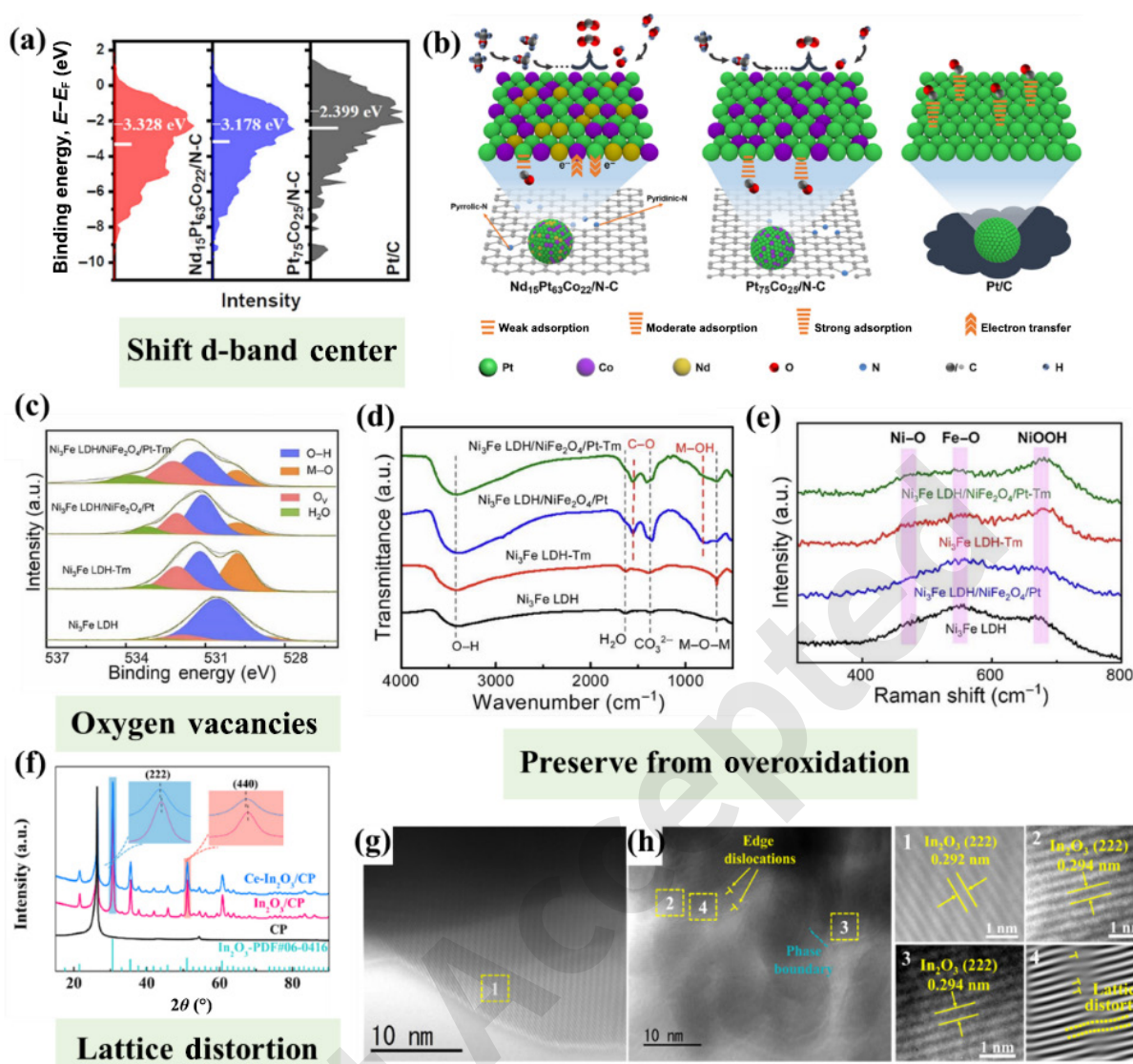
universal effects, such as increasing the density of states (DOS) near the Fermi level and triggering valence electron delocalization, further optimizing electronic conductivity.

In reactions, such as hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), the adsorption/desorption process exerts a decisive influence on reaction kinetics. Since doping can directly alter the electronic structure around active sites, it has become one of the most effective strategies for regulating the adsorption process. In some typical research works, rare earth elements are applied to the above reactions via doping strategies, serving to optimize the adsorption process by modulating the electronic structure. Aiming to synthesize high-performance OER catalysts, Wang et al. [58] grew NiFe-layered double hydroxide (LDH) doped with various proportions of lanthanide elements, such as Sm, Ce, and La, onto nickel foam (NF). Ultimately, they screened a NiFeSm-LDH catalyst with the best OER performance. Through *in situ* analysis and theoretical calculations, the researchers explained that the Sm element in NiFeSm-LDH can attract more electrons from the outermost 3d orbitals of Ni due to the lanthanide contraction effect, resulting in the highest valence state and d-band center of Ni. First-principles calculations also reveal that NiFeSm-LDH significantly reduces the formation energy from  $\text{OOH}^*$  to  $\text{O}_2$ . Additionally, compared to doping with La and Ce, the Sm-doped catalyst requires a lower overpotential to generate the key intermediate NiOOH, thus exhibiting faster kinetics for the Ni(II)–Ni(III) transformation. In another work, Li et al. [59] synthesized an array-like Ce-CoP catalyst for HER and OER through theoretical design and electrodeposition-phosphorization methods. They investigated how the introduction of cerium enhances the catalytic performance. Theoretical calculations and studies reveal that during the HER process, the Ce 4f-band induces a spin-state inversion at the Co site via the Ce–P–Co chain, optimizing the adsorption of the key intermediate  $^*\text{H}$ . In the oxidation potential range for the oxygen evolution reaction, TM oxyhydroxide species are generally the active species for the reaction. The TM–O covalent bonds split into M–O bonds and (M–O)\* antibonding bands, and the (M–O)\* bands further divide into the lower Hubbard band (LHB) and empty upper Hubbard band (UHB). After introducing rare earth elements, the 4f bands with appropriate energy levels can act as electron buffer bands to realize electron compensation. This preserves the lower Hubbard band and thereby maintains the covalency of TM–O bonds. Acting as electron buffer, cerium provides electrons to the system, protecting Co from over-oxidation and promoting its coupling with oxygen intermediates by maintaining Co 3d in a spin-down state. The catalyst achieves overpotentials of only 81 and 240 mV at  $10 \text{ mA}\cdot\text{cm}^{-2}$  for HER and OER, respectively.

In reactions involving the cleavage and formation of C–C bonds, such as carbon dioxide reduction reaction ( $\text{CO}_2\text{RR}$ ) and methanol (MeOH)/ethanol (EtOH) oxidation reaction (MOR/EOR), the adsorption of by-products like CO on active sites can seriously impair the catalytic activity. Meanwhile, in the lattice oxygen mechanism (LOM) mechanism for OER or the direct mechanism of nucleophiles oxidation, the over-oxidation of metal sites severely undermines catalyst stability. Employing doping strategies to leverage the electronic structure modulation effect of rare earth elements can suppress the adsorption of toxic species, inhibit over-oxidation, and enhance the overall robustness of catalysts. In a work of MOR, Zhang et al. [60] synthesized various PtCo-RE/N-C (RE = Nd, Y, La, Ce, Pr, or Sm) catalysts via wet impregnation and high-temperature  $\text{H}_2$  reduction with the

Nd-doping catalyst showing the best performance. The doped Nd leads to a downshift of the d-band center of catalysts. This downshift is anticipated to weaken the binding strength of the CO intermediate, consequently enhancing the anti-poisoning ability. Besides the introduced Nd, it can simultaneously tune the N configuration of  $\text{Nd}_{15}\text{Pt}_{63}\text{Co}_{22}/\text{N-C}$ , effectively improving the reaction kinetics. The optimized  $\text{Nd}_{15}\text{Pt}_{63}\text{Co}_{22}/\text{N-C}$  exhibits the highest mass and specific activities of  $1.95 \text{ A}\cdot\text{mg}_{\text{Pt}}^{-1}$  and  $3.12 \text{ mA}\cdot\text{cm}^{-2}$  among all catalysts, along with excellent CO resistance and MOR stability (Figs. 3(a) and 3(b)). Yang et al. [61] developed a complex  $\text{Ni}_3\text{Fe}$  LDH/ $\text{NiFe}_2\text{O}_4/\text{Pt-Tm}$  catalyst for HER and OER in alkaline conditions. The researchers suggest that Tm doping regulates the LDH through electron-compensated buffer to prevent overoxidation of M–O bonds, making it an excellent OER electrocatalyst. Meanwhile, Pt incorporation enhances HER performance. These structural optimizations also promote NiOOH formation and intermediate adsorption while preserving oxygen vacancies and unsaturated coordination, leading to superior overall water-splitting performance. At  $10 \text{ mA}\cdot\text{cm}^{-2}$ , the OER and HER overpotentials are 224.0 and 125.0 mV, respectively, and only 1.69 V is required for overall water splitting (Figs. 3(c)–3(e)).

While regulating the electronic structure, the doping of rare earth elements may also cause defects or lattice distortion in the catalyst, and even alter the coordination state near the active sites. The vacancies and defects formed thereby are conducive to the exposure or activation of active centers. Zhang et al. [62] prepared a Ce-doped  $\text{Cu}_{2+1}\text{O}/\text{Cu}_3\text{VO}_4$  catalyst. Ce-doping regulates the catalyst's electronic structure, facilitating V–Cu electron transfer and upshifting the d-band center to enhance intermediate adsorption and optimize reaction kinetics. Besides, induced Ce generates abundant oxygen vacancies during redox process, exposing more active sites and strengthening nitrate adsorption/activation to overcome the nitrate reduction reaction ( $\text{NO}_3\text{RR}$ ) high activation barrier. Ce also improves the poor conductivity of copper-based oxides, reducing charge transfer resistance and accelerating electron transport for efficient  $\text{NO}_3\text{RR}$ , while it suppresses the HER side reaction by enhancing nitrate selective adsorption and weakening H adsorption, thus elevating ammonia Faradaic efficiency (FE). Theoretical calculation shows that Ce lowers the free energy barrier of the rate-determining step (RDS) to 0.04 eV, greatly accelerating the overall  $\text{NO}_3\text{RR}$  reaction rate. In another work, Yang et al. [63] collaborated to synthesize an efficient Ce- $\text{In}_2\text{O}_3/\text{CP}$  catalyst by *in situ* growing cerium-doped  $\text{In}_2\text{O}_3$  on carbon paper, with formic acid as the main product of  $\text{CO}_2$  reduction. Cerium doping causes lattice distortion in  $\text{In}_2\text{O}_3$ , thereby promoting the preferential adsorption of  $^*\text{OOCH}$  intermediates on the sites of electrocatalyst surface. DFT calculations show that Ce- $\text{In}_2\text{O}_3$  reduces the Gibbs free energy of adsorption for key intermediates and suppresses the HER. This catalyst achieves a Faradaic efficiency of over 90% in a wide potential range (–1.5 to –1.8 V), reaching a maximum Faradaic efficiency of 97.6% at –1.7 V (Figs. 3(f)–3(h)). Chen et al. [64] utilized the higher electronegativity of rare earth yttrium ions ( $\text{Y}^{3+}$ ). They treated nickel copper foam with dielectric barrier discharge plasma (PNCf) and synthesized NiCo-LDH *in situ*, and then obtained nitrogen-doped YNiCo phosphide (N-YNiCoP/PNCf) after a phosphating process using radio frequency plasma in nitrogen. X-ray absorption spectroscopy (XAS) shows that the addition of Y atoms shortens the bond length and reduces the coordination numbers of Co and Ni atoms, thus inducing an increasing electrocatalytic performance and improving the stability



**Figure 3** (a) Surface valence band photoemission spectra. (b) Schematic illustration of the MOR mechanism with  $\text{Nd}_{15}\text{Pt}_{63}\text{Co}_{22}/\text{N-C}$ ,  $\text{Pt}_{75}\text{Co}_{25}/\text{N-C}$ , and commercial Pt/C as the used catalysts. Reproduced with permission from Ref. [60], © American Chemical Society 2023. (c) O 1s XPS high-resolution spectra. (d) FTIR spectra and (e) Raman spectra of the  $\text{Ni}_3\text{Fe}$  LDH-based composites. Reproduced with permission from Ref. [61], © The Royal Society of Chemistry 2024. (f) XRD patterns of  $\text{In}_2\text{O}_3/\text{CP}$  and  $\text{Ce-In}_2\text{O}_3/\text{CP}$ . ((g) and (h)) High-resolution transmission electron microscopy (HRTEM) images of  $\text{In}_2\text{O}_3/\text{CP}$  and  $\text{Ce-In}_2\text{O}_3/\text{CP}$ . Reproduced with permission from Ref. [63], © Elsevier Ltd. 2025.

of the synthesized catalyst. DFT calculations indicate that the incorporation of Y atoms helps to reduce the energy barriers of the HER and OER processes.

In the aforementioned typical rare earth element doping studies, REEs play a pivotal role, including the interaction between REE 4f orbitals and transition metal 3d orbitals to regulate adsorption, valence-variable REEs enhance the charge transfer efficiency and stability of catalysts, and the relatively large atomic diameter of REEs induces lattice distortion and oxygen vacancies in the host structure.

Additionally, other intrinsic properties of REEs, such as electronegativity and hydrophilicity, can also exert positive effects in certain catalytic systems. These functions often act synergistically to improve electrocatalytic performance. In rare earth element metal-support interaction engineering, these effects will be more pronounced, which will be further reviewed in the next section. The above-mentioned research works in this section may provide valuable references for the design and preparation of REE-doped catalysts.

## 2.2 Rare earth element metal-support interaction engineering

Different from the doping role that relies on trace addition, rare earth elements as carriers or main structural components directly form the framework of the catalyst or provide stable support for active sites. When rare earth elements are used as support for metal active sites (including rare earth oxide carriers or acting as structural materials), they can better exert their advantages of being electron-rich and having fast charge transfer. They provide electron buffering for the metal centers, regulate the electronic structure of the metal centers, and enhance the activity and stability of catalysts. In addition, through reasonable carrier design and preparation, rare earth substrates can also play a role in anti-poisoning while improving activity by regulating the adsorption of intermediates.

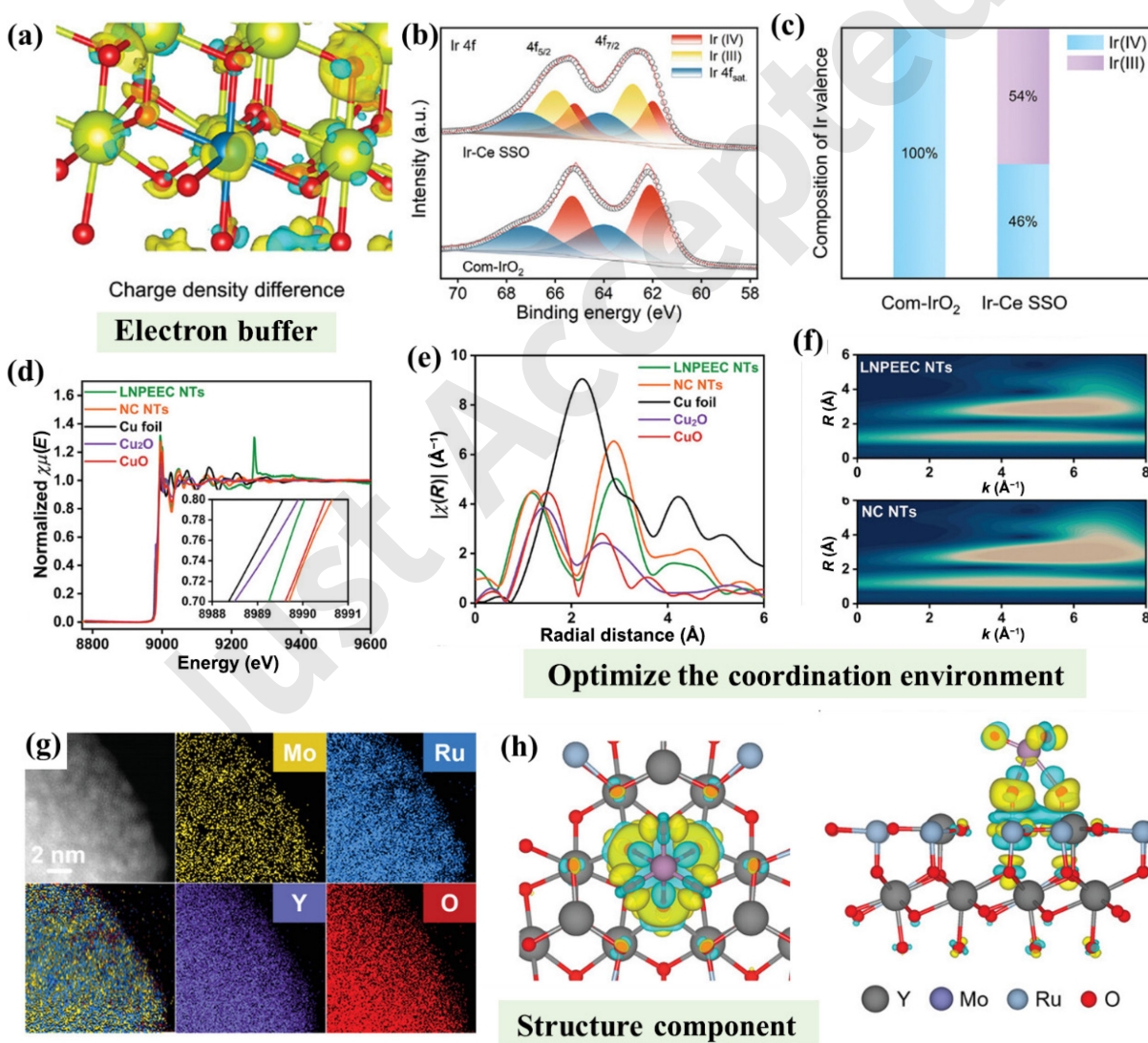
As metal-support, rare earth elements can also interact with active sites, regulate the electronic structure of active sites, and thereby enhance the catalytic activity of catalysts. Dong et al. [65]



prepared an iridium-cerium substitution solid solution oxide catalyst (SSO), with Ir atoms uniformly distributed on the surface of the Ir-Ce SSO. Theoretical studies and *in situ* characterizations confirm that  $\text{CeO}_2$  acts as an electron buffer in the system, promoting charge transfer to Ir atoms, thereby generating abundant active low-valent Ir sites and effectively preventing their oxidation and dissolution. Besides,  $\text{CeO}_2$ -induced downshifts the d-band center of Ir 5d orbitals to  $-2.501$  eV, weakening the excessive adsorption of OER intermediates ( $^*\text{OH}$ ,  $^*\text{O}$ , and  $^*\text{OOH}$ ), reducing the energy barrier of the RDS from 2.41 to 1.67 eV, and accelerating OER kinetics. This endows the Ir-Ce SSO catalyst with an overpotential of 238 mV at  $10 \text{ mA}\cdot\text{cm}^{-2}$ . The anion exchange membrane water electrolyzer (AEMWE) using Ir-Ce SSO can operate continuously for over 100 h at a low Ir loading of  $396 \mu\text{g}_{\text{Ir}}\cdot\text{cm}^{-2}$  and a high current density of  $500 \text{ mA}\cdot\text{cm}^{-2}$  (Figs. 4(a)–4(c)). Luo et al. [66] collaborated to develop an oxygen reduction reaction (ORR) catalyst. The researchers introduced Y into atomically dispersed iron and nitrogen co-doped carbon

materials to integrate nanoparticles (NPs), nanoclusters, and atomic sites ( $\text{FeY}\text{-NC}$ ). The X-ray photoelectron spectroscopy (XPS) shows a downshift of binding energy for Y, indicating that the  $\text{Y}_2\text{O}_3$  tends to pull the electrons from the surrounding coordinated environment, providing a strong synergistic interaction to tune the electronic structure of the components adjacent. The researchers believe that the synergistic effect of  $\text{Y}_2\text{O}_3$  with the dual active sites of  $\text{FeN}_4$  and  $\text{Fe}_4\text{N}$  decreases the binding energy of  $^*\text{OH}$ , improving the reaction performance. In alkaline and acidic systems,  $\text{FeY}\text{-NC}$  achieves half-wave potential ( $E_{1/2}$ ) of 0.926 V. It shows excellent performance in a zinc–air battery, providing a peak power density of  $233 \text{ mW}\cdot\text{cm}^{-2}$ .

In some typical studies, rare earth element carriers are used to enhance the stability of active sites through electronic interactions and optimize the reaction microenvironment. Jiang et al. [67] synthesized a series of Ni/lanthanide oxide heterojunction catalysts for sulfide-resistant hydrogen evolution electrocatalysis, exhibiting the best performance.  $\text{La}_2\text{O}_3$  itself is completely resistant to



**Figure 4** (a) Charge density difference of Ir-Ce SSO and Com-IrO<sub>2</sub> (yellow color represents charge accumulation and blue color represents charge depletion). (b) XPS spectra of Ir-Ce SSO and Com-IrO<sub>2</sub> at the Ir 4f core level. (c) Corresponding compositions of Ir valence states in Ir-Ce SSO and Com-IrO<sub>2</sub>. Reproduced with permission from Ref. [65], © Wiley-VCH GmbH 2024. ((d) and (e)) Cu K-edge XANES and FT-EXAFS spectra. (f) Wavelet transform (WT)-EXAFS contour plots of Cu K-edge for LNPEEC NTs and Nd<sub>2</sub>CuO<sub>4</sub> (NC) NTs. Reproduced with permission from Ref. [69], © Wiley-VCH GmbH 2024. (g) Scanning TEM (STEM)-energy dispersive X-ray spectroscopy (EDS) elemental mapping images of Mo-YRO. (h) Electron localization function (ELF) maps of Mo-YRO. Yellow and cyan refer to electron-rich and electron-deficient areas. Reproduced with permission from Ref. [70], © Wiley-VCH GmbH 2023.



sulfidation during electrolysis in sulfide-rich alkaline electrolytes and does not react with  $S^{2-}$  or polysulfides ( $S_x^{2-}$ ) to form lanthanum sulfides. Besides,  $La_2O_3$ 's fully hydroxylated surface induces electrostatic repulsion to anionic sulfides. Through *in situ* spectroscopy and electrochemical impedance spectroscopy, the presence of  $La_2O_3$  significantly delays the sulfidation of the metallic Ni component. Sulfidation is restricted to the surface layer without penetrating into the bulk structures, retaining the active Ni/ $La_2O_3$  (NLO). The required cell voltage is significantly reduced by 1.05 V for NLO and by 0.77 V for Pt/C to achieve  $100 \text{ mA}\cdot\text{cm}^{-2}$ , respectively. Moreover, the catalyst demonstrates excellent stability in both sulfide-containing (1.0 M KOH + 0.5 M sulfide) and sulfide-free systems. Kim et al. [68] synthesized Ni- $CeO_2$ /carbon (NCC) electrocatalyst via co-precipitation and heat treatment for HER in AEMWE using industrial waste alkaline water. A key highlight is the critical role of the rare earth-derived  $CeO_2$ , which enables strong electronic metal-support interactions with Ni.  $CeO_2$  acts as an electron donor, transferring electrons to Ni active sites—evidenced by a reduced  $Ce^{3+}/Ce^{4+}$  ratio and negative shifts in Ni binding energies, along with an increased Ni<sup>0</sup>/Ni ratio. This electronic modulation optimizes the adsorption strength of  $H^+$  and accelerates the rate-limiting Volmer step. Additionally,  $CeO_2$  enhances the resistance of the catalyst to impurity poisoning by reducing the binding energy of Li, Mo, and W ions with active sites, and stabilizes the Ni- $CeO_2$  interface to prevent particle agglomeration. In AEMWE tests, NCC achieves  $1 \text{ A}\cdot\text{cm}^{-2}$  at 2.03 V and maintains exceptional long-term stability over 2000 h with a degradation rate of only 4.95%.

Introducing rare earth elements into oxides to make them serve as part of the structural composition while continuing to exert their regulatory effect on electronic structures is a classic catalyst design strategy. Chen et al. [69] developed high-entropy perovskite oxide nanotubes (NTs) for  $NO_3RR$ . By introducing multiple rare earth elements (La, Nd, Pr, Er, and Eu) into the A-site via electrospinning, they synthesized  $LaNd_{0.25}Pr_{0.25}Er_{0.25}Eu_{0.25}CuO_4$  NTs (LNPEEC NTs). DFT calculations suggest that introducing multiple rare earth elements into the A-site optimizes the coordination environment of Cu at the B-site, increasing unsaturated Cu sites and providing more active sites. Additionally, it modulates the d-band center of Cu at the B-site and reduces the reaction energy barrier of the rate-determining step. The catalyst exhibits exceptional performance, achieving a  $NH_3$  Faradaic efficiency of 100% at  $-0.7 \text{ V}$  and a  $NH_3$  yield rate of  $1378 \mu\text{g}\cdot\text{h}^{-1}\cdot\text{mg}_{\text{cat}}^{-1}$  at  $-1.0 \text{ V}$  (Figs. 4(d)–4(f)). In a work of Liu et al. [70], surface manipulation strategy involving implanting  $MoO_x$  moieties using wet chemical peroxone method on nano  $Y_2Ru_2O_{7-8}$  (Mo-YRO) was adopted. The implanted  $MoO_x$  successfully contrasts a heterogeneous construction and eliminates the bandgap by inducing Ru 4d delocalization and band alignment rearrangement. In addition,  $MoO_x$  shortens the Ru–O bond, increases the bond angle, thereby alleviating distortion of  $[RuO_6]$ . The electronic and geometric structure tailoring enhances the OER performance, showing a small overpotential of 240 mV at  $10 \text{ mA}\cdot\text{cm}^{-2}$  (Figs. 4(g) and 4(h)).

This section elaborates on another important strategy for the engineering of rare earth element electrocatalysts, namely employing rare earth elements as metal supports or structural components. In catalyst systems, rare earth metal supports can often exert a synergistic effect of electronic structure regulation, electronic buffering, coordination regulation, etc., thereby improving the activity and stability of the catalyst. Additionally, using rare earth elements as structural components in pyrochlore

and high-entropy alloys (HEAs)/oxides, taking advantage of their unique electronic structure and large atomic radius, is also an important approach.

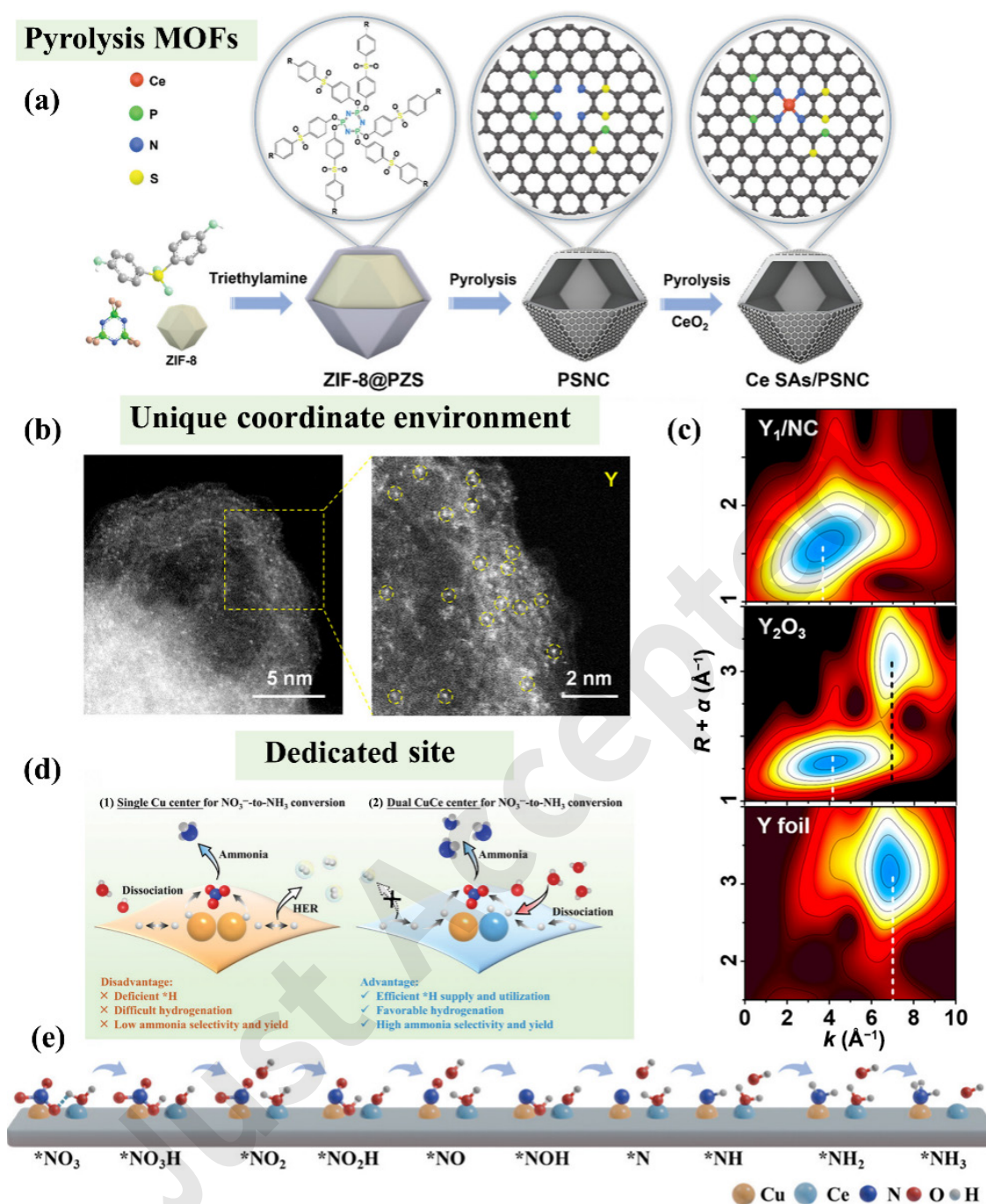
In Sections 2.1 and 2.2, rare earth elements function as regulators whether used as dopants or metal supports. In some studies, rare earth elements can also serve as active sites themselves.

### 2.3 Rare earth element active site engineering

In some specific catalyst systems, rare earth elements themselves can serve as active sites, directly participating in the adsorption, activation, and conversion of reactants. By adopting unique catalyst synthesis strategies, catalysts with rare earth elements as active centers, even rare earth single-atom catalysts, can be synthesized. Through these strategies, leveraging the high electron cloud density and distinctive coordination structure of rare earth elements to fabricate catalysts with rare earth elements as active centers has become one of the important approaches for catalyst synthesis. In addition, in some heterojunction catalysts formed by rare earth elements, rare earth elements have high activity in the adsorption and activation of some intermediates, which is conducive to reducing the energy barrier of key steps and improving reaction kinetics.

Typically, acting as Lewis acid sites, rare earth elements can form oxophilic bonds with several key reaction intermediates in certain studies, which enables them to exert direct effects or synergistic performance in ORR, HER, OER, et. al. Leveraging the versatile coordination properties of rare earth elements, their catalytic activity can also be modulated via electronic effects by regulating their 4f orbitals.

Liu et al. [71] used a mechanochemical method to disperse Y/Sc onto zeolitic imidazolate framework-8 (ZIF-8), and then pyrolyzed it to synthesize single-atom (SA) catalysts of Y and Sc,  $Y_1/NC$  and  $Sc_1/NC$ . Due to their large atomic sizes, Y and Sc can coordinate with six chemical bonds, which is different from the structure of  $M-N_4$ . DFT calculations reveal that coordination modulation regulates the local electronic structure of rare earth single atoms, optimizes the adsorption of reaction intermediates, activates the electrocatalytic activity at room temperature, and successfully breaks through the room-temperature electrochemical catalytic inertness of rare earth elements. This kind of single-atom catalyst of rare earth element exhibits both good nitrogen reduction reaction (NRR) and  $CO_2RR$  performance.  $Y_1/NC$  and  $Sc_1/NC$  have the highest  $CO_2RR$  Faradaic efficiency of 88.3% and 81.3% at  $-0.58$  and  $-0.68 \text{ V}$ , respectively. For NRR, at a lower potential of  $-0.1 \text{ V}$ , the maximum ammonia yields of  $Y_1/NC$  and  $Sc_1/NC$  are  $23.2$  and  $20.4 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ , respectively, and the Faradaic efficiency can reach 12.1% and 11.2% (Figs. 5(b) and 5(c)). In a work of ORR, Yin et al. [72] prepared a cerium single-atom catalyst supported on P, S, N co-doped hollow carbon (PSNC) for ORR. Unlike inactive bulk  $CeO_2$ , Ce SAs in Ce SAs/PSNC form a high-coordination structure ( $Ce-N_4/O_2$ ) via direct coordination with N/O atoms. Critically, the neighboring P and S heteroatoms induce long-range electronic modulation of Ce active sites. They upshift Ce 4f orbitals toward the Fermi level, enhance electron transfer efficiency, and optimize the adsorption strength of ORR intermediates, thus reducing reaction energy barriers. Theoretical studies confirm that the catalyst lowered the energy barrier of the rate-determining step, the conversion of OOH to O. The Ce SAs/PSNC catalyst possessed a half-wave potential of  $0.90 \text{ V}$  and a turnover frequency value of  $52.2 \text{ s}^{-1}$  at  $0.85 \text{ V}$ . When used in a zinc-air battery, it exhibits a high and stable open-circuit voltage



**Figure 5** (a) Schematic of the synthesis procedure of Ce SAs/PSNC. Reproduced with permission from Ref. [72], © Wiley-VCH GmbH 2023. (b) High-angle annular dark-field (HAADF)-STEM images of Y<sub>1</sub>/NC. (c) Wavelet transform analysis of Y<sub>1</sub>/NC, Y<sub>2</sub>O<sub>3</sub>, and Y foil. The white dashed line shows the maximum intensity position. Reproduced with permission from Ref. [71], © American Chemical Society 2020. (d) The proposed different mechanism of nitrate reduction over Cu/MoO<sub>2</sub>@C and 5%Ce-Cu/MoO<sub>2</sub>@C. (e) Proposed reaction pathway of NO<sub>3</sub><sup>-</sup> electroreduction over 5%Ce-Cu/MoO<sub>2</sub>@C. Reproduced with permission from Ref. [76], © Wiley-VCH GmbH 2025.

of 1.49 V and a maximum power density of 212 mW·cm<sup>-2</sup> (Fig. 5(a)). Yin et al. [73] constructed single-atom ORR catalysts La-Cl SAs/N-doped hierarchical porous carbon (NHPC), using axial coordination strategies and nanostructure design. Theoretical calculations demonstrate that Cl coordination modulates the electronic structures of La sites, promoting electron transfer efficiency through d-p orbital coupling. The enhanced electroactivity of La sites optimizes the adsorption of key intermediates, reducing the energy barriers of the potential-determining step. This catalyst achieves a high half-wave potential

(0.91 V) and significant robustness in alkaline media. The aqueous zinc-air battery (AZAB) and flexible zinc-air battery (FZAB) integrating La-Cl SAs/NHPC as the cathode catalyst exhibit maximum power densities of 260.7 and 68.5 mW·cm<sup>-2</sup>. Ajmal et al. [74] developed a dual-functional Tb single-atom catalyst for urea oxidation reaction (UOR) and HER. Tb SAs are topologically stabilized on defect-rich Co<sub>3</sub>O<sub>4</sub> (Tb<sub>SA</sub>@d-Co<sub>3</sub>O<sub>4</sub>) via Tb-O coordination. Theoretical calculations and mechanistic studies suggest that for UOR, the Tb single atoms reduce the energy barrier of the potential-determining step from 1.93 eV for

defective  $\text{Co}_3\text{O}_4$  to 1.44 eV, weaken the interaction between urea and the catalyst, balance the adsorption and desorption of reaction intermediates, and simultaneously facilitate charge transfer. For HER, the Tb single atoms enhance water adsorption capacity with an adsorption free energy of  $-0.80$  eV, much lower than  $-0.31$  eV for  $\text{d-Co}_3\text{O}_4$  and reduce the kinetic energy barrier for water dissociation from 1.53 to 0.84 eV, thus significantly boosting the kinetics of the HER in alkaline media. Through unique Tb–O coordination strategy, this work explores the catalytic properties of rare earth “f-block” elements to create advanced electrocatalysts via structural modulation.

In addition to directly adsorbing reaction intermediates as active centers, rare earth elements can also act as associate sites to participate in partial steps of the reaction, such as providing  $\ast\text{H}$  for the reaction system during hydrogenation reduction. Furthermore, in some reactions, oxygen vacancies themselves can serve as reaction sites. Introducing rare earth oxides into the system to promote the formation of oxygen vacancies is also an important research strategy. Guo et al. [75] collaborated to synthesize a  $\text{Mo}_5\text{O}_{14}\text{-Y(OH)}_3\text{-CoMoO}_4$ /cobalt foam (CF) catalyst rich in a ternary heterojunction structure on CF. Surface energy calculations highlight that the addition of Y facilitates the formation of cumin-like nanoparticles. DFT analysis and *in situ* Raman spectroscopy indicate that the interaction among the three metals forms the  $\text{Mo}_5\text{O}_{14}\text{-Y(OH)}_3\text{-CoMoO}_4$  ternary heterostructure, which effectively reduces the energy barrier of the hydrogen evolution reaction. Among them, the Y site in the  $\text{CoMoO}_4\text{-Y(OH)}_3$  heterostructure shows the lowest free energy of hydrogen adsorption. Therefore, the researchers believe that Y is the main active site in the  $\text{Mo}_5\text{O}_{14}\text{-Y(OH)}_3\text{-CoMoO}_4$ /CF catalyst. The catalyst exhibits an HER overpotential of only 40 mV at  $10\text{ mA}\cdot\text{cm}^{-2}$  and an overpotential of only 219 mV at  $1000\text{ mA}\cdot\text{cm}^{-2}$ . In another work, Dong et al. [76] collaborated to prepare a  $\text{Ce-Cu/MoO}_2\text{@C}$  catalyst through liquid-phase reduction and calcination methods. They investigated the electrocatalytic nitrate reduction mechanism through *in situ* tests and theoretical calculations. The results show that Ce acts as a dedicated site for water dissociation to generate  $\text{H}^\ast$ , while Cu adsorbs and activates  $\text{NO}_3^-$ . The  $\text{H}^\ast$  produced on Ce sites undergoes spillover to adjacent nitrogen-containing intermediates ( $\ast\text{NO}_x$ ) on Cu, promoting efficient hydrogenation and selective ammonia synthesis. Furthermore, Ce modulates the electronic structure of the catalyst, enhances  $\text{NO}_3^-$  adsorption and activation, and reduces the free energy barrier of the rate-determining step (Figs. 5(d) and 5(e)). Xiao et al. [77] prepared  $\text{Sn-CeO}_{2-x}$  nanorods via hydrothermal synthesis and reductive calcination, exploring their NRR performance with Ce as the core matrix and Sn doping as the synergistic regulator. Ce forms defective  $\text{Sn-CeO}_{2-x}$  with oxygen vacancies, which capture electrons for  $\text{N}_2$  p back-donation to activate the  $\text{N}\equiv\text{N}$  bond and serve as the basic NRR active sites. Sn doping inhibits competitive HER, induces charge transfer with Ce to modulate its electronic structure, optimizes N–Ce interaction and lowers the catalyst’s work function for faster electron transfer. It also promotes oxygen vacancy formation, strips pre-adsorbed water from Ce sites to enhance  $\text{N}_2$  adsorption, and expands the electrochemically active surface area (ECSA) to expose more Ce active sites. The optimized 6.7 wt.%  $\text{Sn-CeO}_{2-x}$  achieves a  $\text{NH}_3$  yield of  $41.1\text{ }\mu\text{g}\cdot\text{mg}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$  and a FE of 35.3%, and shows excellent catalytic stability with unchanged core structure after long-term tests.

Rare earth elements are often used as modifiers in electrocatalysis research to adjust the electronic structure and

lattice of catalysts. However, in the above works, rare earth elements, as active centers, also exhibit good catalytic activity. Due to the localized nature of the 4f orbitals of rare earth elements, designing unique structure–activity relationships is essential when employing these 4f orbitals as the primary active sites. A typical approach is to leverage the diverse coordination modes of rare earth elements to adjust the coordination structure and number of surrounding non-metallic coordinating atoms, thereby regulating the 4f orbitals of rare earths. This requires researchers to adopt distinctive catalyst design strategies, such as pyrolysis of metal–organic frameworks (MOFs), defect engineering, and support engineering. Only by fully exposing rare earth sites and precisely modulating the electronic structure can rare earths function as active centers. It should be noted that the activity of rare earth elements does not depend on the type of elements, but on catalyst engineering. Therefore, there are still many reactions/rare earth elements worthy of research regarding the directional regulation of the electronic and coordination structures to activate and better exert the performance of rare earth element active centers.

## 2.4 Summary

REE structural engineering, including doping engineering, metal–support interaction engineering, and REE active site engineering, provides the possibility for the preparation of high-performance rare earth catalysts. Based on the systematic classification and analysis of rare earth element electrocatalysts regulated by three structural engineering strategies, a series of universal and transferable design principles for high-performance rare earth electrocatalysts can be summarized for the rational design and preparation of advanced electrocatalytic materials.

First, rare earth doping engineering serves as a facile and efficient electronic and structural modulation strategy, whose core transferable law lies in utilizing the unique 4f orbital characteristics, variable valence states, and large atomic radius of rare earth elements to realize multi-dimensional optimization of host catalysts. The orbital coupling between rare earth 4f orbitals and transition metal 3d orbitals can precisely tune the d-band center of active metal sites, thereby regulating the adsorption strength of key reaction intermediates and optimizing reaction kinetics. The reversible valence conversion of rare earth ions can build a fast charge transfer channel between the catalyst and reaction system, while effectively inhibiting the over-oxidation of metal active sites and improving catalytic stability. Meanwhile, the lattice distortion and rich oxygen vacancies induced by rare earth doping can expose abundant unsaturated active sites, and the intrinsic electronegativity and hydrophilicity of rare earth elements can further optimize the catalyst–electrolyte interface, reducing mass transfer resistance. The doping strategy is universally applicable to diverse electrocatalytic reactions and can also effectively suppress side reactions and catalyst poisoning failure caused by excessive adsorption of toxic intermediates.

Second, rare earth metal–support interaction engineering relies on rare earth-based substrates (mainly rare earth oxides, perovskites, and high-entropy rare earth composites) to construct strong electronic metal–support interactions, forming a distinct regulation mechanism different from trace doping. The core design rule is to take advantage of the electron-rich properties and electron buffering effect of rare earth supports to directionally transfer electrons to metal active centers, optimize the electronic structure of active sites, and lower the energy barrier of the rate-determining step. In addition, rare earth supports can construct



stable interfacial structures to inhibit the agglomeration, oxidation, and dissolution of metal active components, and their unique surface physicochemical characteristics can also resist sulfide and impurity ion poisoning, optimize the reaction microenvironment, and greatly enhance the long-term cycling stability of catalysts under harsh working conditions, such as high current density and complex electrolyte systems. The structural tunability of rare earth substrates also enables the regulation of coordination environment and band structure of active sites through multi-rare earth doping and defect engineering, which is suitable for the design of high-stability electrocatalysts for electrocatalytic reactions.

Third, rare earth active site engineering breaks the traditional cognition that rare earth elements only act as auxiliary regulators, and realizes the direct utilization of rare earth active centers. The key design principle is to construct rare earth-based active sites (including rare earth single atoms, defect-rich rare earth composites, and heterojunction-associated rare earth active centers) by precise structural modulation. Relying on the unique coordination versatility and high electron cloud density of rare earth elements, the inert electrochemical properties of bulk rare earth materials can be activated through orbital rearrangement, coordination number regulation, and defect construction. Rare earth active sites can act as Lewis acid sites to efficiently adsorb and activate reaction intermediates, and also serve as auxiliary hydrogen production sites to provide active hydrogen species for hydrogenation reduction reactions, realizing the synergistic catalysis of multiple active sites. Moreover, the oxygen vacancies derived from rare earth oxide systems can cooperate with rare earth active centers to optimize reactant adsorption and charge transfer, effectively balancing the adsorption-desorption behavior of intermediates and inhibiting competitive side reactions.

In general, the core universal logic of rare earth electrocatalyst design is to fully exploit the dual advantages of rare earth elements in electronic structure and geometric structure. The synergistic effect of orbital modulation, valence cycling, lattice defect regulation, and interfacial electronic interaction can fundamentally solve the bottleneck problems of insufficient active sites, sluggish reaction kinetics, and poor structural stability of conventional electrocatalysts. By matching different rare earth structural engineering strategies with specific electrocatalytic reaction mechanisms, targeted regulation of intermediate adsorption, charge transport, and reaction pathways can be realized, which is conducive to the development of high-performance, durable, and multi-functional rare earth electrocatalytic materials for diverse energy conversion electrocatalytic systems. The catalysts involved in the relevant references of this chapter and their performances are shown in Table 1 ( $\eta_x$  represents the overpotential at  $x \text{ mA}\cdot\text{cm}^{-2}$ ).

### 3 Rare earth element catalysts reaction type

Rare earth elements rely on their unique 4f electronic configuration, tunable valence states, and strong electronic modulation ability, which can effectively optimize the adsorption/desorption energy of reaction intermediates, induce the formation of catalyst defects and active sites, and stabilize the electronic structure of catalytic active centers. These excellent properties make REEs widely used in the design and preparation of electrocatalysts for various energy conversion and environmental remediation reactions.

Although in Section 2, this review has elaborated on the engineering of rare earth element catalysts from three aspects:

doping, metal-support interaction, and active sites, the author still holds that it is necessary to further discuss rare earth element catalysts classified by different reactions. This is because catalysts for different reactions have distinct design requirements. For instance, catalysts for  $\text{CO}_2\text{RR}$  need to address poisoning issues, while those for ammonia synthesis have to take the supply of  $^*\text{H}$  into account. The author believes that discussion categorized by reactions will help researchers better combine the design strategies of rare earth elements with reaction characteristics, so as to provide more effective guidance for the design of rare earth element catalysts. This chapter classifies and elaborates on the research progress of REE-based electrocatalysts according to different reaction types, including water electrolysis (WE), carbon dioxide reduction reaction, ammonia synthesis reaction, oxygen reduction reaction, nucleophile oxidation reactions, and summarizes the regulatory mechanism and structural design strategy of REEs in different catalytic systems. Owing to space constraints and the authors' limited expertise, certain other electrocatalytic reactions have not been covered herein.

#### 3.1 Water electrolysis

Water electrolysis is the core technology for green hydrogen production, which is composed of HER at the cathode and OER at the anode. Both reactions have slow kinetics and require efficient catalysts to reduce overpotential and improve reaction efficiency. REEs can act as electronic modulators, defect inducers, or active site components in water electrolysis catalysts, and realize the performance optimization of HER and OER catalysts through multiple mechanisms, such as adjusting the d-band center of active sites, optimizing the adsorption energy of  $^*\text{H}$ /oxygen-containing intermediates, and inducing oxygen vacancies. In addition, many REE-modified catalysts have both excellent HER and OER performance, which are ideal bifunctional catalysts for overall water splitting and have important application value in industrial water electrolysis systems.

##### 3.1.1 Hydrogen evolution reaction

HER is a proton/electron water reduction reaction that occurs at the cathode of the water electrolysis system. The key to improving the catalytic performance is to optimize the adsorption free energy of hydrogen intermediate ( $^*\text{H}$ ) and accelerate the water dissociation kinetics (Volmer step). REEs, such as Y, Ce, Sm, and Er, can effectively regulate the electronic structure of HER catalysts, balance the water dissociation energy and  $^*\text{H}$  adsorption energy, and thus significantly reduce the reaction overpotential and improve the catalytic kinetics and stability.

Building on the idea of constructing multi-interface catalysts with RE oxides, Sun et al. [78] implanted oxides of Sc, Y, and La into the catalyst with the purpose of providing  $\text{H}_2\text{O}$  dissociation active sites for the Volmer step. Among the catalysts,  $\text{Ni}/\text{Y}_2\text{O}_3$  shows the best HER performance. The researchers explain that  $\text{Y}_2\text{O}_3$  with compatible oxophilicity can provide a Cu balance between the OH binding energy and  $\text{H}_2\text{O}$  dissociation energy. Moreover, the superhydrophilic self-supported electrode structure of  $\text{Ni}/\text{Y}_2\text{O}_3$  with firm electrocatalyst-substrate interface and weakened electrocatalyst-bubble interfacial force significantly accelerates the removal of generated  $\text{H}_2$  gas bubbles and prevents catalyst from falling off, therefore further improving the catalytic efficiency and stability. The  $\text{Ni}/\text{Y}_2\text{O}_3$  can drive  $10 \text{ mA}\cdot\text{cm}^{-2}$  at a low overpotential of  $61.1 \pm 3.7 \text{ mV}$ , with a low Tafel slope of  $52.8 \text{ mV}\cdot\text{dec}^{-1}$ . It also shows outstanding long-term durability at high current density of  $1000 \text{ mA}\cdot\text{cm}^{-2}$  for 500 h in 1 M KOH. This

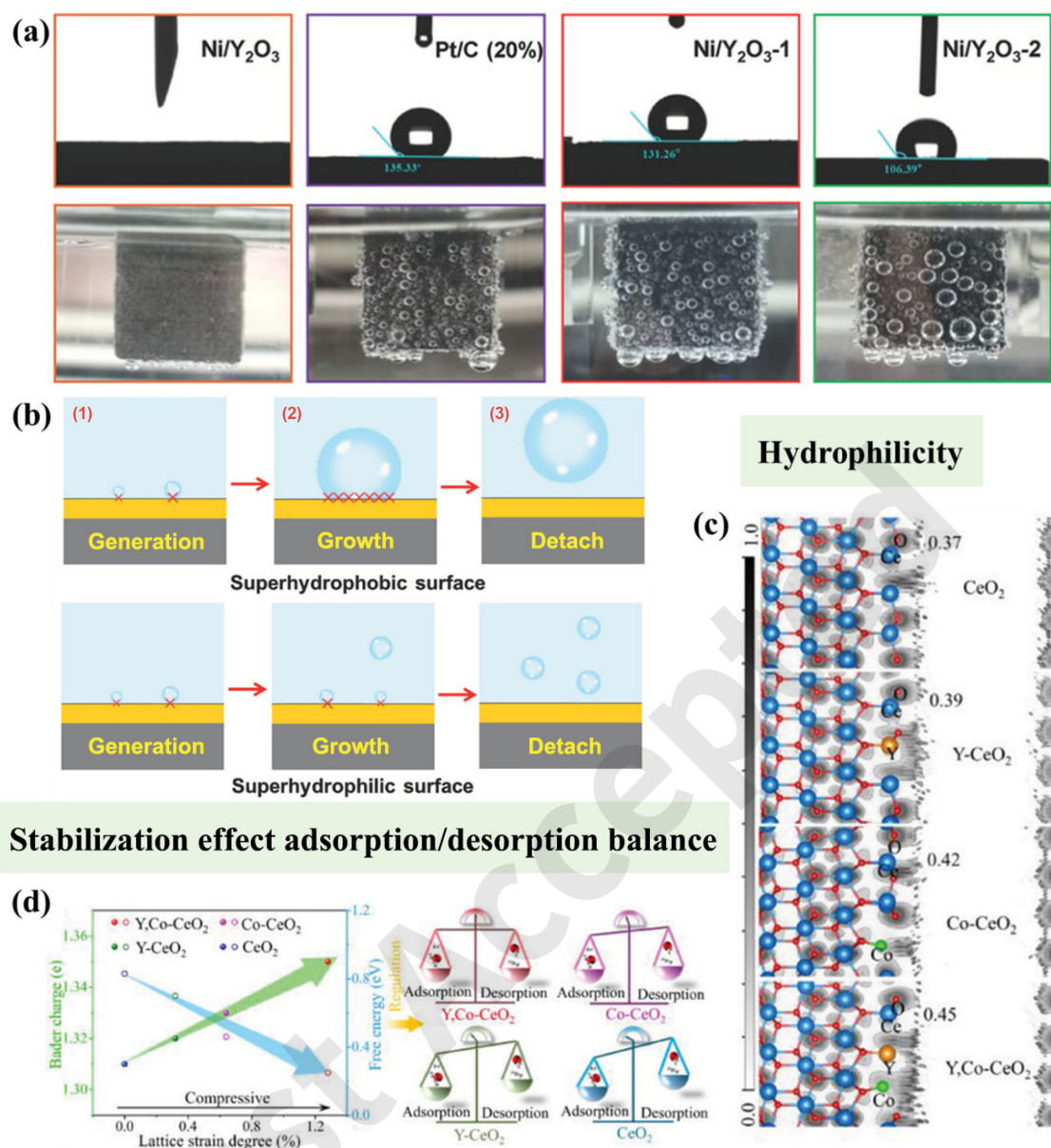
**Table 1** Summary of catalyst performances in Section 2

| References | Name                                                                        | Catalyst                              | Electrolyte                                                                    | Mass loading                                                                                   | Performance                                                                                                                                                                    | Commercial catalysts                                                                                  |
|------------|-----------------------------------------------------------------------------|---------------------------------------|--------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|
| [58]       | NiFeSm-LDH/NF                                                               | OER                                   | 1.0 M KOH                                                                      | 1.8 mg·cm <sup>-2</sup>                                                                        | $\eta_{10} = 203$ mV; NiFeSm-LDH  Pt/C: 100 mA·cm <sup>-2</sup> , 1.59 V, 27 h                                                                                                 | RuO <sub>2</sub> , $\eta_{10} = 310$ mV                                                               |
| [59]       | Ce-CoP                                                                      | HER, OER                              | 1.0 M KOH                                                                      | 0.5 mg·cm <sup>-2</sup>                                                                        | HER: $\eta_{10} = 81$ mV; OER: $\eta_{10} = 240$ mV; Ce-CoP@CC  Ce-CoP@CC: 10 mA·cm <sup>-2</sup> , 1.57 V, 27 h                                                               | HER: Pt/C, $\eta_{10} = 34$ mV; OER: RuO <sub>2</sub> , $\eta_{10} = 340$ mV                          |
| [60]       | Nd <sub>15</sub> Pt <sub>63</sub> Co <sub>22</sub> /N-C                     | MOR                                   | 0.1 M HClO <sub>4</sub> + 0.5 M MeOH                                           | 6 $\mu$ g <sub>Pt</sub> ·cm <sup>-2</sup> ; Pt: 29.12 wt.%                                     | Specific activity: 3.12 mA·cm <sub>Pt</sub> <sup>-2</sup> ; mass activity: 1.95 A·mg <sub>Pt</sub> <sup>-1</sup> ; 80.5% current remained after 0.8 V, 3600 s                  | Pt/C; mass activity: 0.48 A·mg <sup>-1</sup> ; specific activity: 0.69 mA·cm <sup>-2</sup>            |
| [61]       | Ni <sub>3</sub> Fe LDH/NiFe <sub>2</sub> O <sub>4</sub> /Pt-Tm              | HER, OER                              | 1.0 M KOH                                                                      | 5 mg·cm <sup>-2</sup> (20% acetylenen black)                                                   | HER: $\eta_{10} = 125$ mV; OER: $\eta_{10} = 224$ mV; overall: 1.69 V for 10 mA·cm <sup>-2</sup> , CV 5000 cycles                                                              | —                                                                                                     |
| [62]       | Cu <sub>2+1</sub> O/Cu <sub>3</sub> VO <sub>4</sub>                         | NO <sub>3</sub> RR                    | 1.0 M KOH + 0.1 M KNO <sub>3</sub>                                             | —                                                                                              | Y: 18.905 mg·cm <sup>-2</sup> ·h <sup>-1</sup> ; FE = 93.7%; -0.5 V, 12 h                                                                                                      | —                                                                                                     |
| [63]       | Ce-In <sub>2</sub> O <sub>3</sub> /CP                                       | HCOOH-CO <sub>2</sub> RR              | 0.1 M KHCO <sub>3</sub>                                                        | 1 mg·cm <sup>-2</sup>                                                                          | FE = 97.6%, -1.7 V, 60 h, FE remained > 85%                                                                                                                                    | —                                                                                                     |
| [64]       | N-YNiCoP/PNCF                                                               | HER, OER                              | 1 M KOH                                                                        | 18.5 mg·cm <sup>-2</sup>                                                                       | HER: $\eta_{2000} = 331$ mV; OER: $\eta_{2000} = 464$ mV, 10 mA·cm <sup>-2</sup> ; overall: 50 h, 10 mA·cm <sup>-2</sup> , 1.51 V                                              | Pt/C/PNCF, $\eta_{10} = 26$ mV                                                                        |
| [65]       | Ir-Ce SSO                                                                   | OER                                   | 0.5 M H <sub>2</sub> SO <sub>4</sub>                                           | Three-electrode: 1 mg·cm <sup>-2</sup> , PEM: 2 mg·cm <sup>-2</sup>                            | $\eta_{10} = 238$ mV; flow-cell: 500 mA·cm <sup>-2</sup> , 1.67 V, 100 h                                                                                                       | IrO <sub>2</sub> , $\eta_{10} = 297$ mV                                                               |
| [66]       | FeY-NC                                                                      | ORR                                   | 0.1 M KOH/0.1 M HClO <sub>4</sub>                                              | Rotating ring-disk electrode (RRDE): 0.2 mg·cm <sup>-2</sup> ; Zn-air: 1.0 mg·cm <sup>-2</sup> | $E_{1/2} = 0.926/0.809$ V; Zn-air: 20 mA·cm <sup>-2</sup> , 25 h, stable at ~ 1.31 V                                                                                           | Pt/C, $E_{1/2} = 0.853/0.839$ V                                                                       |
| [67]       | Ni/La <sub>2</sub> O <sub>3</sub>                                           | HER, sulfide oxidation reaction (SOR) | 1.0 M KOH + 0.5 M sulfide                                                      | —                                                                                              | Overall: 1.05 V for 100/200 mA·cm <sup>-2</sup> with/without S, ~ 90 h                                                                                                         | Pt/C, $\eta_{200} = 128/211$ mV (with/without S)                                                      |
| [68]       | Ni-CeO <sub>2</sub> /C                                                      | HER                                   | Industrial waste alkaline water                                                | ~ 4 mg·cm <sup>-2</sup>                                                                        | 2.03 V for 1000 mA·cm <sup>-2</sup> , Coulombic efficiency (CE): 72.79%; AEMWE: 2000 h; current 4.95% decreased                                                                | Ni/C, $\eta_{10} = 110$ mV                                                                            |
| [69]       | LNPEEC NTs                                                                  | NO <sub>3</sub> RR                    | 0.5 M K <sub>2</sub> SO <sub>4</sub> + 500 mg·L <sup>-1</sup> KNO <sub>3</sub> | 0.2 mg·cm <sup>-2</sup>                                                                        | Y: 1378 $\mu$ g·h <sup>-1</sup> ·mg <sub>cat</sub> <sup>-1</sup> at -1.0 V; FE = 100% at -0.7 V, 10 cycles/-0.7 V, 10 cycles/-1.0 V, 10cycles                                  | —                                                                                                     |
| [70]       | Mo-YRO                                                                      | OER                                   | 0.1 M HClO <sub>4</sub>                                                        | 1.2 mg·cm <sup>-2</sup>                                                                        | $\eta_{10} = 240$ mV; 10 mA·cm <sup>-2</sup> for 30 h                                                                                                                          | RuO <sub>2</sub> , $\eta_{10} = 306$ mV; IrO <sub>2</sub> , $\eta_{10} = 304$ mV                      |
| [71]       | Y <sub>1</sub> /NC                                                          | CO-CO <sub>2</sub> RR/NRR             | 0.5 M KHCO <sub>3</sub> /0.1 M HCl                                             | 0.4 mg·cm <sup>-2</sup>                                                                        | CO <sub>2</sub> RR: FE = 88.3%; NRR: Y: 23.2 $\mu$ g·cm <sup>-2</sup> ·h <sup>-1</sup> , FE = 12.1%, -0.68 V, 10 h                                                             | —                                                                                                     |
| [72]       | Ce SAs/PSNC                                                                 | ORR                                   | 0.1 M KOH                                                                      | 0.5 mg·cm <sup>-2</sup>                                                                        | $E_{1/2} = 0.9$ V, CV 5000 cycles, Zn-air: 5 mA·cm <sup>-2</sup> for more than 300 h                                                                                           | Pt/C, $E_{1/2} = 0.86$ V                                                                              |
| [73]       | La-Cl SAs/NHPC                                                              | ORR                                   | 0.1 M KOH/6.0 M KOH + 0.2 M Zn(OAc) <sub>2</sub>                               | 0.5 mg·cm <sup>-2</sup>                                                                        | $E_{1/2} = 0.91$ V, AZAB/FZAB: 260.7/68.5 mW·cm <sup>-2</sup> , CV 6000 cycles; $E_{1/2} = 0.85$ V, 94.8% retention of the initial current after ~ 30 h of operation at 0.85 V | Pt/C, $E_{1/2} = 0.87$ V                                                                              |
| [74]       | Tb <sub>SA</sub> @d-Co <sub>3</sub> O <sub>4</sub>                          | HER, UOR                              | 1.0 M KOH (+ 0.5 M urea)                                                       | —                                                                                              | HER: $\eta_{10} = 35$ mV; UOR: 1.27 V for 10 mA·cm <sup>-2</sup> ; overall: 1.22 V for 10 mA·cm <sup>-2</sup> , 93% retention of the initial current after 100 h at 1.44 V     | UOR: 10 mA·cm <sup>-2</sup> , Pt/C; 1.42 V, RuO <sub>2</sub> : 1.37 V; HER: Pt/C, $\eta_{10} = 35$ mV |
| [75]       | Mo <sub>5</sub> O <sub>14</sub> -Y(OH) <sub>3</sub> -CoMoO <sub>4</sub> /CF | HER                                   | 1 M KOH                                                                        | ~ 13.93 mg·cm <sup>-2</sup>                                                                    | $\eta_{10} = 40$ mV, $\eta_{1000} = 219$ mV, CV 10,000 cycles, 800 mA·cm <sup>-2</sup> , 18 h                                                                                  | Pt/C, $\eta_{10} = 88$ mV                                                                             |
| [76]       | 5%Ce-Cu/MoO <sub>2</sub> @C                                                 | NO <sub>3</sub> RR                    | 1.0 M KOH + 0.1 M KNO <sub>3</sub>                                             | 0.4 mg·cm <sup>-2</sup>                                                                        | Y: 20.3 ± 0.7 mg·mg <sub>cat</sub> <sup>-1</sup> ·h <sup>-1</sup> , FE = 92% ± 3%, -0.4 V, 7 cycles                                                                            | —                                                                                                     |
| [77]       | Sn-CeO <sub>2-x</sub>                                                       | NRR                                   | 0.1 M HCl                                                                      | 0.2 mg·cm <sup>-2</sup>                                                                        | Y: 41.1 $\mu$ g·mg <sub>cat</sub> <sup>-1</sup> ·h <sup>-1</sup> , FE = 35.3%, -0.4 V, 15 h, 8 cycles                                                                          | —                                                                                                     |

work provides a reference for the application of rare earth elements in regulating reactions for environmental purposes (Figs. 6(a) and 6(b)).

Solid solution is another effective structural form for RE catalyst design. Su et al. [79] synthesized a series of cerium dioxide (CeO<sub>2-x</sub>) based solid solution materials via hydrothermal methods.

Through a series of characterizations and theoretical studies, it demonstrates that cerium and cobalt, through electron transfer, optimize the band structure and stabilize the electronic configuration of the catalyst. The Co<sub>0.07</sub>Ce<sub>0.93</sub>O<sub>2- $\delta$</sub>  solid solution increases protonation capability, facilitating the formation of H in alkaline media. In addition to being used in conjunction with Co



**Figure 6** (a) The wettability test and the optical images of the electrodes during the HER tests (200 mA·cm<sup>-2</sup>). (b) Schematic illustration of the evolution of gas bubbles on the hydrophobic/hydrophilic electrode during HER. Reproduced with permission from Ref. [78], © Wiley-VCH GmbH 2024. (c) ELF of Y<sub>2</sub>Co-CeO<sub>2</sub>, Co-CeO<sub>2</sub>, Y-CeO<sub>2</sub>, and CeO<sub>2</sub> models. (d) Dependence of ΔG<sub>H+</sub> on the Bader change of O site. Reproduced with permission from Ref. [83], © Wiley-VCH GmbH 2024.

for the preparation of electrolytic water catalysts, Ce can also be utilized in the preparation of catalysts with other metals. The Co<sub>0.07</sub>Ce<sub>0.93</sub>O<sub>2-δ</sub> shows the best catalytic performance. In an anion exchange membrane water electrolysis system, Co<sub>0.07</sub>Ce<sub>0.93</sub>O<sub>2-δ</sub>/NiFe-LDH achieves a current density of 1000 mA·cm<sup>-2</sup> at ~1.86 V in alkaline seawater at 80 °C and exhibits long-term stability for 450 h. This study verifies the great potential of Ce-based solid solutions for practical seawater electrolysis.

Highly dispersed RE species on metal substrates have also been proven effective for HER. Wang et al. [80] employed a high-temperature spray-coating method to highly disperse Ce onto a nickel mesh (NM), resulting in the NiCe/NM catalyst. Through theoretical calculations and research, the researchers conclude that both the dissociation of water and the release of hydrogen on the catalyst surface are accelerated. On the NiCe/NM electrode, the distinct distribution of unoccupied orbitals near the Fermi level for the Ni-slab and NiCe-slab improves the water dissociation step. These factors contribute to the catalyst's excellent HER

performance, exhibiting an overpotential of 169 mV at a current density of 500 mA·cm<sup>-2</sup>. Moreover, the electrolyzer using this catalyst requires only 1.67 V to achieve a current density of 800 mA·cm<sup>-2</sup> under the conditions of 7 M KOH and 80 °C, and it can operate stably for 2000 h.

Heterojunction engineering strategy of RE catalyst is also applied to pH-universal HER catalysts. Chen et al. [81] synthesized a complex CeP<sub>5</sub>O<sub>14</sub>/WP/WS<sub>2</sub> heterojunction catalyst on carbon paper through sequential hydrothermal, electrodeposition, sulfidation, and phosphorization processes. Characterization and theoretical calculations suggest that the heterojunction structure of the catalyst can regulate the electronic structure, thereby accelerating charge transfer, optimizing the Gibbs free energy of hydrogen adsorption (ΔG<sub>H+</sub>), and lowering the d-band center. The introduction of CeP<sub>5</sub>O<sub>14</sub> increases oxygen vacancies in the catalyst, which enhances catalytic activity. This catalyst demonstrates excellent HER performance across various pH environments, with overpotentials at 10 mA·cm<sup>-2</sup> of 105, 154,



and 119 mV in acidic, alkaline, and neutral solutions, respectively, and Tafel slopes of 52, 78, and 93 mV·dec<sup>-1</sup>. Such pH-universal catalysts are highly desirable for complex and practical electrolysis environments.

High-entropy alloys modified by RE elements have attracted wide attention in recent years. Zhang et al. [82] successfully prepared a Ce-tailored PdCeMoCuRu high-entropy alloy using a facile wet-chemical synthesis method. Theoretical studies and calculations indicate that the introduction of cerium increases the electron density around the active sites of Pd, Cu, and Ru, shifting the d-band center away from the Fermi level and strengthening the adsorption of intermediates. This catalyst shows excellent HER ability, which requires only 12.8 mV to achieve a current density of 10 mA·cm<sup>-2</sup> and can operate stably at an industrial-level current density of 1000 mA·cm<sup>-2</sup> for 100 h.

Lattice strain and oxygen vacancy regulation are core advantages of RE doping. Liu et al. [83] collaborated to develop a Y and Co-doped CeO<sub>2</sub> catalyst (Y<sub>2</sub>Co-CeO<sub>2</sub>) for alkaline HER. Through characterizations and theoretical calculations, the researchers attribute the superior HER efficiency to a synergistic lattice strain and oxygen vacancy stabilization strategy. Lattice strain creates more oxygen vacancies with water-splitting activity, while Y doping stabilizes oxygen vacancies through stronger Y–O bonding compared to Ce–O, which endows the catalyst with excellent stability. The catalyst exhibits an overpotential of only 27 mV at 10 mA·cm<sup>-2</sup> and a Tafel slope of 48 mV·dec<sup>-1</sup>, along with excellent stability at high current densities. In AEMWE with Y<sub>2</sub>Co-CeO<sub>2</sub> cathode shows outstanding stability at 600 mA·cm<sup>-2</sup> and 1.67 V in 500 h test (Figs. 6(c) and 6(d)).

For Ni-based non-precious metal catalysts, RE doping can effectively inhibit metal leaching. Wang et al. [84] synthesized a NiMoSmO<sub>x</sub> catalyst on nickel mesh via hydrothermal, water bath, and annealing methods. By introducing Sm doping, a stable Sm<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> phase is formed in the alkaline HER system, which expresses molybdenum leaching and greatly improves the stability of nickel–molybdenum-based catalysts. Characterizations and DFT calculations verify that Sm interacts with the Mo 3d orbital, tuning the electronic states of molybdenum by Mo–Sm bonding in the newly formed Sm<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>, which may result in the improved electrocatalytic HER activity on NiMoSmO<sub>x</sub>. The catalyst exhibits a flower-shaped morphology and exceptional stability, maintaining operation at 500 mA·cm<sup>-2</sup> for over 850 h. Compared to the undoped sample, the HER overpotential at 500 mA·cm<sup>-2</sup> decreases from 159 to 100 mV. This work offers a new route to improve the long-term durability of NiMo-based HER catalysts.

RE-alloy engineering is also promising for acidic HER systems. Chen et al. [85] developed a bifunctional catalyst consisting of Pt–Er alloy clusters and atomically dispersed Pt and Er single atoms, which exhibits high mass activity, stability, and CO tolerance in acidic HER and hydrogen oxidation reaction (HOR). The researchers propose that Pt–Er active sites are formed by several Pt atoms bonded with neighboring Er atoms in the bimetallic Pt–Er alloy cluster, providing more types of active sites. DFT calculations indicate that the multi-site configuration optimizes the adsorption of hydrogen and CO. The Pt-skin and near-atomic scale reduce alloy dissolution and enhance catalyst stability. The Pt–Er/h-NC exhibits excellent acidic HER performance with a low overpotential of 25 mV at 10 mA·cm<sup>-2</sup> and can operate stably in acidic electrolyte at 1000 mA·cm<sup>-2</sup> for over 1200 h. Additionally, Pt–Er/h-NC as the anode for acidic HOR demonstrates remarkable mass activity, impressive stability,

and outstanding CO tolerance. This work highlights the value of RE-alloy engineering for acidic electrocatalytic systems.

### 3.1.2 Oxygen evolution reaction

OER is a four-electron transfer oxidation reaction with slow kinetics and high overpotential, which is the main bottleneck restricting the efficiency of water electrolysis. The key to catalyst design is to optimize the adsorption energy of oxygen-containing intermediates (\*O and \*OOH) and accelerate the rate-determining step of O–O bond formation. REEs, such as Y, Ce, Pr, Nd, Sm, Eu, and Gd, can stabilize the high-valence active sites of transition metals, induce the formation of oxygen vacancies and lattice defects, and adjust the d-band center of active sites, thus significantly improving the OER activity and stability of catalysts in both acidic and alkaline systems.

Ce-based composite catalysts are widely studied for OER. Jiao et al. [86] sequentially electrodeposited NiFeO<sub>x</sub>H<sub>y</sub> hydroxide and CeO<sub>2</sub> onto nickel foam, followed by cyclic voltammetry (CV) activation, to prepare the NiFeO<sub>x</sub>H<sub>y</sub>/CeO<sub>2</sub> catalyst, which exhibits excellent HER performance and stability. Through theoretical research, the researchers conclude that high-valence Ni serves as the active site for the reaction, while the addition of CeO<sub>2</sub> enhances the stability of the catalyst. The catalyst demonstrates a low overpotential of 240 mV at 100 mA·cm<sup>-2</sup> and durability exceeding 2000 h at 200 mA·cm<sup>-2</sup> for OER.

To address the poor performance of traditional NiFe-LDH at high current densities, researchers adopted RE doping strategies. Byaruhanga et al. [87] developed an anion-environment-controlled synthesis strategy, aiming to address the limitations of NiFe LDHs in alkaline oxygen evolution reaction under high current densities. By replacing NH<sub>4</sub>F with NH<sub>4</sub>Cl as the anion precursor in hydrothermal synthesis, they achieved uniform Ce doping into NiFe LDH, avoiding insoluble Ce–F complexes and ensuring structural homogeneity. *Operando* Raman, XAS, and DFT analyses reveal that Ce doping accelerates Ni oxidation, stabilizes the active β-NiOOH phase, and modulates the electronic structure to enhance charge transfer. The optimized NiFe<sub>0.95</sub>Ce<sub>0.05</sub> LDH requires only 307 mV overpotential to reach 1000 mA·cm<sup>-2</sup> in 1 M KOH, with a small Tafel slope of 35.3 mV·dec<sup>-1</sup>. Paired with a Ni&Ni<sub>0.2</sub>Mo<sub>0.8</sub>N HER cathode in AEMWE, it delivers 1 A·cm<sup>-2</sup> at 1.616 V and 8 A·cm<sup>-2</sup> at 2.185 V, maintaining stability for over 400 h.

For acidic OER, multi-RE/transition metal co-doping is an effective solution. Chong et al. [88] prepared La–Mn codoped cobalt spinel nanofibrous catalyst (LMCF) via electrospinning Co-ZIF precursor with La/Mn and thermal activation. As the key rare earth dopant, La is localized on the Co<sub>3</sub>O<sub>4</sub> surface due to its large ionic radius, which induces lattice strain and *in situ* formation of oxygen vacancies on the catalyst surface, optimizing the local electronic structure of Co active sites. It also forms stable OH\*-bridged structures with Co at proton exchange membrane WE (PEMWE) operating potentials, effectively inhibiting Co dissolution and enhancing the acid corrosion resistance of the cobalt spinel, and its strong affinity for surface –OH groups further boosts OER kinetics. Mn is uniformly doped in the Co<sub>3</sub>O<sub>4</sub> bulk lattice, substituting octahedral Co<sup>3+</sup> with Mn<sup>3+</sup> to introduce partially occupied defect states in the bandgap, realizing delocalization of d-electrons, significantly improving the intrinsic conductivity of the oxide, and synergistically regulating the Co<sup>2+</sup>/Co<sup>3+</sup> ratio to expose more active sites. The hierarchical porous nanofibrous structure of LMCF further facilitates mass/charge transfer, and the catalyst achieves a low overpotential of 353 mV at

10 mA·cm<sup>-2</sup> in 0.1 M HClO<sub>4</sub>. Assembled into PEMWE anode, LMCF delivers 2000 mA·cm<sup>-2</sup> at 2.47 V and 4000 mA·cm<sup>-2</sup> at 3.0 V. A mild loss of Co, Mn, and La ions by ~ 1.9 wt.%, ~ 2.8 wt.%, and ~ 1.1 wt.% over their stoichiometric loadings in the LMCF catalyst, respectively, in a period of 80 h was observed during the chronopotentiometry at 10 mA·cm<sup>-2</sup>.

Rare earth doping can optimize the electronic structure of precious metal Ir alloys. Zhang et al. [89] used lanthanide elements to modulate the electronic structure of Ir alloys to enhance acidic OER performance. The researchers mixed graphene, Ir-lanthanide compounds, and cyanamide solids, followed by nano-steam reduction. The researchers conclude that lanthanide elements adjusted the alloy's d-band center, making it more favorable for acidic OER. Moreover, the highest electroactivity of Ir<sub>2</sub>Pr is attributed to improved electron transfer via 4f orbitals and the optimal binding strength of intermediates. Among the catalysts, Ir<sub>2</sub>Pr achieves a maximum mass activity of 2.10 A·mg<sub>Ir</sub><sup>-1</sup> at an overpotential of 300 mV and stability over 200 h at 10 mA·cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>. This work proves that lanthanide regulation is an effective way to enhance the performance of precious metal OER catalysts.

Erbium doping is also proven to create abundant defects for OER. Pan et al. [90] developed an Er-doped cobalt oxide catalyst for the OER. The researchers demonstrate that the introduction of Er induced structural defects and oxygen vacancies, increasing the ratio of Co<sup>3+</sup> to Co<sup>2+</sup>. Both the activity and stability of the catalyst are enhanced. *In situ* Raman spectroscopy reveals that the catalyst accelerates the formation of the key intermediate \*O. Theoretical studies demonstrate an optimized \*O-\*OOH value at Er-Co<sub>3</sub>O<sub>4</sub>, which is close to the theoretical optimal OER activity at the current density of interest. The catalyst requires an overpotential of only 321 ± 5 mV to achieve a current density of 10 mA·cm<sup>-2</sup> and can operate stably for 250 h.

Perovskite oxides modified by RE elements show excellent OER activity. Wang et al. [91] synthesized various mesoporous perovskite oxide nanosheets (MPONs), including LaFeO<sub>3</sub>, A-site-doped LaFeO<sub>3</sub> (A-LaFeO<sub>3</sub>, where A is Pr, Nd, Sm, Eu, or Gd), and B-site-doped LaFeO<sub>3</sub> (B-LaFeO<sub>3</sub>, where B is Mn, Co, Ni, Cu, or Zn), via a self-sacrificial template-induced nanostructure modulation strategy. Combining experimental and theoretical studies, the researchers prove that introducing rare earth elements at the A-site not only increases the density of active sites but also enhances lattice oxygen participation, thereby improving intrinsic activity. Through extensive research, they found that the best-performing catalyst among them, Eu-LaFeO<sub>3</sub> requires OER overpotential of only 267 mV to achieve a current density of 10 mA·cm<sup>-2</sup>.

Gadolinium can regulate the phase composition of cerium-based materials. Liao et al. [92] prepared Gd-doped CeO<sub>2</sub>/Ce(OH)CO<sub>3</sub> nanohybrids on copper foam via a one-step hydrothermal method, with rare earth Gd serving as the regulatory dopant. Gd with smaller ionic radius embeds into the cerium-based lattice to induce lattice contraction, inhibit crystal growth and regulate the phase composition of the nanohybrid—Its doping accelerates the redox conversion between CeO<sub>2</sub> and Ce(OH)CO<sub>3</sub> increasing the content of Ce(OH)CO<sub>3</sub> which promotes OER via hydrogen bonding with adsorbed water. Gd also modulates the catalyst's morphology, driving the transformation from leaf-like to uniform nanosheet/nanoflower structures with more exposed active sites, and most importantly, it elevates the Ce<sup>3+</sup> ratio and induces abundant oxygen vacancies in the cerium-based matrix, optimizing the electronic structure,

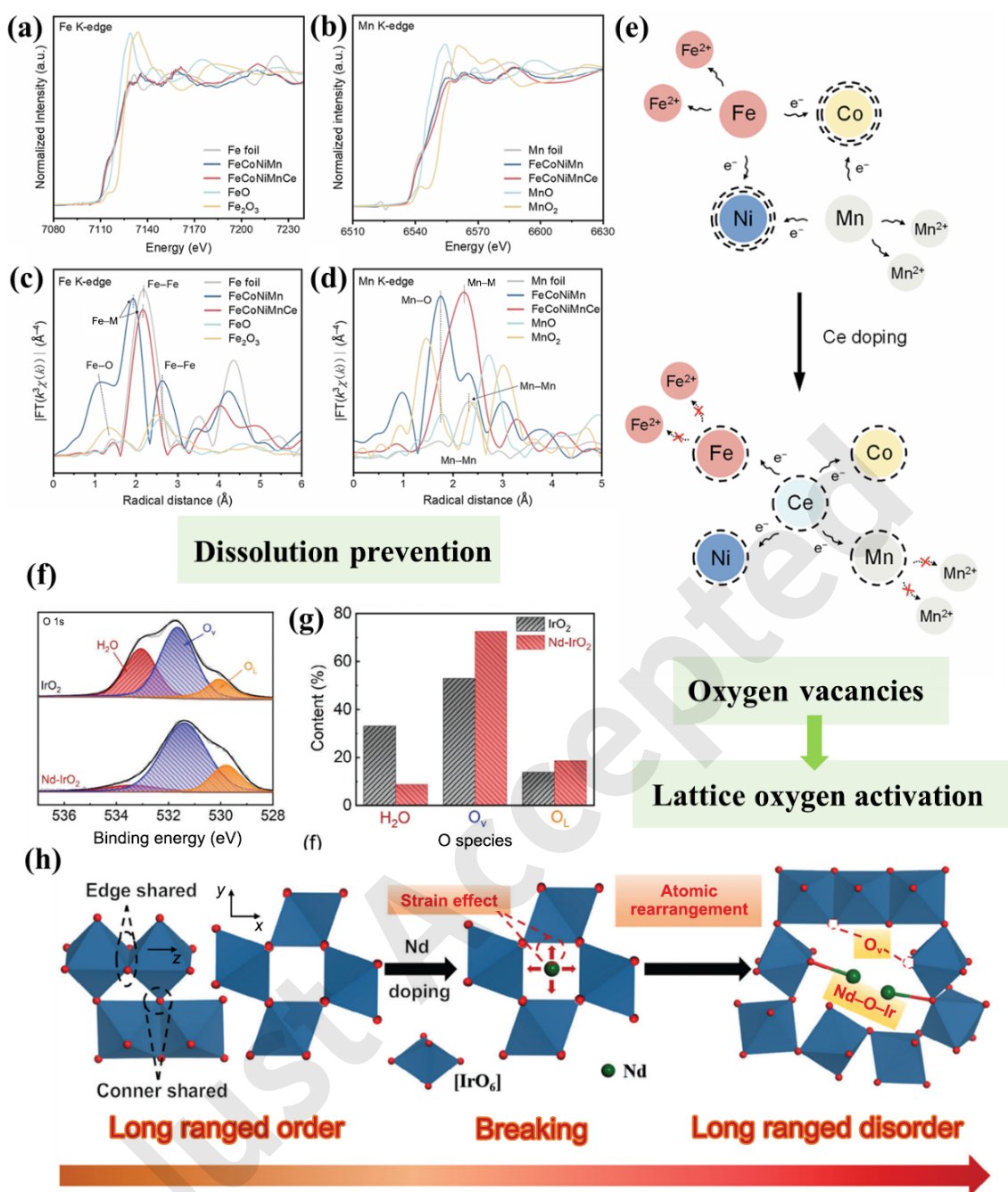
enhancing the material's conductivity, and facilitating the adsorption/migration of oxygen intermediates. The optimized 2% Gd-doped CeO<sub>2</sub>/Ce(OH)CO<sub>3</sub>/CF exhibits superior OER activity with a low overpotential of 292 mV at 10 mA·cm<sup>-2</sup> and good stability.

Aiming at seawater electrolysis, RE doping can resist chloride corrosion. Uddin et al. [93] reported a Ce-doped SrCoO<sub>x</sub> electrocatalyst for stable oxygen evolution reaction in simulated alkaline saline water and real seawater. Synthesized via a sol-gel method, the optimized 0.5% Ce-doped 5% SrCoO<sub>x</sub> (0.5% Ce-SCO) forms a protective CeO<sub>x</sub> passivation layer and generates lattice defects by Ce substituting Sr. This dual effect blocks corrosive Cl<sup>-</sup> ions, suppresses the competitive chlorine evolution reaction (CER), and enhances OER kinetics. Post-reaction characterizations confirm preserved crystal structure and morphology. This work provides a feasible strategy for developing corrosion-resistant electrocatalysts using rare earth doping, promising for seawater electrolysis applications. The catalyst exhibits a low corrosion current of ~1.10 μA·cm<sup>-2</sup> and a high corrosion potential of 0.90 V vs. reversible hydrogen electrode (RHE), with a Tafel slope of 81.7 mV·dec<sup>-1</sup>. It maintains stable OER performance for 45 h in real seawater and shows minimal degradation after 500 CV cycles. This work provided a feasible strategy for seawater electrolysis catalysts.

High-entropy alloys with RE components are emerging OER candidates. Hu et al. [94] proposed a Ce-mediated charge redistribution strategy, synthesizing FeCoNiMnCe HEA via rapid Joule heating. The electron-rich Ce acts as an efficient electron donor, inducing charge transfer to neighboring TMs (Fe, Co, Ni, and Mn) and regulating their electronic structures. This modulate increases the dissolution activation energy of Fe/Mn, suppressing their oxidative dissolution, and optimizes the electronic orbitals of Co/Ni by lowering antibonding state energies. The FeCoNiMnCe HEA exhibits excellent OER performance, requiring an overpotential of only 267.5 mV to reach 10 mA·cm<sup>-2</sup> in 1 M KOH with a Tafel slope of 50.35 mV·dec<sup>-1</sup>. More notably, it achieves exceptional durability, retaining negligible decay over 1000 h of OER operation at 10 mA·cm<sup>-2</sup>. When applied as the air cathode in zinc-air batteries, it enables stable cycling for 4600 h at 2 mA·cm<sup>-2</sup>, with a peak power density of 205.7 mW·cm<sup>-2</sup> and a high specific capacity of 804.97 mAh·g<sup>-1</sup>. This work reflected the great potential of RE-containing high-entropy alloys (Figs. 7(a)–7(e)).

Aiming to optimize IrO<sub>2</sub> by neodymium doping, Wang et al. [95] doped Nd into IrO<sub>2</sub>, resulting in Nd-IrO<sub>2</sub>. The researchers attribute the improvement to Nd doping disrupting the long-range ordered structure by triggering the strain effect. Besides, Nd-doping created more oxygen vacancies, triggering Nd-IrO<sub>2</sub> to catalyze OER mainly through LOM by activating lattice oxygen owing to abundant O<sub>v</sub>. The formed Nd-O-Ir bonds tailor the electronic structure of Ir, leading to a lowered d-band center that weakens intermediate absorption on Ir sites. The catalyst requires a relatively low overpotential of 263 mV at 10 mA·cm<sup>-2</sup>, demonstrating significantly higher mass activity than commercial IrO<sub>2</sub> (Com-IrO<sub>2</sub>). Moreover, the catalyst can operate stably at 50 mA·cm<sup>-2</sup> for 20 h, far surpassing commercial IrO<sub>2</sub> due to the oxidation-suppressing effect induced by Nd doping (Figs. 7(f)–7(h)).

Similarly, Nd modification works well for Ru-based OER catalysts. Researchers Li et al. [96] synthesized Nd<sub>0.1</sub>RuO<sub>x</sub> via dip-coating and annealing. Theoretical studies reveal that Nd doping decreased the d-band center energy, balancing the adsorption and desorption of oxygen intermediates. Additionally, doping Nd leads



**Figure 7** XANES spectra of (a) Fe K-edge and (b) Mn K-edge. EXAFS spectra of (c) Fe K-edge and (d) Mn K-edge. (e) Mechanism of electron transfer before and after the introduction of Ce. Reproduced with permission from Ref. [94], © American Chemical Society 2026. (f) The XPS high-resolution spectra of O 1s. (g) The relative content of O species for Nd-IrO and IrO. (h) Scheme of Nd doping process in IrO<sub>2</sub> and illustration of strain effect and atomic rearrangement. Reproduced with permission from Ref. [95], © Wiley-VCH GmbH 2024.

to the formation of higher valence Ru<sup>4+</sup> during OER, indicating that the introduction of Nd can effectively suppress the dissolution of Ru in acidic electrolytes, enhancing stability in acidic OER conditions and reducing Ru dissolution. The catalyst achieves an overpotential of 211 mV at 10 mA·cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. A PEM electrolyzer using Nd<sub>0.1</sub>RuO<sub>x</sub>/carbon cloth (CC) as the anode can operate stably at 10 mA·cm<sup>-2</sup> for 50 h.

Dual RE/metal doping is also a reliable design route. Li et al. [97] synthesized a Nd and Ni co-doped Co<sub>2</sub>O<sub>3</sub> catalyst. Through *in situ* Raman spectroscopy and DFT calculations, the researchers elucidate the reaction mechanism. Nd incorporation enables the critical step of CoOOH formation on the catalyst surface to occur

at a lower potential. Furthermore, Ni and Nd doping optimizes the electronic structure, facilitating intermediate reactions and accelerating the rate-determining step (i.e., O → OOH\*), thereby reducing the energy barrier for OOH\* formation. These improvements collectively enhance the catalyst's performance, exhibiting excellent water-splitting performance with an OER overpotential of 269 mV at 10 mA·cm<sup>-2</sup> and a Tafel slope of 54 mV·dec<sup>-1</sup>.

Samarium-doped perovskite also exhibits outstanding OER performance. Researchers from multiple countries [98] collaborated to develop Sm-doped AgNbO<sub>3</sub> perovskite electrocatalyst via a sonication method. Sm doping induces lattice



distortion in  $\text{AgNbO}_3$  due to its distinct ionic radius, reducing particle agglomeration and increasing the specific surface area, which exposes more active sites. As a rare earth element with unique 4f orbital characteristics, Sm optimizes the charge density distribution of the perovskite, and lowers the charge transfer resistance. Besides, Sm doping improves electrical conductivity, accelerating OER reaction kinetics. It also enlarges the electrochemical surface area and increases the roughness factor, further boosting catalytic activity. The optimized catalyst exhibits exceptional OER performance: a low overpotential of 203 mV at  $10 \text{ mA}\cdot\text{cm}^{-2}$  and a small Tafel slope of  $35.22 \text{ mV}\cdot\text{dec}^{-1}$ .

### 3.1.3 Bifunctional catalysts for overall water splitting

Bifunctional catalysts with both excellent HER and OER performance can simplify the device structure of water electrolysis systems, reduce the cost of catalyst loading, and are the key to the industrialization of water electrolysis technology. REE-modified bifunctional catalysts rely on the electronic modulation and structural regulation ability of REEs, realize the simultaneous optimization of HER and OER performance, and exhibit excellent catalytic activity and long-term stability in overall water splitting, even at industrial-level high current densities.

In a typical work of yttrium doping, Wang et al. [99] synthesized a Y-doped heterogeneous bifunctional catalyst  $\text{Y-MSe}_x/\text{NF}$  on NF through a two-step hydrothermal method. The researchers believed that the hydrophilicity of Y causes it to combine with water vapor in the air to form  $\text{Y-O-H}$  compounds, which promote the binding and conversion of water. The doping of Y also changes the electron density around Ni due to the enhanced synergistic interaction between metal elements, improving the electrochemical activity of the catalyst. In addition, the researchers believe that the connected structure of nanosheets and nanoscale microspheres generated by hydrothermal selenium increases the catalytic reaction area. This catalyst can achieve overpotentials of only 350 mV for HER and 340 mV for OER at a current density of  $1000 \text{ mA}\cdot\text{cm}^{-2}$  and can operate stably for 50 h.

In another representative work of Yttrium, Zhang et al. [100] reported a method for preparing phosphorus and yttrium co-doped cobalt hydroxide compound on nickel foam. The researchers synthesized the  $(\text{YP-Co}(\text{OH})\text{F})$  catalyst through a hydrothermal and phosphating method, which exhibits good catalytic performance for both HER and OER. Although Y only accounts for a very small part of the catalyst, through controlled experiments, the researchers demonstrate that the co-doping of Y and P optimizes the electronic environment of  $\text{Co}(\text{OH})\text{F}$ , facilitates electron transfer, enlarges the ECSA, and thus improves the catalytic activity of water electrolysis. At a current density of  $10 \text{ mA}\cdot\text{cm}^{-2}$ , the OER and HER overpotentials are 238 and 55 mV, respectively.

Ding et al. [101] used MOFs as templates and introduced cerium into CoP through ultrasonic synthesis followed by phosphorization. Characterizations indicate that cerium introduces abundant catalytic site defects, and superior conductivity. Besides, theoretical studies prove that doped Ce modulates the electronic structure of CoP, optimizing the adsorption and desorption energies of various reaction intermediates at the reactive sites, thereby reducing the overall energy barrier of the rate-limiting step and enhancing catalytic activity. The catalyst achieves overpotentials of 152 mV for HER at  $10 \text{ mA}\cdot\text{cm}^{-2}$  and 352 mV for OER at  $50 \text{ mA}\cdot\text{cm}^{-2}$ , respectively. Additionally, in an alkaline medium, using  $\text{Ce}_{0.04}\text{Co}_{0.96}\text{P}$  as both cathode and anode delivers a cell voltage of 1.55 V at  $10 \text{ mA}\cdot\text{cm}^{-2}$ .

Electrodeposited RE mixed-phase oxides are easy to scale up. Inamdar et al. [102] synthesized a cobalt oxide/cerium mixed-phase oxide heterocomposite nanoflakes catalyst via electrodeposition. Combining characterization methods, such as XPS spectra, X-ray diffraction (XRD) patterns, Raman spectra, and Fourier transform infrared (FTIR) spectra, the researchers demonstrate that the synthesized catalyst is a mixture of metal oxides. Among them, Ce forms both  $\text{Ce}_2\text{O}_3$  and  $\text{CeO}_2$  phases. This catalyst requires only 177 and 76 mV to achieve  $20 \text{ mA}\cdot\text{cm}^{-2}$  for OER and  $10 \text{ mA}\cdot\text{cm}^{-2}$  for HER, respectively, and exhibits excellent stability. A  $\text{Co}_{0.85}\text{Ce}_{0.15}||\text{Co}_{0.85}\text{Ce}_{0.15}$  electrolyzer achieves a current density of  $10 \text{ mA}\cdot\text{cm}^{-2}$  at a very low cell voltage of 1.56 V, which further decreases to 1.48 V at  $55^\circ\text{C}$ . At an industrial-level current density of  $1000 \text{ mA}\cdot\text{cm}^{-2}$ , the cell voltage is only 2.07 V. This study provides a useful reference for the electrodeposition of rare earth oxide catalytic materials.

In order to improve the stability and activity of NiFe-based electrocatalysts, a strategy of Ce-modification was employed. Yaseen et al. [103] synthesized a self-supported porous network  $\text{Ni}(\text{OH})_2\text{-CeO}_x$  heterostructure layer on a  $\text{FeOOH}$ -modified Ni-mesh ( $\text{NiCe/Fe@NM}$ ) electrode via an electrodeposition method. The researchers attribute the enhanced catalytic performance to the following reasons: well-optimized surface and electronic structures facilitated by an optimal Ce ratio, rapid reaction kinetics, and a superhydrophilic/superaerophobic interface. The best-performing  $\text{NiCe}_{0.05}/\text{Fe@NM}$  requires overpotentials of only 163 and 262 mV to achieve a current density of  $100 \text{ mA}\cdot\text{cm}^{-2}$  for HER and OER, respectively, and requires only 1.701 V to achieve  $100 \text{ mA}\cdot\text{cm}^{-2}$  with robust stability over 1000 h in an alkaline medium.

La-based nanowire (NW) heterojunctions are also promising candidates. Zhang et al. [104] conducted sequential annealing, electrodeposition, and electrochemical reduction on pretreated nickel foam, ultimately developing a porous  $\text{Co}(\text{OH})_2/\text{La}(\text{OH})_3@Cu$  NW ( $\text{CH/LH@Cu}$  NW) heterojunction catalyst with excellent catalytic performance for both OER and HER. Modeling and theoretical calculations reveal that the strong interaction within the heterojunction structure can modulate the electronic structure of the active centers and optimize the adsorption energy of intermediates. The porous structure and highly conductive substrate also contribute to the catalyst's superior catalytic activity. In alkaline HER and OER, the catalyst requires overpotentials of only 75 and 273 mV, respectively, to achieve a current density of  $100 \text{ mA}\cdot\text{cm}^{-2}$ . A cell using this catalyst as both the anode and cathode requires only 1.56 V to reach a current density of  $20 \text{ mA}\cdot\text{cm}^{-2}$ . The multistep chronopotentiometric curve at the current densities of 10, 20, 50, and  $100 \text{ mA}\cdot\text{cm}^{-2}$  for the  $\text{CH/LH@Cu}$  NW-based cell has no obvious potential fluctuations after about 50 h.

La-doped molybdenum phosphide improves dual activity. Ye et al. [105] developed a nitrogen-doped carbon-encapsulated La-doped MoP nanoparticle catalyst ( $\text{La-MoP@N/C}$ ). The induction of La increases the exposed active sites and electrochemically active area, decreases charge transfer resistance, and redistributes charge density. Theoretical studies reveal that La doping not only effectively adjusts the electron density around Mo and P atoms, accelerating adsorption and desorption processes, but also increases the number of active sites. Overall, the La plays the role of both improving the activity of active sites and increasing the number of active sites. The optimal  $\text{La}_{0.025}\text{-Mo}_{0.975}\text{P@N/C}$  requires overpotentials of only 113 and 388 mV for HER and OER, respectively, to reach  $10 \text{ mA}\cdot\text{cm}^{-2}$ . A two-electrode electrolyzer

assembled with  $\text{La}_{0.025}\text{-Mo}_{0.975}\text{P@N/C}$  requires an initial cell voltage of just 1.73 V to drive a current density of 10  $\text{mA}\cdot\text{cm}^{-2}$  in an alkaline medium and exhibits excellent stability for over 24 h.

La-doped molybdate catalysts show unique surface reconstruction behavior. Arumugam et al. [106] doped La into  $\text{CoMoO}_4$ . *In situ* testing and theoretical calculations demonstrate that La doping lowered the d-band center of Co, optimizes the adsorption energy of intermediates, and improves HER and OER activity. In addition, the researchers investigate the surface dynamic reconstruction of  $\text{La}_x\text{CoMoO}_4$  in OER and HER systems, which illustrates the catalytic mechanism and the reason of the improving performance. In the OER process, the transformation of  $\beta\text{-CoOOH}$  to  $\gamma\text{-CoOOH}$  is considered to be the reaction mechanism of the catalyst. At the same time,  $\text{La}_x\text{CoMoO}_4$  is favorable for promoting faster surface reconstruction kinetics in an alkaline environment, thus exposing the abundant active sites of  $\gamma\text{-CoOOH}$  as the major active component. While in HER, initially formed  $\gamma\text{-CoOOH}$  gradually converts to  $\alpha\text{-Co(OH)}_2$ , and the exsolution of Mo as  $\text{MoO}_4^{2-}$  recombines to form  $\text{MoO}_x/\text{Co(OH)}_2/5\% \text{La}_x\text{CoMoO}_4$  hybrids under strong reduction potentials and acts as the active component for HER. The best-performing 5%  $\text{La}_x\text{CoMoO}_4$  requires overpotentials of only 0.219 and 0.272 V for HER and OER, respectively, to reach 20  $\text{mA}\cdot\text{cm}^{-2}$ .

Based on typical NiFe-LDH and RE doping strategy, Nagappan et al. [107] synthesized Sm-doped NiFe-LDH catalysts on nickel foam via a one-step hydrothermal method. The researchers believe that tuning the Ni-to-Fe ratios in NiFeLDH and doping with Sm ions improves the electrical structure and intrinsic activity. DFT calculations indicate that the OER overpotential of  $\text{SmNi}_{0.02}\text{Fe-LDH}$  is significantly reduced compared to the undoped sample. Additionally, the Gibbs free energy change ( $\Delta G$ ) value for HER is close to 0 eV for Sm-doped  $\text{SmNi}_{0.02}\text{Fe-LDH}$  (−0.28 eV), explaining the performance enhancement. Among the catalysts,  $\text{SmNi}_{0.02}\text{Fe-LDH}$  achieves 10  $\text{mA}\cdot\text{cm}^{-2}$  at lower overpotentials (230 mV for OER, 95 mV for HER). In AEMWE cells, the  $\text{SmNi}_{0.02}\text{Fe-LDH}$  cathode and anode pair exhibits outstanding activity (0.9  $\text{A}\cdot\text{cm}^{-2}$  at 2 V) and stability over 120 h.

REEs, such as Y, Ce, La, Sm, Nd, Pr, Er, Tm, Eu, and Gd, play a multi-faceted regulatory role in water electrolysis catalysts, and the optimization mechanisms for HER and OER are highly targeted. For HER, REEs balance the water dissociation energy and  $\text{H}^+$  adsorption energy by constructing heterogeneous interfaces, inducing oxygen vacancies, and adjusting the d-band center of active sites, thus reducing the reaction overpotential and accelerating the catalytic kinetics. For OER, REEs stabilize high-valence active sites, optimize the adsorption energy of oxygen-containing intermediates, and enhance lattice oxygen participation by inducing structural defects and oxygen vacancies, thereby improving the intrinsic activity and stability of the catalyst.

REE-based bifunctional catalysts for overall water splitting integrate the above regulatory mechanisms and realize the simultaneous optimization of HER and OER performance through strategies, such as heteroatom doping, heterojunction construction, and alloying. These catalysts exhibit excellent performance in both acidic and alkaline systems, can maintain long-term stability at industrial-level high current densities, and even have good catalytic activity in seawater electrolysis systems, showing broad industrial application prospects. The catalysts involved in the relevant references of Section 3.1 and their performances are shown in Table 2.

## 3.2 Carbon dioxide reduction reaction

$\text{CO}_2\text{RR}$  can convert greenhouse gas  $\text{CO}_2$  into high-value carbon-based chemicals and fuels (such as formic acid, CO, methane, ethanol, ethylene, etc.), which have important environmental and economic benefits. However,  $\text{CO}_2\text{RR}$  faces the problems of high C=O bond activation energy, many reaction paths, and low product selectivity. REEs can effectively regulate the electronic structure of  $\text{CO}_2\text{RR}$  catalysts, optimize the adsorption and activation of  $\text{CO}_2$  molecules and reaction intermediates, and suppress the competitive HER, thus improving the catalytic activity and product selectivity of  $\text{CO}_2\text{RR}$  catalysts. According to the different target products, the research progress of REE-based  $\text{CO}_2\text{RR}$  catalysts is classified and elaborated below.

### 3.2.1 $\text{CO}_2\text{RR}$ to $\text{C}_1$ products

Formic acid, methane, and carbon monoxide are the main  $\text{C}_1$  products obtained from electrocatalytic carbon dioxide reduction without C–C coupling. When used in  $\text{CO}_2\text{RR}$  catalysts, REEs play a crucial role in advancing these transformations by stabilizing catalyst active sites, optimizing the adsorption energy of key intermediates (such as  $\text{*OCHO}$  for formate or  $\text{*CO}$  and  $\text{*CHO}$  for methane), and modulating electronic structures to lower reaction energy barriers. Consequently, REE doping significantly improves selectivity, catalytic activity, and stability across various  $\text{C}_1$  product pathways.

Cerium-modified bismuth catalysts are widely used for formic acid production. In a work of Wang et al. [108], the researchers utilized the unique electronic structure of rare earth cerium ions. They prepared Ce-doped Bi@C nanorods via pyrolysis of Ce-doped Bi-MOF precursors. This catalyst features a modulated electronic structure around Bi active sites, shortening the Bi–Bi bond length, strengthening  $\text{CO}_2$  adsorption capacity. XPS, X-ray absorption near-edge spectroscopy (XANES), and extended X-ray absorption fine structure (EXAFS) characterizations confirm that Ce doping increases the electron density of Bi sites and optimizes the adsorption of the  $\text{*OCHO}$  intermediate. Ce incorporation lowers the energy barrier for  $\text{*OCHO}$  formation and accelerates electron transfer, thereby promoting formate production and suppressing the competitive HER. It exhibits excellent electrocatalytic performance for  $\text{CO}_2$ -to-formate conversion, achieving a Faradaic efficiency of over 90% in an ultra-wide potential window of 1000 mV (from −0.9 to −1.9 V vs. RHE) in an H-cell, with a maximum FE of 96.1% at −1.5 V vs. RHE. In a flow cell configuration, it delivers a high current density of 225.82  $\text{mA}\cdot\text{cm}^{-2}$  at −1.3 V vs. RHE while maintaining FE > 90%.

In another work of Bi and Ce for  $\text{CO}_2\text{RR}$  to  $\text{C}_1$  production. Palanimuthu et al. [109] reported a cerium and sulfur-doped hierarchical bismuth oxide nanosheet ( $\text{Ce@S-Bi}_2\text{O}_3$ ) for the electrochemical  $\text{CO}_2\text{RR}$  ( $\text{ECO}_2\text{RR}$ ). Characterizations confirm that the S and Ce doping induces a modification in the Bi site electronic configuration that facilitates  $\text{CO}_2$  adsorption and improves electron transfer to produce a high conversion rate of formate. Theoretical studies indicate that the doping of cerium and sulfur weakens the OH and  $\text{H}^+$  species, strengthening the OCHO pathway and making it dominant. This catalyst achieves a maximum Faradaic efficiency of 92.5% and a current density of 42.09  $\text{mA}\cdot\text{cm}^{-2}$  at −1.16 V vs. RHE in an H-cell system. Using a three-chamber gas diffusion electrode reactor with  $\text{Ce@S-Bi}_2\text{O}_3$ , a maximum FE of 85% is achieved over a wide range of applied potentials (−0.86 to −1.36 V vs. RHE).

Through a MOF-derived strategy, in a work of Zhang et al. [110] on Bi and Ce for  $\text{CO}_2\text{RR}$ , researchers synthesized a Ce-Bi@C

**Table 2** Summary of catalyst performances in Section 3.1

| References | Name                                                     | Catalyst | Electrolyte                                                                           | Mass loading                                                                            | Performance                                                                                                                              | Commercial catalysts                                                                                                                                                      |
|------------|----------------------------------------------------------|----------|---------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| [78]       | Ni/Y <sub>2</sub> O <sub>3</sub>                         | HER      | 1.0 M KOH                                                                             | 3.5 mg·cm <sup>-2</sup>                                                                 | $\eta_{10} = 61.1 \pm 3.7$ mV, 1000 mA·cm <sup>-2</sup> , 500 h                                                                          | Pt/C, $\eta_{10} = 70$ mV                                                                                                                                                 |
| [79]       | Co <sub>0.07</sub> Ce <sub>0.93</sub> O <sub>2-δ</sub>   | HER      | 1.0 M alkaline seawater                                                               | 0.05 mg·cm <sup>-2</sup>                                                                | $\eta_{10} = 160$ mV; overall: 1.86 V for 1000 mA·cm <sup>-2</sup> , 450 h                                                               | Pt/C, $\eta_{10} = 70$ mV (KOH)                                                                                                                                           |
| [80]       | NiCe/NM                                                  | HER      | 1.0 M KOH                                                                             | —                                                                                       | $\eta_{500} = 169$ mV, 7 M KOH, 80 °C, 800 mA·cm <sup>-2</sup> , 2000 h                                                                  | —                                                                                                                                                                         |
| [81]       | CeP <sub>5</sub> O <sub>14</sub> /WP/WS <sub>2</sub> /CC | HER      | 0.5 M H <sub>2</sub> SO <sub>4</sub> /1.0 M KOH/1.0 M phosphate-buffered saline (PBS) | —                                                                                       | $\eta_{10} = 105, 154$ , and 119 mV, 5000 cycles CV in acidic, alkaline, and neutral                                                     | Pt/C, $\eta_{10} = 52/70$ mV in acidic/alkaline                                                                                                                           |
| [82]       | PdCeMoCuRu HEA                                           | HER      | 0.5 M H <sub>2</sub> SO <sub>4</sub>                                                  | 0.25 mg·cm <sup>-2</sup>                                                                | $\eta_{10} = 12.8$ mV; 1 A·cm <sup>-2</sup> , 7% current decrease after 100 h; steady for 10,000 CV cycles                               | Pt/C, $\eta_{10} = 24.8$ mV                                                                                                                                               |
| [83]       | Y <sub>2</sub> Co-CeO <sub>2</sub>                       | HER      | 1.0 M KOH                                                                             | 1.5 mg·cm <sup>-2</sup>                                                                 | $\eta_{10} = 27$ mV; overall: 600 mA·cm <sup>-2</sup> , 500 h                                                                            | Pt/C, $\eta_{10} = 70$ mV                                                                                                                                                 |
| [84]       | NiMoSmO <sub>x</sub> /NM                                 | HER      | 1.0 M KOH                                                                             | —                                                                                       | $\eta_{500} = 10$ mV, 500 mA·cm <sup>-2</sup> , 850 h                                                                                    | —                                                                                                                                                                         |
| [85]       | Pt-Er/h-NC                                               | HER, HOR | 0.5 M H <sub>2</sub> SO <sub>4</sub>                                                  | 81 μg·cm <sup>-2</sup> (Pt: 4.78 wt.%)                                                  | HER: $\eta_{10} = 25$ mV; HOR: 428 mA·mg <sub>Pt</sub> <sup>-1</sup> at 20 mV; PEM: 1 A·cm <sup>-2</sup> , 40 h                          | Pt/C, $\eta_{10} = 24.8$ mV                                                                                                                                               |
| [86]       | NiFeO <sub>x</sub> H <sub>y</sub> /CeO <sub>2</sub>      | OER      | 1.0 M KOH                                                                             | —                                                                                       | $\eta_{100} = 240$ mV, 200 mA·cm <sup>-2</sup> , 2100 h                                                                                  | RuO <sub>2</sub> /NF, $\eta_{100} = 445$ mV                                                                                                                               |
| [87]       | NiFe <sub>0.95</sub> Ce <sub>0.05</sub> LDH              | OER      | 1.1 M KOH                                                                             | —                                                                                       | $\eta_{1000} = 307$ mV, AEMWE: 1 A·cm <sup>-2</sup> , 400 h, 0.133 mV·h <sup>-1</sup> required potential increasing                      | IrO <sub>2</sub> , $\eta_{10} = 280$ mV, $\eta_{100} = 350$ mV                                                                                                            |
| [88]       | LMCF                                                     | OER      | 0.1 M HClO <sub>4</sub>                                                               | 0.9 mg·cm <sup>-2</sup>                                                                 | OER: $\eta_{10} = 353$ mV; PEMWE: 2000 mA·cm <sup>-2</sup> at 2.47 V, 4000 mA·cm <sup>-2</sup> at 3.00 V, 100 h, 210 mA·cm <sup>-2</sup> | Ir, 0.4 mg·cm <sup>-2</sup> ; 2000 mA·cm <sup>-2</sup> , 1.93 V                                                                                                           |
| [89]       | Ir <sub>2</sub> Pr                                       | OER      | 0.5 M H <sub>2</sub> SO <sub>4</sub>                                                  | Ir, 14.1–15.3 μg·cm <sup>-2</sup>                                                       | $\eta_{10} = 300$ mV, 200 h                                                                                                              | Ir/G, $\eta_{10} = 371$ mV                                                                                                                                                |
| [90]       | 4% Er-Co <sub>3</sub> O <sub>4</sub>                     | OER      | 0.5 M H <sub>2</sub> SO <sub>4</sub>                                                  | 0.5–1 mg·cm <sup>-2</sup>                                                               | $\eta_{10} = 321 \pm 5$ mV, 100 mA·cm <sup>-2</sup> , 30 h, 99 mV, overpotential increasing                                              | RuO <sub>2</sub> , $\eta_{10} = 298$ mV; IrO <sub>2</sub> , $\eta_{10} = 295$ mV                                                                                          |
| [91]       | Eu-LaFeO <sub>3</sub>                                    | OER      | 1.0 M KOH                                                                             | 4 mg·cm <sup>-2</sup>                                                                   | $\eta_{10} = 267$ mV, 24 h, 10 mA·cm <sup>-2</sup> , 90.7% retention of the initial current after 24 h at 10 mA·cm <sup>-2</sup>         | Commercial IrO <sub>2</sub> : $\eta_{10} = 270$ –290 mV; commercial RuO <sub>2</sub> : $\eta_{10} = 280$ –300 mV; commercial RuO <sub>2</sub> : $\eta_{10} = 280$ –300 mV |
| [92]       | CeO <sub>2</sub> /Ce(OH)CO <sub>3</sub>                  | OER      | 1.0 M KOH                                                                             | —                                                                                       | $\eta_{10} = 292$ mV; 0.3% current decrease after 40 h at 1.56 V                                                                         | RuO <sub>2</sub> , $\eta_{10} = 359$ mV                                                                                                                                   |
| [93]       | 0.5% Ce-SCO                                              | OER      | 1.1 M KOH + 0.5 M NaCl/seawater                                                       | 8 mg·cm <sup>-2</sup>                                                                   | Tafel: 81.7 mV·dec <sup>-1</sup> ; 45 h, 1.62 V, seawater                                                                                | IrO <sub>2</sub> , Tafel: 131.2 mV·dec <sup>-1</sup>                                                                                                                      |
| [94]       | FeCoNiMnCe HEA                                           | OER      | 1.0 M KOH                                                                             | Rotating disk electrode (RDE): 0.383 mg·cm <sup>-2</sup> ; NF: 0.25 mg·cm <sup>-2</sup> | $\eta_{10} = 267.5$ mV, 4600 h at 2 mA·cm <sup>-2</sup>                                                                                  | IrO <sub>2</sub> , $\eta_{10} = 347.4$ mV                                                                                                                                 |
| [95]       | Nd-IrO <sub>2</sub>                                      | OER      | 0.5 M H <sub>2</sub> SO <sub>4</sub>                                                  | 0.78 mg·cm <sup>-2</sup>                                                                | $\eta_{10} = 263$ mV, 400 mA·cm <sup>-2</sup> , 60 h                                                                                     | IrO <sub>2</sub> , $\eta_{10} = 284$ mV                                                                                                                                   |
| [96]       | Nd <sub>0.1</sub> RuO <sub>x</sub>                       | OER      | 0.5 M H <sub>2</sub> SO <sub>4</sub>                                                  | —                                                                                       | $\eta_{10} = 211$ mV, $\eta_{10}$ increases by 7 mV after 3000 CV cycles                                                                 | RuO <sub>2</sub> /CC, $\eta_{10} = 359$ mV                                                                                                                                |
| [97]       | NdNi-Co <sub>3</sub> O <sub>4</sub>                      | OER      | 1.0 M KOH                                                                             | 0.71 mg·cm <sup>-2</sup> , Zn-air, 2.0 mg·cm <sup>-2</sup>                              | $\eta_{10} = 269$ mV; $\eta_{10}$ increased by 12 mV and $\eta_{50}$ increases by 28 mV after 50 h                                       | RuO <sub>2</sub> , $\eta_{10} = 292$ mV                                                                                                                                   |
| [98]       | Sm-doped AgNbO <sub>3</sub> /NF                          | OER      | 1.0 M KOH                                                                             | —                                                                                       | $\eta_{10} = 203$ mV, 50 h, 5000 CV cycles                                                                                               | —                                                                                                                                                                         |

catalyst. The researchers successfully synthesized porous framework by annealing the MOF-based precursor. *In situ* characterizations and DFT calculations show that cerium doping increases the electron density around Bi, thereby enhancing the binding energy of the key OCHO intermediate and boosting the catalyst's activity toward formate. The best-performing Ce<sub>2</sub>-Bi@C catalyst achieves a current density of 13.7 mA·cm<sup>-2</sup> and a selectivity of 97.2% toward the formate product at −1.1 V vs. RHE. Additionally, Ce<sub>2</sub>-Bi@C exhibits a stable current density and maintains a high average FE (HCOO<sup>-</sup>) of 93.6% during 48 h electrolysis at −1.1 V vs. RHE.

In a work of Bi and another RE element yttrium, Xie et al. [111] conducted research on carbon dioxide reduction to formic acid using rare earth elements. In the work, they employed the strong anti-reductive property of rare earth yttrium ions to stabilize Bi<sub>2</sub>O<sub>3</sub>. They synthesized Y-doped Bi<sub>2</sub>O<sub>3</sub> nanosheets via a solvothermal method. The Y doping modulates the Bi–O electronegativity difference, stabilizes the Bi<sup>3+</sup> oxidation state, and enhances the adsorption of the key \*OCHO intermediate. *In situ* Raman spectroscopy confirms the stabilization of Bi<sub>2</sub>O<sub>3</sub> by Y doping, while *in situ* FTIR identifies \*OCHO as the critical intermediate. DFT calculations verify that Y doping reduces



electron transfer between Bi and O, strengthening Bi–O bond covalency and lowering the energy barriers for CO<sub>2</sub> adsorption and activation, thus improving catalytic activity and stability. The optimized 3% Y-doped Bi<sub>2</sub>O<sub>3</sub> catalyst demonstrates outstanding performance, achieving a record formate FE of 97.9% at –1.05 V vs. RHE and maintaining FE > 90% over a 350 mV potential window. In a flow cell, it sustains FE > 90% at industrial-grade current densities up to 160 mA·cm<sup>–2</sup>.

In another work, syngas is used as the raw material for the electrocatalytic synthesis of C<sub>1</sub> products. The doping strategy of La plays an important role in this process. Liu et al. [112] synthesized multiple La<sub>x</sub>-Zn<sub>3</sub>Al<sub>2–x</sub>-layered double oxide (LDO) electrocatalysts with varying La doping ratios. By adjusting the La doping ratio, the catalyst can achieve different CO/H<sub>2</sub> product ratios. The researchers conclude that La introduction facilitates the activation of ZnAlLa-LDO active sites by modifying electron interactions and the coordination environment of the elements, thereby promoting CO<sub>2</sub> adsorption onto the catalyst surface. In addition, characterization proves that La doping changes the chemical environment of Zn<sup>2+</sup>/Al<sup>3+</sup> and optimizes the structure of layered bimetallic oxide, consequently augmenting the electrochemically active surface area of ZnAl-LDO. The optical catalyst achieves a combined Faradaic efficiency for CO<sub>2</sub> reduction and HER close to 100%. The La<sub>0.2</sub>-Zn<sub>3</sub>Al<sub>1.8</sub>-LDO catalyst, which exhibits the best CO<sub>2</sub> reduction performance, reaches a maximum CO FE of 59.12% at 1.3 V vs. RHE, with an H<sub>2</sub> FE of 40.88% and a CO/H<sub>2</sub> ratio of 1.45.

Cu based electrocatalyst is another promising electrocatalyst for CO<sub>2</sub>RR to C<sub>1</sub> production. In a work of Cu and Ce, Zhang et al. [113] synthesized a Cu/CeO<sub>2</sub>@C catalyst through the pyrolysis of MOFs for the electrocatalytic reduction of CO<sub>2</sub> to CH<sub>4</sub>. Mechanistic studies reveal that the high selectivity of Cu/CeO<sub>2</sub>@C primarily benefits from the synergistic effect of the carbon encapsulation and the Cu/CeO<sub>2</sub> active component, which optimizes CO<sub>2</sub> and intermediate adsorption, accelerates charge transfer and reaction kinetics, and effectively prevents the reduction of Cu active sites. The optical catalyst achieves a Faradaic efficiency of 80.3% and a current density of 138.6 mA·cm<sup>–2</sup> (Figs. 8(a)–8(c)).

In another work of Cu and Ce for CO<sub>2</sub>RR to C<sub>1</sub> production, Chen et al. [114] exploited the unique 4f electronic structure and large ionic radius of cerium to modify Cu-based catalysts. They prepared atomic Ce-doped CuO<sub>x</sub> NPs (Ce/CuO<sub>x</sub>-NPs) via cyclic voltammetry pretreatment of Ce-doped HKUST-1 precursors. Structural characterizations reveal that atomic Ce doping induces lattice strain in the Cu lattice, modulates the local electron density of Cu atoms, and enhances the dispersion of Cu nanoparticles. *In situ* attenuated total reflection surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) confirms the formation of key intermediates (\*CO, \*CHO, and \*CH<sub>3</sub>O), while DFT calculations demonstrate that Ce doping lowers the energy barrier for \*CO-to-\*CHO conversion and facilitates the cleavage of the C–O bond in \*CH<sub>3</sub>O, thereby promoting CH<sub>4</sub> formation. This catalyst exhibits high selectivity for CO<sub>2</sub>-to-CH<sub>4</sub> conversion, with a maximum FE of 67.4% and a partial current density of 293 mA·cm<sup>–2</sup> at –1.6 V vs. RHE. The FE of CH<sub>4</sub> remains above 62% over a 350 mV potential window (Figs. 8(d) and 8(e)).

La doping can regulate product distribution of Cu-based catalysts. Guo et al. [115] synthesized Cu-based bimetallic catalysts with varying La doping ratios for the electrocatalytic reduction of CO<sub>2</sub> to methane. La doping alters the phase composition of oxide-derived (OD)-La-CuO<sub>x</sub> catalysts and correlates positively with

higher concentrations of \*H, allowing for tunable electron selectivity and kinetics of CO<sub>2</sub>RR products. Through *in situ* analysis and theoretical calculations, the researchers conclude that La doping accelerates water dissociation and electron transfer, thereby speeding up the key intermediate step \*CHO → \*CH<sub>2</sub>O and improving reaction activity. The OD-La<sub>0.10</sub>-CuO<sub>x</sub> catalyst exhibits a Faradaic efficiency over 80% for C<sub>2+</sub> products at 300 mA·cm<sup>–2</sup>, while OD-La<sub>0.40</sub>-CuO<sub>x</sub> achieves a 61.4% FE for CH<sub>4</sub> at 400 mA·cm<sup>–2</sup>.

### 3.2.2 CO<sub>2</sub>RR to C<sub>2+</sub> products

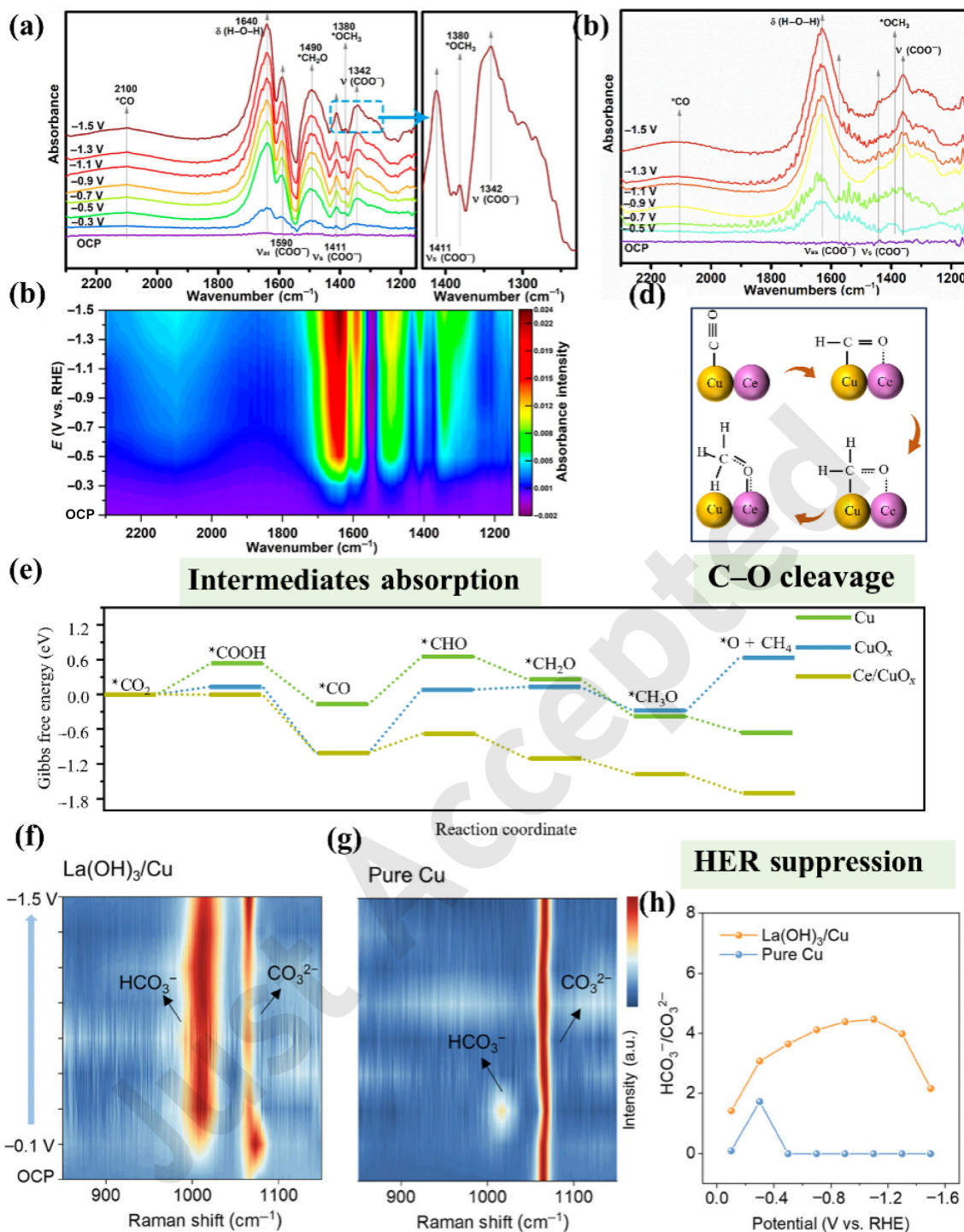
C<sub>2+</sub> products, such as ethanol and ethylene, have higher economic value and energy density, and CO<sub>2</sub>RR to C<sub>2+</sub> products is a multi-electron transfer reaction involving C–C coupling, which is the key research direction of CO<sub>2</sub>RR. REEs, such as Ce, La, and Pr, can regulate the electronic structure of catalyst active sites, promote the adsorption and coupling of CO<sub>2</sub> reduction intermediates, and thus improve the selectivity and yield of C<sub>2+</sub> products.

Aiming to promote ethylene formation, Lu et al. [116] introduced rare earth yttrium to construct Cu<sub>2</sub>Y<sub>2</sub>O<sub>5</sub> nanoclusters via a citric acid sol-gel method. The high electrophilicity of Y acts as an “electron dock” to attract \*CO intermediates, regulate the electronic structure of Cu, and protect the stability of Cu<sup>2+</sup> during reduction. *In situ* IR detects distinct \*OCCO intermediates, indicating promoted C–C dimerization. DFT calculations confirm that the interaction between Cu and Y lowers the energy barrier for CO<sub>2</sub>-to-ethylene conversion, reduces the HER Gibbs free energy, and enhances the adsorption of \*CO, thereby directing the reaction pathway toward ethylene. The optimized CYO-850 catalyst exhibits exceptional ethylene selectivity, achieving a FE of 70% and a partial current density of 200 mA·cm<sup>–2</sup> in a flow cell.

In a typical work, gadolinium doping optimizes copper oxide for ethylene synthesis. Cao et al. [117] employed the solvent shielding effect to precisely regulate the doping amount of rare earth gadolinium in CuO catalysts via a solvothermal method. Structural characterizations show that solvent polarity modulates Gd doping, which enriches the electron density of Cu active sites. *In situ* ATR-FTIR identifies \*COCOH as the key intermediate for ethylene formation. DFT calculations demonstrate that moderate Gd doping reduces the Gibbs free energy of the C–C coupling step, promoting \*COCOH formation and improving ethylene selectivity. The Gd-doped CuO (Gd-CuO-E) with moderate Gd content exhibits superior CO<sub>2</sub>-to-ethylene performance, achieving a FE of 58.6% at –1.2 V vs. RHE in an H-cell and 52.4% with a current density of 397.8 mA·cm<sup>–2</sup> in a flow cell.

Sha et al. [118] also constructed a La-Cu catalyst for CO<sub>2</sub> electroreduction to C<sub>2+</sub> study. The researchers synthesized La<sub>2</sub>CuO<sub>4</sub> via sol-gel and high-temperature oxidation methods. This La<sub>2</sub>CuO<sub>4</sub> catalyst is used to reduce CO<sub>2</sub> to ethylene. Under the influence of CO<sub>2</sub> and H<sub>2</sub>O, La<sub>2</sub>CuO<sub>4</sub> undergoes partial surface reconstruction, forming carbonate and amorphous layers. Due to the electronegativity difference between C and O, interfacial electron redistribution creates electron-rich and electron-deficient layers, lowering the d-band center and regulating \*CO adsorption strength. The formation of amorphous electron-rich layers containing Cu<sup>+</sup> provides additional active sites. The catalyst demonstrates high catalytic performance, achieving a C<sub>2</sub>H<sub>4</sub> FE of 58.67% at –1.3 V vs. RHE in an H-cell reactor.

In a representative work, lanthanum hydroxide modified copper catalysts achieve high C<sub>2+</sub> yield at Ampere-level current. Hu et al. [119] utilized the electron-modulating effect of rare earth



**Figure 8** (a) and (b) Operando ATR-FTIR spectra on Cu/CeO<sub>2</sub>@C at different potentials. Reproduced with permission from Ref. [113], © American Chemical Society 2023. (c) Operando ATR-FTIR spectra on Cu/CeO<sub>2</sub> at different potentials. Reproduced with permission from Ref. [114], © Elsevier B.V. 2024. (d) Proposed reaction pathways of ECO<sub>2</sub>RR to CH<sub>4</sub> on the Ce/CuO<sub>x</sub>-NPs surface. (e) The calculated Gibbs free energy for Cu, CuO<sub>x</sub>, and Ce/CuO<sub>x</sub>. Reproduced with permission from Ref. [114], © Elsevier B.V. 2024. ((f) and (g)) In situ Raman spectroscopy investigating the HER of (f) the La(OH)<sub>3</sub>/Cu and (g) the pure Cu. (h) The HCO<sub>3</sub><sup>-</sup> to CO<sub>3</sub><sup>2-</sup> ratios of the La(OH)<sub>3</sub>/Cu and Cu catalysts. Reproduced with permission from Ref. [119], © Wiley-VCH GmbH 2023.

lanthanum in the form of La(OH)<sub>3</sub> to modify Cu catalysts. They synthesized La(OH)<sub>3</sub>/Cu via a surfactant-assisted coprecipitation method. The La(OH)<sub>3</sub> modification optimizes the electronic structure of Cu, promotes \*CO adsorption, hydrogenation, and \*CO-\*COH coupling, and suppresses HER. In situ ATR-FTIR detects enhanced signals of \*CO (bridge and atop adsorption) and \*OCCOH intermediates, confirming promoted C-C coupling. DFT calculations reveal that La(OH)<sub>3</sub> increases electron transfer

from Cu to \*CO, reduces the energy barrier for the rate-determining step (\*CO + \*CO → \*CO + \*COH), and strengthens the interaction between Cu and reaction intermediates. At an Ampere-level current density of 1000 mA·cm<sup>-2</sup>, the catalyst achieves a C<sub>2+</sub> FE of 71.2% and maintains stability for 8 h (Figs. 8(f)–8(h)).

In a work of Shen et al. [120]. The researchers utilized rare earth yttrium doping to induce the formation of amorphous low-

valent Cu species in CuS catalysts via electrochemical codeposition and sulfidation. Structural characterizations confirm that Y doping expands the CuS lattice, weakens Cu-S bonds, and increases the density of active Cu sites. *In situ* ATR-FTIR detected ethanol-related intermediates ( $^*\text{OCCOH}$  and  $^*\text{OC}_2\text{H}_5$ ), while *in situ* ultraviolet-visible (UV-vis) spectroscopy verify the presence of amorphous low-valent Cu species as the primary active sites. *Ab initio* molecular dynamics simulations support that Y doping modulates the electronic structure of CuS, promoting C-C coupling and ethanol formation. The Y-CuS catalyst exhibits high selectivity for  $\text{CO}_2$ -to-ethanol conversion, achieving an ethanol FE of 52% at a current density of  $400 \text{ mA}\cdot\text{cm}^{-2}$  and an energy efficiency of 23.8% when the ethanol-producing current density exceeds  $200 \text{ mA}\cdot\text{cm}^{-2}$ .

In another work, rare earth element Pr was composited with Cu. Wang et al. [121] developed a series of rare earth-Cu-based topological catalysts for the electrocatalytic reduction of  $\text{CO}_2$  to ethanol. Ultimately, they identified  $\text{Pr}_2\text{CuO}_4$  as the best candidate due to its robust topological surface states and potential selectivity for  $\text{C}_{2+}$  products. *In situ* tests and theoretical calculations reveal a strong interaction between the C p orbital of key intermediates and the Cu  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals, significantly promoting charge transfer and forming an energetically favorable pathway toward ethanol. This catalyst achieves a Faradaic efficiency of up to 67% and a current density of  $220 \text{ mA}\cdot\text{cm}^{-2}$  at a potential of  $-1.1 \text{ V}$ .

In a work of Ce and Cu for  $\text{CO}_2\text{RR}$  to  $\text{C}_{2+}$ , Cerium oxide stabilizes cuprous sites in copper sulfide for ethanol synthesis. Yang et al. [122] synthesized a series of rare earth element oxide and CuS heterojunction catalysts via a solvothermal method for the electrocatalytic reduction of  $\text{CO}_2$  to ethanol. In the catalytic system, cerium is used as a self-sacrificing agent to stabilize the  $\text{Cu}^+$  of CuS. Theoretical studies suggest that in this catalyst, cerium stabilizes the Cu(0) and Cu(I) active sites through the  $\text{Ce}^{3+}/\text{Ce}^{4+}$  conversion. Meanwhile, the remaining S atoms are adsorbed on the surface of Cu as an electronic regulator and promote the conversion of  $\text{CO}_2$  to CO. *In situ* electrochemical Raman spectra and ATR-FTIR tests suggest the rapid C-C coupling on  $\text{CeO}_2/\text{CuS}$  compared with the CuS, and the pathway of  $^*\text{CO}$  dimerization to form ethanol. Among the series of catalysts, the  $\text{CeO}_2/\text{CuS}$  nanoplates catalyst exhibits the best performance, achieving high ethanol selectivity with a FE up to 54% and  $\text{FE}_{\text{C}_{2+}} = 75\%$  in a flow cell, and shows no significant decay over 180 h.

REEs, such as Ce, La, and Pr, play an important regulatory role in  $\text{CO}_2\text{RR}$  catalysts, and their optimization mechanisms for different products are highly targeted. For formic acid, REEs stabilize the catalyst active sites and enhance the binding energy of the key intermediate  $^*\text{OCHO}$  by doping and heterojunction construction, thus improving the selectivity of formic acid; for CO, REEs modify the electron interaction and coordination environment of the catalyst, promote the adsorption and activation of  $\text{CO}_2$  molecules, and realize the efficient conversion of  $\text{CO}_2$  to CO. For methane, REEs optimize the adsorption of  $\text{CO}_2$  and reaction intermediates, accelerate the protonation process of intermediates, and thus improve the catalytic activity and selectivity of methane. For  $\text{C}_{2+}$  products, such as ethanol and ethylene, REEs regulate the electronic structure of the catalyst active sites, promote the adsorption and coupling of  $\text{CO}_2$  reduction intermediates, and lower the energy barrier of C-C coupling reaction, which is the key to the efficient synthesis of  $\text{C}_{2+}$  products.

It can be easily concluded from the above research that Cu-based catalysts, Bi-based catalysts, and noble metal catalysts remain the most reliable types of catalysts for electrocatalytic

$\text{CO}_2\text{RR}$ . The core strategy of applying rare earth elements to electrocatalytic  $\text{CO}_2$  reduction is to composite rare earth elements with these metal systems via alloying, doping, and other methods, so as to adjust the adsorption and desorption capacity of active sites for key intermediates.

Among all rare earth elements, Ce is the most widely used REE in  $\text{CO}_2\text{RR}$  catalysts, and La, Pr, and other REEs also show excellent regulatory effects. Apart from tuning adsorption and desorption behaviors, rare earth elements can effectively suppress the competitive HER reaction in several representative studies, and deliver high catalytic activity and product selectivity across various electrolyte systems. The catalysts involved in the relevant references of Section 3.2 and their performances are shown in Table 3.

### 3.3 Ammonia synthesis

Ammonia is an important chemical raw material and hydrogen storage carrier, and electrocatalytic ammonia synthesis under mild conditions is a promising alternative to the traditional Haber-Bosch process with high energy consumption and high carbon emission. Electrocatalytic ammonia synthesis mainly includes NRR and  $\text{NO}_3\text{RR}$ . NRR directly reduces  $\text{N}_2$  to  $\text{NH}_3$ , but faces the problems of strong  $\text{N}\equiv\text{N}$  bond and low Faradaic efficiency;  $\text{NO}_3\text{RR}$  reduces nitrate ions ( $\text{NO}_3^-$ ) in wastewater to  $\text{NH}_3$  which can realize the resource utilization of wastewater while producing ammonia, and has higher reaction kinetics and Faradaic efficiency. REEs can effectively activate  $\text{N}_2/\text{NO}_3^-$  molecules, optimize the adsorption and hydrogenation of reaction intermediates, and suppress the competitive HER reaction, thus improving the catalytic activity and selectivity of ammonia synthesis catalysts.

#### 3.3.1 Nitrate reduction reaction

$\text{NO}_3\text{RR}$  is an electrocatalytic reaction that converts nitrate ions to ammonia, which has the advantages of low reaction barrier and high Faradaic efficiency, and can realize the simultaneous treatment of nitrate wastewater and production of high-value ammonia. REEs, such as Y and Ce, can act as active sites or electronic modulators in  $\text{NO}_3\text{RR}$  catalysts, provide  $\text{H}^+$  intermediates for the hydrogenation step, optimize the electronic structure of the catalyst, and thus significantly improve the ammonia production rate and Faradaic efficiency of  $\text{NO}_3\text{RR}$ .

In a noticeable work, yttrium single atom combined with copper phosphide achieves high-efficiency  $\text{NO}_3\text{RR}$ . Cai et al. [123] loaded single atom Y and copper phosphide nanoparticles on an N, P-doped carbon (CNP) substrate to form the  $\text{Y}_{\text{SA}}\text{-Cu}_3\text{P/CNP}$  catalyst. *In situ* XAS proves that both Cu and Y sites transfer electrons to  $\text{NO}_3^-$  and play a crucial role in the catalytic system. Employing *in situ* differential electrochemical mass spectrometry (DEMS), researchers detect the N-containing intermediates and identify the NO-pathway. Through DFT calculations, the researchers believe that the efficient nitrate reduction on  $\text{Y}_{\text{SA}}\text{-Cu}_3\text{P/CNP}$  is attributed to the reduction of the energy barrier of the rate-determining step, as well as the increase in the activity and hydrogen stability beneficial to the hydrogenation step. Besides, the researchers believe that Y single atoms facilitate the pre-deoxygenation process. This catalyst can achieve a maximum Faradaic efficiency of 92% at a potential of  $-0.5 \text{ V}$  vs. RHE and a maximum ammonia production rate of  $11.4 \text{ mg}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$  at  $-0.6 \text{ V}$  vs. RHE. In addition, the researchers assembled a zinc nitrate battery, using the  $\text{Y}_{\text{SA}}\text{-Cu}_3\text{P/CNP}$  as the cathode with a sustained high open circuit voltage of  $1.1 \text{ V}$ .



**Table 3** Summary of catalyst performances in Section 3.2

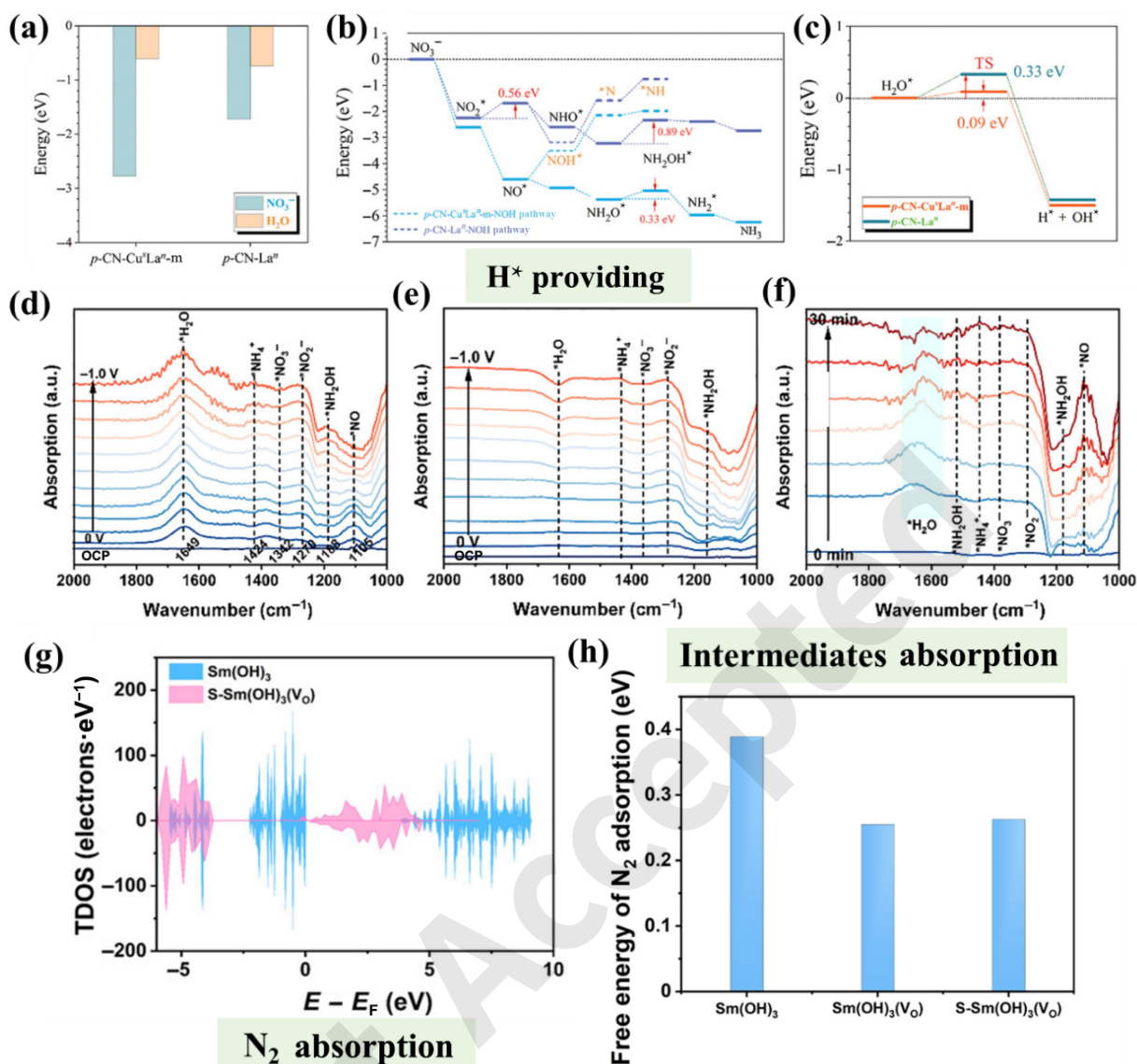
| References | Name                                                    | Catalyst                                          | Electrolyte                           | Mass loading                                                     | Performance                                                                                                                        | Commercial catalysts                                          |
|------------|---------------------------------------------------------|---------------------------------------------------|---------------------------------------|------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------|
| [108]      | Ce-doped Bi@C NRs                                       | HCOOH-CO <sub>2</sub> RR                          | 0.1 M KHCO <sub>3</sub>               | 20 mg·cm <sup>-2</sup> (50% carbon black)                        | FE > 90% (−0.9 to −1.9 V vs. RHE); 96.1% at −1.5 V, 36 h                                                                           | —                                                             |
| [109]      | Ce@S-Bi <sub>2</sub> O <sub>3</sub>                     | CO/HCOOH-CO <sub>2</sub> RR                       | 0.5 M KHCO <sub>3</sub>               | —                                                                | FE = 92.5%, current density = 42.09 mA·cm <sup>-2</sup> ; H-cell: steady for 25 h, −0.96 V, FE remained unchanged 86% ± 2%         | —                                                             |
| [110]      | Ce <sub>2</sub> -Bi@C                                   | HCOOH-CO <sub>2</sub> RR                          | 0.1 M KHCO <sub>3</sub>               | —                                                                | FE = 93.6%, current density = 13.7 mA·cm <sup>-2</sup> ; 48 h                                                                      | —                                                             |
| [111]      | Y-Bi <sub>2</sub> O <sub>3</sub>                        | HCOOH-CO <sub>2</sub> RR                          | 0.5 M KHCO <sub>3</sub>               | 5.0 mg·cm <sup>-2</sup>                                          | FE = 97.9% at 1.05 V; flow-cell: 80 mA·cm <sup>-2</sup> ; 6.4 h, FE = 95.48%                                                       | —                                                             |
| [112]      | La <sub>x</sub> -Zn <sub>3</sub> Al <sub>2-x</sub> -LDO | HER, CO-CO <sub>2</sub> RR                        | 0.1 M KHCO <sub>3</sub>               | 0.56 mg·cm <sup>-2</sup> (28.6% carbon black)                    | FE of CO = 59.12%, FE of H <sub>2</sub> = 40.88%, at 1.3 V vs. RHE, 7000 s                                                         | —                                                             |
| [113]      | Cu/CeO <sub>2</sub> @C                                  | CH <sub>4</sub> -CO <sub>2</sub> RR               | 0.5 M KHCO <sub>3</sub>               | 1 mg·cm <sup>-2</sup>                                            | FE = 80.3%, current density = 138.6 mA·cm <sup>-2</sup> ; −1.5 V, 9 h                                                              | —                                                             |
| [114]      | Ce/CuO <sub>x</sub> -NPs                                | CH <sub>4</sub> -CO <sub>2</sub> RR               | 1 M KOH                               | 0.4 mg·cm <sup>-2</sup>                                          | FE = 67.4%, current density = 293 mA·cm <sup>-2</sup> at −1.6 V vs. RHE; steady for 10 h                                           | —                                                             |
| [115]      | (OD)-La-CuO <sub>x</sub>                                | CH <sub>4</sub> -CO <sub>2</sub> RR               | 1.0 M KCl/<br>1.0 M KOH               | 1 mg·cm <sup>-2</sup>                                            | La <sub>0.10</sub> : FE = 80.4% at 300 mA·cm <sup>-2</sup> , 16 h/La <sub>0.40</sub> : FE = 61.5% at 400 mA·cm <sup>-2</sup> , 8 h | —                                                             |
| [116]      | Cu <sub>2</sub> Y <sub>2</sub> O <sub>5</sub>           | C <sub>2</sub> H <sub>4</sub> -CO <sub>2</sub> RR | 1 M KOH                               | 0.5 mg·cm <sup>-2</sup>                                          | FE = 70%, current density = 200 mA·cm <sup>-2</sup> , 10 h                                                                         | —                                                             |
| [117]      | Gd-CuO                                                  | C <sub>2</sub> H <sub>4</sub> -CO <sub>2</sub> RR | 0.5 M KHCO <sub>3</sub>               | —                                                                | FE = 58.6% at −1.2 V; FE = 52.4% at 397.8 mA·cm <sup>-2</sup> ; 12 h                                                               | —                                                             |
| [118]      | La <sub>2</sub> CuO <sub>4</sub>                        | C <sub>2</sub> H <sub>2</sub> -CO <sub>2</sub> RR | 0.1 M KHCO <sub>3</sub>               | ~ 1 mg·cm <sup>-2</sup> (50% carbon black)                       | FE = 58.67% at −1.3 V, 8 h                                                                                                         | Commercial Cu foil, FE (C <sub>2</sub> H <sub>4</sub> ) = 26% |
| [119]      | La(OH) <sub>3</sub> /Cu                                 | C <sub>2</sub> +CO <sub>2</sub> RR                | 0.1 M KHCO <sub>3</sub> //<br>1 M KOH | 1 mg·cm <sup>-2</sup>                                            | FE <sub>C<sub>2</sub>+</sub> : 71.2% at 1000 mA·cm <sup>-2</sup> for 8 h                                                           | —                                                             |
| [120]      | Y-CuS                                                   | EtOH-CO <sub>2</sub> RR                           | 1 M KOH                               | 1.0 mg·cm <sup>-2</sup>                                          | FE = 52% at 400 mA·cm <sup>-2</sup> for 5 h                                                                                        | —                                                             |
| [121]      | Pr <sub>2</sub> CuO <sub>4</sub>                        | EtOH-CO <sub>2</sub> RR                           | 1.0 M KOH                             | 1 mg·cm <sup>-2</sup>                                            | FE = 67%; current density = 220 mA·cm <sup>-2</sup> at −1.1–1.0 V, 15 h, FE > 60%                                                  | —                                                             |
| [122]      | CeO <sub>2</sub> /CuS                                   | EtOH-CO <sub>2</sub> RR                           | 0.1 M KHCO <sub>3</sub>               | H-cell: 5 mg·cm <sup>-2</sup> ; flow-cell: 1 mg·cm <sup>-2</sup> | FE <sub>C<sub>2</sub>+</sub> = 75%; −0.51 V, FE (C <sub>2</sub> H <sub>5</sub> OH) = ~ 45%, 180 h                                  | —                                                             |

Employing a strategy of using Lanthanum-based clusters as proton donors, Zuo et al. [124] proposed a proton donor strategy via a synergistic catalyst design. They synthesized a model catalyst *p*-CNCuLa<sup>m</sup>-m by anchoring Cu single atoms on La-based nanoparticles, using ultraviolet radiation reduction, confined synthesis, and microwave treatment. La-based clusters act as proton donors, providing abundant active H<sup>+</sup> that spills over to Cu sites to accelerate N-intermediate hydrogenation. *In situ* characterizations confirm an O-end adsorption mechanism for NO<sub>3</sub>RR, with key intermediates (\*NO and \*NOH) stabilized by the catalyst. DFT calculations reveal that low-coordinated Cu sites enhance electroactivity, while La modulates electron transfer and proton supply, lowering the rate-determining step energy barrier to 0.29 eV. This work provides insights for designing proton donor-cooperated catalysts, enabling efficient NO<sub>3</sub>RR and potential C–N coupling reactions. The catalyst achieves an exceptional Faradaic efficiency of 97.7% for NH<sub>3</sub> and a high yield rate of 10.6 mol·g<sub>metal</sub><sup>-1</sup>·h<sup>-1</sup>. It exhibits robust stability in both H-cell and flow cell (Figs. 9(a)–9(c)).

In order to optimize the intermediate adsorption, Zhou et al. [125] developed La(OH)<sub>3</sub>@CuCo alloy heterostructures via a facile *in situ* exsolution strategy, aiming to address the limited NH<sub>3</sub> production efficiency of Cu-based catalysts in electrocatalytic nitrate reduction due to strong \*NO<sub>2</sub> adsorption. Synthesized

from LaCu<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> perovskites through thermal reduction, the optimal La(OH)<sub>3</sub>/CuCo (Cu:Co = 7:3) exhibits superior performance under neutral conditions. Mechanistic studies and DFT calculations reveal that Co alloying and La(OH)<sub>3</sub> heterostructure construction synergistically modulate Cu electronic structure. This optimizes intermediate adsorption strength, promotes \*NO hydrogenation to \*NOH, and accelerates NH<sub>3</sub> desorption. The optimal catalyst achieves a high NH<sub>3</sub> yield rate of 8.80 mg·h<sup>-1</sup>·mg<sub>cat</sub><sup>-1</sup> and a Faradaic efficiency of 76.6% at −0.9 V vs. RHE in neutral electrolyte, outperforming La(OH)<sub>3</sub>/Cu (Figs. 9(d)–9(f)).

Shang et al. [126] proposed a strategy of RE metal doping to induce 4f–2p–3d orbital hybridization. Single-atom RE metals (Y, La, Pr, and Sm) are incorporated into the octahedral sites of Co<sub>3</sub>O<sub>4</sub> hollow nanoribbons, with Pr-doped Co<sub>3</sub>O<sub>4</sub> (Pr-Co<sub>3</sub>O<sub>4</sub>) exhibiting optimal performance. Mechanistic studies and DFT calculations reveal that Pr-induced 4f–2p–3d orbital hybridization optimizes Co 3d orbital configuration, enhancing NO<sub>3</sub><sup>-</sup> and \*NO adsorption strengths. It also promotes electron transfer from Co to \*NO, reducing the energy barrier of the rate-determining step (\*NO → \*NOH) from 1.22 to 0.96 eV. The catalyst shows excellent stability over 21 cycles and 5 h continuous operation, with unchanged structure and composition. This work provides a new pathway for improving NO<sub>3</sub>RR performance via f–p–d orbital hybridization



**Figure 9** (a) The adsorption energies comparisons of NO<sub>3</sub><sup>-</sup> and H<sub>2</sub>O. (b) The reaction energy trends of NO<sub>3</sub>RR on p-CN-Cu<sup>0</sup>/La<sup>0</sup>-m and p-CN-La<sup>0</sup> of different reaction pathways. (c) The dissociation barriers of water in p-CN-Cu<sup>0</sup>/La<sup>0</sup>-m and p-CN-La<sup>0</sup>. Reproduced with permission from Ref. [124], © Zuo, Y. P. et al. 2025. ((d) and (e)) *In situ* FTIR spectra of (d) R-LaCu<sub>0.7</sub>Co<sub>0.3</sub>O<sub>3</sub> and (e) R-La<sub>2</sub>CuO<sub>4</sub> during the NO<sub>3</sub>RR process under different potentials from open circuit potential (OCP) to -1.0 V. (f) *In situ* FTIR spectra of R-LaCu<sub>0.7</sub>Co<sub>0.3</sub>O<sub>3</sub> (R- stands for reduced) during the NO<sub>3</sub>RR process under -0.8 V after reaction for different time lengths (0–30 min). Reproduced with permission from Ref. [125], © Wiley-VCH GmbH 2025. (g) Total DOS (TDOS) of Sm(OH)<sub>3</sub> and S-Sm(OH)<sub>3</sub>(V<sub>O</sub>). (h) The free energy of N<sub>2</sub> adsorption on the mode of Sm(OH)<sub>3</sub>, Sm(OH)<sub>3</sub>(V<sub>O</sub>), and S-Sm(OH)<sub>3</sub>(V<sub>O</sub>). Reproduced with permission from Ref. [131], © Lv, Z. X. et al. 2023.

engineering. Pr-Co<sub>3</sub>O<sub>4</sub> achieves an ammonia yield rate of 6.3 mol·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup> at -0.7 V vs. RHE, and a maximum Faradaic efficiency of 98.0% at -0.5 V vs. RHE.

Xu et al. [127] proposed a rare earth-mediated strategy via lattice expansion and electronic restructuring. By doping large-radius RE ions (La, Sm, and Gd) into Co<sub>3</sub>O<sub>4</sub>, the optimized Gd-Co<sub>3</sub>O<sub>4</sub> exhibits pronounced Co–Co bond elongation and elevated Co oxidation state. These modifications switch active sites from bridge-coordinated Co to top-coordinated Co, altering the adsorption pathway from bidentate to N-end adsorption for NO<sub>3</sub><sup>-</sup>. Mechanistic studies confirm N-end adsorption stabilizes key intermediates (\*NO and \*NOH) and reduces the rate-determining step energy barrier from 1.10 eV (pristine Co<sub>3</sub>O<sub>4</sub>) to 0.55 eV. The catalyst achieves a Faradaic efficiency of 96.2% for NH<sub>4</sub><sup>+</sup> at -0.6 V vs. RHE, a record yield rate of 5.34 mol·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>, and an industrial-level current density of 400 mA·cm<sup>-2</sup> at 1.9 V cell voltage. This strategy is universal across La/Sm doping, providing a general

electronic modulation approach to overcome NO<sub>3</sub>RR bottlenecks, with potential for environmental remediation and sustainable ammonia synthesis.

### 3.3.2 Nitrogen reduction reaction

NRR is an electrocatalytic reaction that directly reduces N<sub>2</sub> molecules to NH<sub>3</sub> under mild conditions, which is the most ideal ammonia synthesis method, but faces the problems of high N≡N bond activation energy, slow reaction kinetics, and serious competitive HER reaction. REEs, such as Ce, Sm, and La, can introduce defects and active sites into the catalyst, optimize the electronic structure of the catalyst, and suppress the competitive HER reaction, thus improving the ammonia production rate and Faradaic efficiency of NRR.

In this typical study, the multiple effects of Ce doping work synergistically to enhance the performance of the catalyst. Nan et al. [128] reported a solvothermal method for preparing two-

dimensional (2D) Ce-doped  $\text{Bi}_2\text{Te}_3$  nanosheets and used this catalyst for NRR. Characterizations prove that the content of metallic Bi on the surface of Ce- $\text{Bi}_2\text{Te}_3$  decreases after doping. The researchers believe it may cause the charge imbalance of  $\text{Ce}^{4+}$  after the introduction of Ce, leading to Te vacancies and unsaturated Bi atoms, which serve as active sites for the reaction. Additionally, cerium doping improves the catalyst's conductivity, enhancing its performance in the electrocatalytic system. By adjusting the cerium doping ratio, they prepared a series of  $\text{Ce}_x\text{-Bi}_2\text{Te}_3$  catalysts. Among them,  $\text{Ce}_{0.3}\text{-Bi}_2\text{Te}_3$  achieves an ammonia production rate of  $78.2 \mu\text{g}\cdot\text{h}^{-1}\cdot\text{mg}_{\text{cat}}^{-1}$  and a Faradaic efficiency of 19.3% at a potential of  $-0.6 \text{ V}$  vs. RHE in a  $0.1 \text{ M Na}_2\text{SO}_4$  solution, demonstrating good stability.

In another work, Lanthanum doping generates oxygen vacancies in iron molybdate. Zhang et al. [129] synthesized  $\text{Fe}_2(\text{MoO}_4)_3$  and  $x\%$  La-doped FeMo ( $x\%$  represents different La molar ratios) via a hydrothermal method. La doping induces oxygen vacancies and tunes the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  molar ratio, forming a fast electron transport channel through  $\text{Fe}^{2+}\text{-O}^{2-}\text{-Fe}^{3+}$  superexchange. Characterizations confirm that 5% La-FeMo has the highest oxygen vacancy content and a  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio close to 1, synergistically enhancing  $\text{N}_2$  adsorption, activation, and electron transfer. The catalyst follows an associative distal pathway, with oxygen vacancies serving as active sites and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  cycling accelerating hydrogenation. The optimal 5% La-FeMo exhibits superior NRR performance at  $-0.8 \text{ V}$  vs. RHE, with an  $\text{NH}_3$  yield rate of  $29.6 \mu\text{g}\cdot\text{h}^{-1}\cdot\text{mg}_{\text{cat}}^{-1}$  and a Faradaic efficiency of 5.8%.

For high-temperature NRR, Ferree et al. [130] prepared a composite  $\text{Co}_3\text{Mo}_3\text{N}$  nitride and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  (LSCF) perovskite cathode for high-temperature electrocatalytic nitrogen reduction. *In situ* testing and theoretical studies confirm that the catalyst's superior performance is due to the synergy between the nitrogen activation ability of  $\text{Co}_3\text{Mo}_3\text{N}$  and the mixed ionic–electronic conductive properties of LSCF. Characterizations reveal that the rare earth components (La and Sr) effectively regulate the electronic structure and ionic conductivity of the catalyst, induce charge redistribution and favorable oxygen vacancies, and create active sites for  $\text{N}_2$  adsorption and activation. Meanwhile, the outstanding mixed ionic–electronic conducting

(MIEC) property of the rare earth perovskite boosts charge transport and  $\text{H}_2\text{O}$  dissociation, synergizing strongly with the Mars-van Krevelen mechanism of  $\text{Co}_3\text{Mo}_3\text{N}$ . In a solid-oxide electrolysis cell, ammonia is electrochemically produced from  $3\% \text{ H}_2\text{O}/\text{N}_2$  on the button cell cathode with a formation rate of  $4.0 \times 10^{-11} \text{ mol}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$  at  $550^\circ\text{C}$  and current density of  $0.65 \text{ mA}\cdot\text{cm}^{-2}$ .

In another work, the hydroxide of rare earth element Sm is taken as the main catalyst, and S is introduced into the catalyst system as a dopant. Lv et al. [131] synthesized S-doped  $\text{Sm}(\text{OH})_3$  nanowires rich in oxygen vacancies via a two-step solvothermal method for NRR. DFT calculations confirm that oxygen vacancies reduce the adsorption energy of  $\text{N}_2$  on the catalyst. Moreover, the S sites improve the adsorption of hydrogen produced via the Volmer reaction, accelerating the formation of the key intermediate  $^*\text{N-NH}$  on Sm sites during the rate-determining step and significantly promoting NRR reaction kinetics. The catalyst achieves an  $\text{NH}_3$  yield rate of  $21 \mu\text{g}\cdot\text{h}^{-1}\cdot\text{mg}_{\text{cat}}^{-1}$  and an  $\text{NH}_3$  Faradaic efficiency of over 29% at  $-0.3 \text{ V}$  in an H-cell using a neutral electrolyte, while maintaining long-term stability (Figs. 9(g) and 9(h)).

Rare earth elements play a key role in both electrocatalytic reactions (NRR and  $\text{NO}_3\text{RR}$ ). They can effectively activate  $\text{N}_2/\text{NO}_3^-$  molecules, optimize the adsorption and hydrogenation of reaction intermediates, regulate the electronic structure of catalysts, and suppress the competitive HER, thereby significantly improving the catalytic activity and selectivity of ammonia synthesis catalysts.

Overall, REE-based electrocatalysts show great potential in the field of electrocatalytic ammonia synthesis, providing important ideas and technical paths for efficient, low-energy-consumption, and sustainable ammonia synthesis as well as environmental remediation. The catalysts involved in the relevant references of the Section 3.3 and their performances are shown in Table 4.

### 3.4 Oxygen reduction reaction

ORR is the core cathodic reaction of fuel cells and metal–air batteries, a multi-electron transfer reaction with slow kinetics, and the main factor restricting the performance of energy storage and conversion devices. According to the electron transfer path, ORR

**Table 4** Summary of catalyst performances in Section 3.3

| References | Name                                                     | Catalyst               | Electrolyte                                          | Mass loading                         | Performance                                                                                                                                                                                                                | Commercial catalysts                                                                                   |
|------------|----------------------------------------------------------|------------------------|------------------------------------------------------|--------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|
| [123]      | $\text{Y}_{\text{SA}}\text{-Cu}_3\text{P/CNP}$           | $\text{NO}_3\text{RR}$ | $1.0 \text{ M KOH} + 0.1 \text{ M KNO}_3$            | $0.4 \text{ mg}\cdot\text{cm}^{-2}$  | Y: $11.4 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ ( $-0.6 \text{ V}$ ); FE = 92%, $-0.5 \text{ V}$ , 16 cycles                                                                                                     | —                                                                                                      |
| [124]      | $p\text{-CNCu}^{\text{I}}\text{La}^{\text{II}}\text{-m}$ | $\text{NO}_3\text{RR}$ | $1.0 \text{ M KOH} + 0.5 \text{ M KNO}_3$            | $1.4 \text{ mg}\cdot\text{cm}^{-2}$  | Y: $10.6 \text{ mol}\cdot\text{mg}_{\text{metal}}^{-1}\cdot\text{h}^{-1}$ ; FE = $97.7\% \pm 2.8\%$ at $-0.45 \text{ V}$ ; H-cell: 110 h, 9% decrease in current density; flow-cell: 111 h, 9% decrease in current density | —                                                                                                      |
| [125]      | $\text{La}(\text{OH})_3/\text{CuCo}$                     | $\text{NO}_3\text{RR}$ | $0.5 \text{ M K}_2\text{SO}_4 + 0.5 \text{ M KNO}_3$ | $0.8 \text{ mg}\cdot\text{cm}^{-2}$  | Y: $8.80 \text{ mg}\cdot\text{mg}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$ ; FE = 76.6% at $-0.9 \text{ V}$ ; steady for 10 cycles at $-0.8 \text{ V}$ ,                                                                       | —                                                                                                      |
| [126]      | $\text{Pr-Co}_3\text{O}_4$                               | $\text{NO}_3\text{RR}$ | $1.0 \text{ M KOH} + 0.1 \text{ M KNO}_3$            | $2 \text{ mg}\cdot\text{cm}^{-2}$    | Y: $6.3 \text{ mol}\cdot\text{mg}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$ at $-0.7 \text{ V}$ ; FE = 98% at $-0.5 \text{ V}$ , 21 cycles, 5 h                                                                                 | $\text{Co}_3\text{O}_4$ ; Y: $1.8 \text{ mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ at $-0.7 \text{ V}$ |
| [127]      | $\text{Gd-Co}_3\text{O}_4$                               | $\text{NO}_3\text{RR}$ | $1.0 \text{ M KOH} + 0.1 \text{ M KNO}_3$            | $0.2 \text{ mg}\cdot\text{cm}^{-2}$  | Y: $5.34 \text{ mol}\cdot\text{mg}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$ ; FE = 96.2% at $-0.6 \text{ V}$ , steady for 6 cycles, 40 h; membrane electrode assembly (MEA): $400 \text{ mA}\cdot\text{cm}^{-2}$               | —                                                                                                      |
| [128]      | $\text{Ce}_{0.3}\text{-Bi}_2\text{Te}_3$                 | NRR                    | $0.1 \text{ M Na}_2\text{SO}_4$                      | —                                    | Y: $78.2 \mu\text{g}\cdot\text{mg}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$ ; FE = 19.3% at $-0.6 \text{ V}$ , 6 cycles, 48 h                                                                                                  | —                                                                                                      |
| [129]      | 5% La-FeMo                                               | NRR                    | $0.1 \text{ M Na}_2\text{SO}_4$                      | $0.45 \text{ mg}\cdot\text{cm}^{-2}$ | Y: $29.6 \mu\text{g}\cdot\text{mg}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$ ; FE = 5.8% at $-0.8 \text{ V}$ , 5 cycles                                                                                                         | —                                                                                                      |
| [130]      | $\text{Co}_3\text{Mo}_3\text{N}$ and LSCF                | High-temperature NRR   | $3\% \text{ H}_2\text{O}/\text{N}_2$                 | —                                    | Y: $4.0 \times 10^{-11} \text{ mol}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$ at $550^\circ\text{C}$ ; current density = $0.65 \text{ mA}\cdot\text{cm}^{-2}$ ; 6 h                                                            | —                                                                                                      |
| [131]      | S- $\text{Sm}(\text{OH})_3$                              | NRR                    | $0.1 \text{ M Na}_2\text{SO}_4$                      | $0.2 \text{ mg}\cdot\text{cm}^{-2}$  | Y: $21 \mu\text{g}\cdot\text{h}^{-1}\cdot\text{mg}_{\text{cat}}^{-1}$ ; FE = 29% at $-0.3 \text{ V}$ , 10 cycles, 55 h                                                                                                     | —                                                                                                      |



can be divided into the  $4e^-$  path (generating  $H_2O$ ) and the  $2e^-$  path (generating  $H_2O_2$ ). Rare earth elements, such as Y, Ce, La, and Sm, can act as core active sites or electronic modulators in ORR catalysts, optimize the adsorption energy of ORR intermediates ( $^*OOH$ ,  $^*O$ , and  $^*OH$ ), accelerate electron transfer, and improve the catalytic activity, selectivity and stability of ORR, thus being widely used in the design of ORR catalysts for fuel cells and zinc-air batteries [132].

Yttrium single-atom catalysts derived from MOFs show good alkaline ORR activity. In a typical work, Parida et al. [133] synthesized a single-atom catalyst of Y using MOFs. During the synthesis process, the researchers loaded Y onto ZIF-8 to form  $nY$ -ZIF ( $n = 0, 20$ , and  $30$ ), and then pyrolyzed it. The synthesized series of catalysts,  $20Y$ -N-C, in addition to Zn and N co-doping, also have ORR active  $Y-N_4$  sites, thus showing better catalytic activity in alkaline electrolytes. Compared with the catalyst without Y, this catalyst also shows higher selectivity for the  $4e^-$  ORR process. By anchoring Y on nitrogen-doped carbon-based materials, the formed Y-N-C catalyst has an onset potential ( $E_{on}$ ) of  $0.931$  V and an  $E_{1/2}$  of  $0.770$  V vs. RHE in  $0.1$  M KOH, and demonstrates good stability.

The pore-confinement strategy optimizes cerium single-atom ORR catalysts. Liu et al. [134] collaborated to report another method to enhance the activity of  $Ce-N_4$  ORR active sites. Believing that pore-coupling with single-metal cerium sites can accelerate the electron transfer, they designed and synthesized a high-performance and stable Ce single-atom catalyst (Ce SA/MC) using a pore-confinement-pyrolysis strategy. Theoretical studies and calculations show that Ce SA/MC can form a wide range of positively charged areas, and the calculated potential-determining step in Ce SA/MC ( $0.24$  eV) is also lower than that of  $CeN_4$  ( $0.36$  eV). This catalyst achieves a half-wave potential of  $0.845$  V. In a zinc-air battery, it exhibits high energy density ( $924$  Wh·kg $_{Zn}^{-1}$ ) and good long-term cycling durability.

In a typical work, the researchers found that cerium oxide with different morphologies regulates  $H_2O_2$  selectivity for  $2e^-$  ORR. Fernandes et al. [135] synthesized various Ce oxide nanomaterials with different morphologies, including nanosheets, nanocubes, and nanoparticles on conductive carbon black. The researchers propose that in the presence of a magnetic field, energy level splitting occurs due to the spin interaction between  $Ce^{3+}$  and oxygen vacancies, which have different energies, leading to the formation of polarons and so-called bound magnetic polarons (BMPs). These interactions with the effective mass carriers in localized states through exchange interactions enhance the energy states of electron spins within the cerium oxide. This accelerates the reaction. The best results are achieved with  $5\%$  (w/w)  $CeO_2$  for all three morphologies, enhancing hydrogen peroxide selectivity to  $84\%$ – $89\%$  and modifying the onset potential to less negative values. The presence of a magnetic field further increases the ring currents with  $5\%$  (w/w)  $CeO_2$ , resulting in  $H_2O_2$  selectivity of  $88\%$ – $96\%$  and an even greater shift in the onset potential (Figs. 10(a)–10(c)).

In a work of Luo et al. [136], the researchers introduced  $CeO_2$  to enhance ORR performance while reducing or even eliminating the impact of  $H_2O_2$ . They synthesized a single-atom catalyst by pyrolyzing ZIF-8, introducing cerium during the assembly stage of Fe single atoms. Through theoretical studies and *in situ* tests, the researchers confirm that the introduced  $CeO_2$  strengthened the adsorption of key ORR reaction intermediates, generating more  $OOH^*$  intermediates while reducing the production of  $O^*$  and  $OH^*$ .  $CeO_2@Fe$ -NC achieves a half-wave potential of  $0.89$  V and a

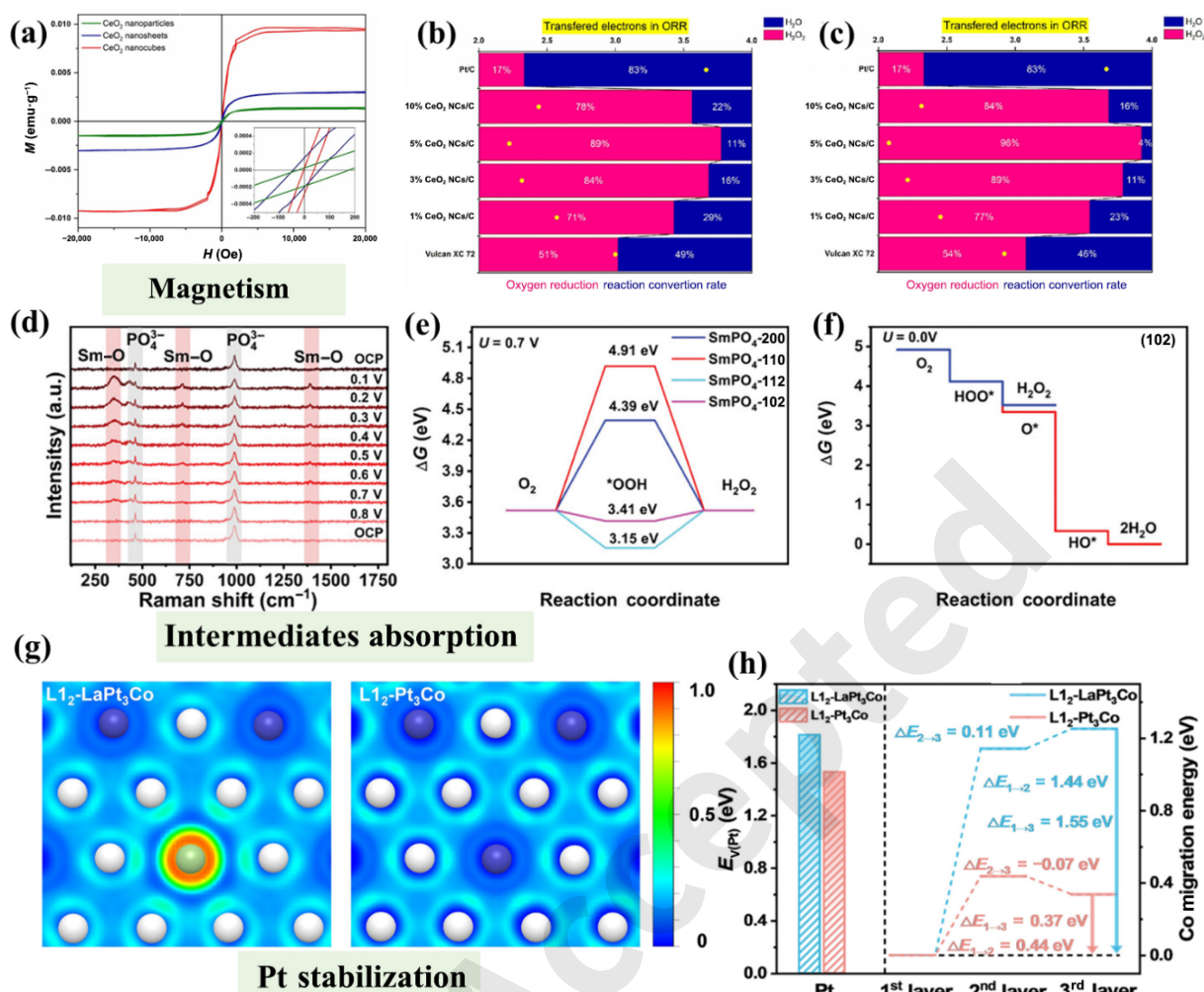
limiting current density of  $6.2$  mA·cm $^{-2}$ .  $CeO_2@Fe$ -NC also shows a half-wave potential loss of only  $1\%$  after  $10,000$  CV cycles, which is better than that of Fe-NC ( $7\%$ ).

In perovskite system, B-site cerium doping may optimize air electrodes for solid oxide fuel cells (SOFCs). Hao et al. [137] developed a cation off-size engineering strategy, aiming to address the limited performance of perovskite air electrodes in SOFCs caused by detrimental secondary phases. By doping  $Ce^{4+}$  into the B-site (instead of the conventional A-site) of  $Sr_2Fe_{1.5}Mo_{0.4}O_{6-\delta}$  (SFM), they deliberately tune cation lattice mismatch from under-mismatch to over-mismatch. This transformation converts the insulating  $SrMoO_4$  secondary phase into beneficial  $SrCeO_3/CeO_2$  composites, accompanied by enriched oxygen vacancies. The optimized  $Sr_2Fe_{1.5}Mo_{0.4}Ce_{0.1}O_{6-\delta}$  (SFMC $_{0.1}$ ) electrode exhibits an area-specific polarization resistance (ASR) of  $0.0091$   $\Omega$ ·cm $^2$  at  $850$  °C, a  $76.1\%$  reduction compared to pristine SFM. DFT calculations and characterizations confirm that B-site Ce doping lowers oxygen vacancy formation energy and enhances oxygen exchange/charge transfer kinetics. The SFMC $_{0.1}$ -based single cell achieves a maximum power density of  $1.71$  W·cm $^{-2}$  at  $850$  °C and maintains stability for over  $350$  h at  $750$  °C.

In another perovskite electrocatalyst for ORR, lanthanum aluminate-based perovskite precipitates low-content Pt nanoparticles. Ozkan et al. [138] developed a low-Pt ( $0.5$  wt.%) perovskite electrocatalyst  $La_{0.9925}Ba_{0.0075}Al_{0.995}Pt_{0.005}O_3$  via solid-state synthesis, enabling Pt nanoparticle exsolution upon reduction in  $H_2/N_2$  at  $400$ – $800$  °C. Low-temperature reduction ( $500$ – $600$  °C) yields uniformly dispersed  $1$ – $3$  nm Pt nanoparticles, while higher temperatures ( $700$ – $800$  °C) produce larger particles ( $3$ – $10$  nm). The catalyst exhibits superior ORR performance in alkaline media ( $0.1$  M KOH) compared to acidic conditions. The  $500$  °C-reduced sample achieves an onset potential of  $0.97$  V vs. RHE and a limiting current density of  $2.8$  mA·cm $^{-2}$ , with enhanced stability. Its mass activity ( $4.66$ – $4.78$  A·mg $_{Pt}^{-1}$ ) surpasses Pt/C ( $2.09$  A·mg $_{Pt}^{-1}$ ) despite half the Pt loading. This work demonstrates that perovskite-derived Pt exsolution offers a promising strategy for low-cost and high-efficiency ORR catalysts in fuel cells.

Hollow samarium phosphate nanospheres were proven to be selective for  $2e^-$  ORR. Liu et al. [139] synthesized hierarchical hollow  $SmPO_4$  nanospheres with open channels via a two-step hydrothermal method. Through *in situ* tests and DFT calculations, the researchers attribute the catalyst's performance to its hexagonal crystal structure with proton/ion-rich channels, and hollow hierarchical features. They appropriate spatial distance between adjacent Sm atoms, high compositional stability, and the synergistic effect of surrounding  $PO_4^{3-}$  units, which create abundant active sites on the  $SmPO_4$  surface. The resulting Sm electronic configuration optimizes the adsorption free energy of the key intermediate  $^*OOH$ , reduces the kinetic barrier for  $OOH$  desorption, and enhances structural stability. This uniquely structured catalyst exhibits excellent  $2e^-$  ORR performance, showing over  $93\%$  selectivity in a broad potential range of  $0$  to  $0.6$  V in  $0.1$  M KOH, with a peak of  $96\%$  at  $0.45$  V. When used as the cathode in a flow cell, the  $SmPO_4$  demonstrates impressive stability at  $100$  mA·cm $^{-2}$  for  $12$  h, maintaining a Faradaic efficiency above  $90\%$  (Figs. 10(d)–10(f)).

In order to address the stability challenges of Pt-based intermetallic catalysts in PEM fuel cells (PEMFCs), Li et al. [140] strategically incorporated La into  $Ll_2$ -Pt $_3$ Co intermetallics, developing a novel structural engineering strategy. The La-doped  $Ll_2$ -LaPt $_3$ Co catalyst was synthesized via a MOF-derived ligand-coordination method, featuring ordered atomic arrangement and



**Figure 10** (a) Magnetization as a function of the external magnetic field of different CeO<sub>2</sub> nanostructures measured at 300 K. The insert shows the low-field region. Electron transferred number and O<sub>2</sub> conversion rate on H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O comparison among the CeO<sub>2</sub>/C electrocatalyst NCs, Vulcan XC-72, and Pt/C, within an O<sub>2</sub>-saturated 1 mol·L<sup>-1</sup> NaOH solution: (b) in the absence of a magnetic field at -0.6 V and (c) in the presence of a magnetic field (2000 Oe) at -0.6 V. Reproduced with permission from Ref. [135], © Elsevier B.V. 2024. (d) *In situ* Raman spectra for SmPO<sub>4</sub>-12 electrocatalyst in O<sub>2</sub>-saturated 0.1 M KOH within a voltage window 0.1–0.8 V versus RHE, together with the Raman spectra backing to 0.0 V versus RHE after forward direction test from 0.1 to 0.8 V versus RHE. (e) Free energy diagram of 2e<sup>-</sup> ORR on different crystal faces of SmPO<sub>4</sub> at U = 0.70 V (U denotes the applied electrode potential). (f) Free energy diagrams for 2e<sup>-</sup> ORR and 4e<sup>-</sup> ORR on (102) facet of SmPO<sub>4</sub>. Reproduced with permission from Ref. [139], © Liu, Z. W. et al. 2025. (g) Sliced ELF for L<sub>1,2</sub>-LaPt<sub>3</sub>Co and L<sub>1,2</sub>-Pt<sub>3</sub>Co. (h) The vacancy formation energy of Pt (E<sub>v(Pt)</sub>) and the layer-by-layer exchange energy between Co and Pt. Reproduced with permission from Ref. [140], © American Chemical Society 2026.

uniform La distribution. Experimental studies and DFT calculations reveal that La induces a transition from metallic to quasi-covalent Pt–La bonding, strengthening Pt–Co/La interactions and increasing Pt vacancy formation energy. This modulation bridges the core–shell chemical potential gradient, suppressing Co migration and oxidative dissolution of both Pt and Co. The catalyst exhibits exceptional ORR performance: a mass activity of 1.29 A·mg<sub>Pt</sub><sup>-1</sup> at 0.9 V<sub>IR-free</sub> and a peak power density of 1.27 W·cm<sup>-2</sup> under H<sub>2</sub>–air conditions. More notably, it retains 87% of initial mass activity and shows only 12 mV voltage loss at 0.8 A·cm<sup>-2</sup> after 30,000 accelerated durability cycles, surpassing United States Department of Energy (U.S. DOE) 2026 targets (Figs. 10(g) and 10(h)).

ORR catalysts require precise reactive sites to boost reaction activity, which is why single-atom catalysis is pursued for ORR catalysts. For this very reason, regulating the electronic structure of the catalyst's active sites is extremely critical. This creates opportunities for the application of rare earth elements in ORR.

REEs can function in various ways in ORR systems. They can

serve directly as active sites, be introduced into catalyst systems to enhance the activity of other elemental catalysts, or be used to synthesize multifunctional catalysts. In addition, REE doping strategies can regulate the crystal structure, oxygen vacancy content, and secondary phases of catalysts, further optimizing ORR performance. Overall, REE-based strategies provide effective approaches for the design of high-performance ORR catalysts, contributing to the development of efficient energy storage and conversion devices. The catalysts involved in the relevant references of the Section 3.4 and their performances are shown in Table 5.

### 3.5 Nucleophile oxidation

Nucleophiles are a class of Lewis base compounds that can provide lone pairs of electrons to attack electropositive atoms. Typical nucleophiles include amines, alcohols, and aldehydes. The nucleophile oxidation reactions usually take place in an alkaline electrolyte environment, which requires precise regulation of the

Table 5 Summary of catalyst performances in Section 3.4

| References | Name                                                                                             | Catalyst | Electrolyte                            | Mass loading                                                                                                                                                                         | Performance                                                                                                                                                                                        | Commercial catalysts                                                    |
|------------|--------------------------------------------------------------------------------------------------|----------|----------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|
| [133]      | 20-Y-N                                                                                           | ORR      | 0.1 M KOH                              | 0.4 mg·cm <sup>-2</sup>                                                                                                                                                              | $E_{1/2} = 0.770$ V, $E_{1/2}$ decreases by 14 mV after 5000 CV cycles                                                                                                                             | Pt/C; 5000 cycles CV; $E_{1/2}$ decreases by 15 mV after 5000 CV cycles |
| [134]      | Ce SA/MC                                                                                         | ORR      | 0.1 M KOH                              | RRDE: 0.384 mg·cm <sup>-2</sup> ; Zn-air: 0.5 mg·cm <sup>-2</sup>                                                                                                                    | $E_{1/2} = 0.845$ V, $E_{1/2}$ decreases by 9 mV after 5000 CV cycles, 98.2% retention of the initial current after 10,000 s potentiostatic test                                                   | Pt/C, $E_{1/2} = 0.845$ V                                               |
| [135]      | CeO <sub>2</sub>                                                                                 | ORR      | 1.0 M NaOH                             | 0.1617 mg·cm <sup>-2</sup>                                                                                                                                                           | H <sub>2</sub> O <sub>2</sub> selectivity = 88%–96%                                                                                                                                                | Pt/C, H <sub>2</sub> O <sub>2</sub> selectivity = 13%, –0.6 V           |
| [136]      | CeO <sub>2</sub> @Fe-NC                                                                          | ORR      | 0.1 M KOH                              | RRDE: ~1 mg·cm <sup>-2</sup> ; Zn-air: 4 mg·cm <sup>-2</sup> (20% carbon black)                                                                                                      | $E_{1/2} = 0.89$ V, $E_{1/2}$ decreases by 1% after 10,000 CV cycles                                                                                                                               | Pt/C, $E_{1/2} = 0.83$ V                                                |
| [137]      | SFMC <sub>0.1</sub>                                                                              | ORR      | Samarium-doped ceria (SDC)-electrolyte | —                                                                                                                                                                                    | 1.71 W·cm <sup>-2</sup> at 850 °C; 350 h at 750 °C                                                                                                                                                 | —                                                                       |
| [138]      | La <sub>0.9925</sub> Ba <sub>0.0075</sub> Al <sub>0.995</sub> Pt <sub>0.005</sub> O <sub>3</sub> | ORR      | 0.1 M KOH                              | 0.59 μg <sub>Pt</sub> ·cm <sup>-2</sup>                                                                                                                                              | Onset potential: 0.97 V, 60,000 s, $i$ decreased ≤ 30%                                                                                                                                             | 1% Pt/C, $E_{1/2} = 0.79$ V                                             |
| [139]      | SmPO <sub>4</sub>                                                                                | ORR      | 0.1 M KOH                              | RRDE: 0.18 mg·cm <sup>-2</sup> ; H-cell/flow-cell: 0.5 mg·cm <sup>-2</sup>                                                                                                           | FE = 96% at –0.45 V; H-cell: 12 h; flow-cell: 100 mA·cm <sup>-2</sup> , 12 h, FE > 90%                                                                                                             | —                                                                       |
| [140]      | Li <sub>2</sub> -LaPt <sub>3</sub> Co                                                            | ORR      | 0.1 M HClO <sub>4</sub>                | RDE: 20 μg <sub>Pt</sub> ·cm <sup>-2</sup> ; MEA: cathode/anode (C/A) 0.1/0.1 μg <sub>Pt</sub> ·cm <sup>-2</sup> ; MEA (high-load): C/A 0.13/0.05 μg <sub>Pt</sub> ·cm <sup>-2</sup> | $E_{1/2} = 0.945$ V; 1.27 W·cm <sup>-2</sup> for H <sub>2</sub> ; stability with 87% MA retention and only 12 mV voltage loss at 0.8 A cm <sup>-2</sup> after 30,000 accelerated durability cycles | 1% Pt/C, $E_{1/2} = 0.884$ V                                            |

adsorption strength of OH<sup>-</sup>. The typical indirect oxidation pathway of nucleophiles also involves the reconstruction of catalyst species. All these processes are expected to be optimized and regulated by introducing rare earth elements. Therefore, rare earth elements are also widely used in nucleophile oxidation reactions, including UOR, MOR, EOR, formic acid oxidation reaction (FAOR), glucose oxidation reaction (GOR), etc. These oxidation reactions are important anodic reactions in energy storage and conversion devices (e.g., urea electrolyzers and direct alcohol fuel cells). It is also expected to replace the anodic OER in water electrolysis for hydrogen production, enabling hydrogen generation at lower potentials while yielding high-value-added products.

Electrochemical nucleophile oxidation reactions face the problems of slow reaction kinetics and low catalytic activity. In the direct mechanism of nucleophile oxidation, the catalyst itself is first oxidized through dehydrogenation or even oxygen acquisition, and then reduced by capturing electrons from the nucleophile, thereby catalyzing the oxidation of the nucleophile. In this mechanism, rare earth elements are expected to regulate the valence state changes of reaction sites and improve the activity and stability of the reaction by virtue of their high electron cloud density and variable valence properties. In the indirect oxidation mechanism of nucleophiles, the catalyst needs to adsorb OH first before carrying out subsequent reactions. The introduction of rare earth elements is expected to optimize the microscopic adsorption behavior of catalysts and enhance reaction kinetics and selectivity.

### 3.5.1 Urea oxidation reaction

UOR is an important anodic reaction of urea electrolyzers, which can replace OER to reduce the cell voltage of water electrolysis and realize the simultaneous treatment of urea-containing wastewater and hydrogen production. Rare earth elements, such as Y, Ce, and Tb, can induce the formation of high-valence active sites in UOR catalysts, optimize the electronic structure of active sites, and

accelerate the cleavage of C–N bonds, thus improving the catalytic activity and stability of UOR.

High-valence species are critical for the oxidation of nucleophiles, and in this work, yttrium doping generates high-valence nickel sites for UOR. Wu et al. [141] introduced Y into α-Ni(OH)<sub>2</sub> by hydrothermal method to synthesize a series of catalysts, and the best performing one was YNi-10. The doping of Y induces the formation of Ni<sup>3+</sup> in the lattice, which is beneficial to the initiation of the UOR process. The researchers compared the performances before and after Y doping through a series of controlled experiments. The doping of Y successfully adjusts the electronic structure of α-Ni(OH)<sub>2</sub>, promoting the Ni<sup>3+</sup>/Ni<sup>2+</sup> redox. All these reduce the activation energy of the reaction and improve the UOR activity of the catalyst. The catalyst shows a current density of 127 mA·cm<sup>-2</sup> at 1.5 V, a low Tafel slope of 48 mV·dec<sup>-1</sup>, a larger potential difference between UOR and the oxygen evolution reaction, and a higher reaction rate constant.

In another work, samarium substitution adjusts spin configuration of ruthenium pyrochlore. Jiang et al. [142] proposed a strategy to modulate Ru spin configuration in pyrochlore oxide Y<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> via Sm substitution. The synthesized Y<sub>1.5</sub>Sm<sub>0.5</sub>Ru<sub>2</sub>O<sub>7</sub> (YRuO-Sm) achieves Sm (4f)–O (2p)–Ru (4d) gradient orbital coupling, transforming Ru from a low-spin to a high-spin (HS) configuration. This HS state enhances Ru–O covalency and electron localization, optimizing \*COO intermediate adsorption and dissociation. DFT calculations confirm Sm substitution eliminates the Mott–Hubbard gap, lowers the energy barrier of the rate-determining step (\*COO → CO<sub>2</sub>) from 0.85 to 0.66 eV. Integrated into a hybrid water electrolyzer, it achieves 100 mA·cm<sup>-2</sup> at 1.65 V with > 98% Faradaic efficiency. As a bifunctional catalyst in urea-assisted Zn–air batteries (ZAB), it narrows the charge–discharge voltage gap to 0.72 V and enables stable cycling for 180 h. YRO-Sm exhibits excellent UOR activity, reaching 100 mA·cm<sup>-2</sup> at 1.43 V vs. RHE with a Tafel slope of 75 mV·dec<sup>-1</sup>, and maintains stability for 200 h.



Based on  $\text{Ni}(\text{OH})_2$ , Ce and N co-doping strategy improved the electrocatalytic performance. Tao et al. [143] designed porous Ce and N co-doped  $\text{Ni}(\text{OH})_2$  (Ce, N- $\text{Ni}(\text{OH})_2$ ) nanosheets as a bifunctional electrocatalyst via hydrothermal synthesis followed by calcination. The porous structure enhances active site exposure and mass transfer, while Ce/N co-doping optimizes the Ni d-band center and improves electron transport. *In situ* Raman spectroscopy and DFT calculations confirm that  $\gamma\text{-NiOOH}$  generated during UOR is the real active species, and the modulated electronic microenvironment shifts the UOR rate-determining step from  $\text{CONNH}^*$  to  $\text{CONHNH}^*$  dehydrogenation, reducing the thermodynamic barrier. The catalyst exhibits excellent UOR activity (1.39 V at  $100 \text{ mA}\cdot\text{cm}^{-2}$ , Tafel slope  $18.4 \text{ mV}\cdot\text{dec}^{-1}$ ) and superior HER performance. The assembled urea electrolyzer achieves  $10 \text{ mA}\cdot\text{cm}^{-2}$  at 1.49 V and maintains stable operation for 70 h.

In order to optimize the reconstruction of Ni species, Wang et al. [144] synthesized Ce-doped  $\text{Ni}_5\text{P}_4$  porous nanosheets via hydrothermal and phosphorization processes. Ce doping induces electron transfer from Ni and P to Ce, elevating Ni's chemical state and promoting surface reconstruction into active  $\text{NiOOH}$  species. The catalyst retains the stable (210) crystal plane of  $\text{Ni}_5\text{P}_4$  while activating it for efficient UOR. DFT calculations reveal Ce doping weakens Ni–N bond binding energy, shifts the UOR rate-determining step to a lower energy barrier (1.51 vs. 1.94 eV for undoped). The assembled anion exchange membrane water electrolyzer with Ce-doped  $\text{Ni}_5\text{P}_4$  as anode delivers  $1 \text{ A}\cdot\text{cm}^{-2}$  at 2.37 V and maintains stability for 60 h, demonstrating industrial application potential. Experimental results show the optimal Ce-doped  $\text{Ni}_5\text{P}_4$  achieves a low potential of 1.33 V at  $500 \text{ mA}\cdot\text{cm}^{-2}$  and exceptional stability over 120 h in 1 M KOH + 0.33 M urea. It exhibits a small Tafel slope of  $20.16 \text{ mV}\cdot\text{dec}^{-1}$  and low charge-transfer resistance, outperforming undoped  $\text{Ni}_5\text{P}_4$  and commercial  $\text{RuO}_2$ .

Meng et al. [145] synthesized a series of  $\text{Ni}_{0.2}\text{Mo}_{0.8}\text{N}/\text{CeO}_{2-x}/\text{NF}$  ( $x = n(\text{Ce})/n(\text{Ni}) = 0.1, 0.3, \text{ and } 0.5$ , where  $n$  presents amount of substance) catalysts on nickel foam using a hydrothermal-annealing method. Among them,  $\text{Ni}_{0.2}\text{Mo}_{0.8}\text{N}/\text{CeO}_{2-0.3}/\text{NF}$  exhibits the best performance, serving as a bifunctional catalyst for both the HER and UOR. The researchers attribute the high performance to the formation of a nanonetwork structure, where a large number of nanoparticles adhered to the nanosheets, enhancing the electrochemical catalytic activity. For HER, the catalyst requires only a potential of 120 mV to achieve a current density of  $100 \text{ mA}\cdot\text{cm}^{-2}$ . For UOR, the potential is only 1.462 V at  $100 \text{ mA}\cdot\text{cm}^{-2}$ . A two-electrode electrolyzer,  $\text{Ni}_{0.2}\text{Mo}_{0.8}\text{N}/\text{CeO}_{2-0.3}/\text{NF}||\text{Ni}_{0.2}\text{Mo}_{0.8}\text{N}/\text{CeO}_{2-0.3}/\text{NF}$ , requires only 1.672 V to reach a current density of  $100 \text{ mA}\cdot\text{cm}^{-2}$ . Additionally, the catalyst demonstrates excellent stability.

In another piece of work, the co-doping of V and Ce provides support for achieving bifunctional catalytic activity of the catalyst. Sheng et al. [146] synthesized a VCe-FeCoNiP/NF dual-doped medium-energy phosphide catalyst via a two-step hydrothermal and phosphorization method for HER and UOR. The researchers attribute the improved performance to the synergetic effect of dual cation doping and medium-entropy structure. In the UOR reaction system, the catalyst requires only 1.308 and 1.338 V vs. RHE to achieve current densities of 10 and  $100 \text{ mA}\cdot\text{cm}^{-2}$ , respectively. For the HER system, the catalyst needs only an overpotential of 173 mV to reach a current density of  $100 \text{ mA}\cdot\text{cm}^{-2}$ . When used as both the anode and cathode in a two-electrode system, it requires only 1.56 V to achieve a current

density of  $100 \text{ mA}\cdot\text{cm}^{-2}$  and can operate stably for 225 h at a current density of  $25 \text{ mA}\cdot\text{cm}^{-2}$ .

In addition to functioning in nitride systems, rare earth elements are also expected to play a role in sulfide systems. Zhang et al. [147] synthesized a nanoparticle-rich Fe-( $\text{CeS}_2/\text{Ni}_3\text{S}_2$ ) hybrid material via a hydrothermal method. This material, with abundant heterointerfaces and sulfur defects, can catalyze the oxidation of water, urea, and ethanol. The researchers employed *in situ* tests and DFT calculations to study the OER process of the catalyst, and the results indicate that electrons are transferred from  $\text{CeS}_2$  to  $\text{Ni}_3\text{S}_2$ , with electron-rich Ni enhancing OER performance. The cerium species can modulate the internal electronic state and stabilize some of the surface sulfide against self-oxidation during OER process. For OER, Fe-( $\text{CeS}_2/\text{Ni}_3\text{S}_2$ ) requires overpotentials of only 254 and 372 mV to reach a high current density of 100 and  $500 \text{ mA}\cdot\text{cm}^{-2}$ , respectively. Additionally, the electrocatalyst presents eminent UOR activity, requiring only 1.36 V to reach  $10 \text{ mA}\cdot\text{cm}^{-2}$ , and outstanding EOR activity, requiring only 1.32 V to reach  $10 \text{ mA}\cdot\text{cm}^{-2}$ . This work provides valuable references and insights for OER catalysts based on the adsorbate evolution mechanism (AEM) in the indirect oxidation of nucleophiles.

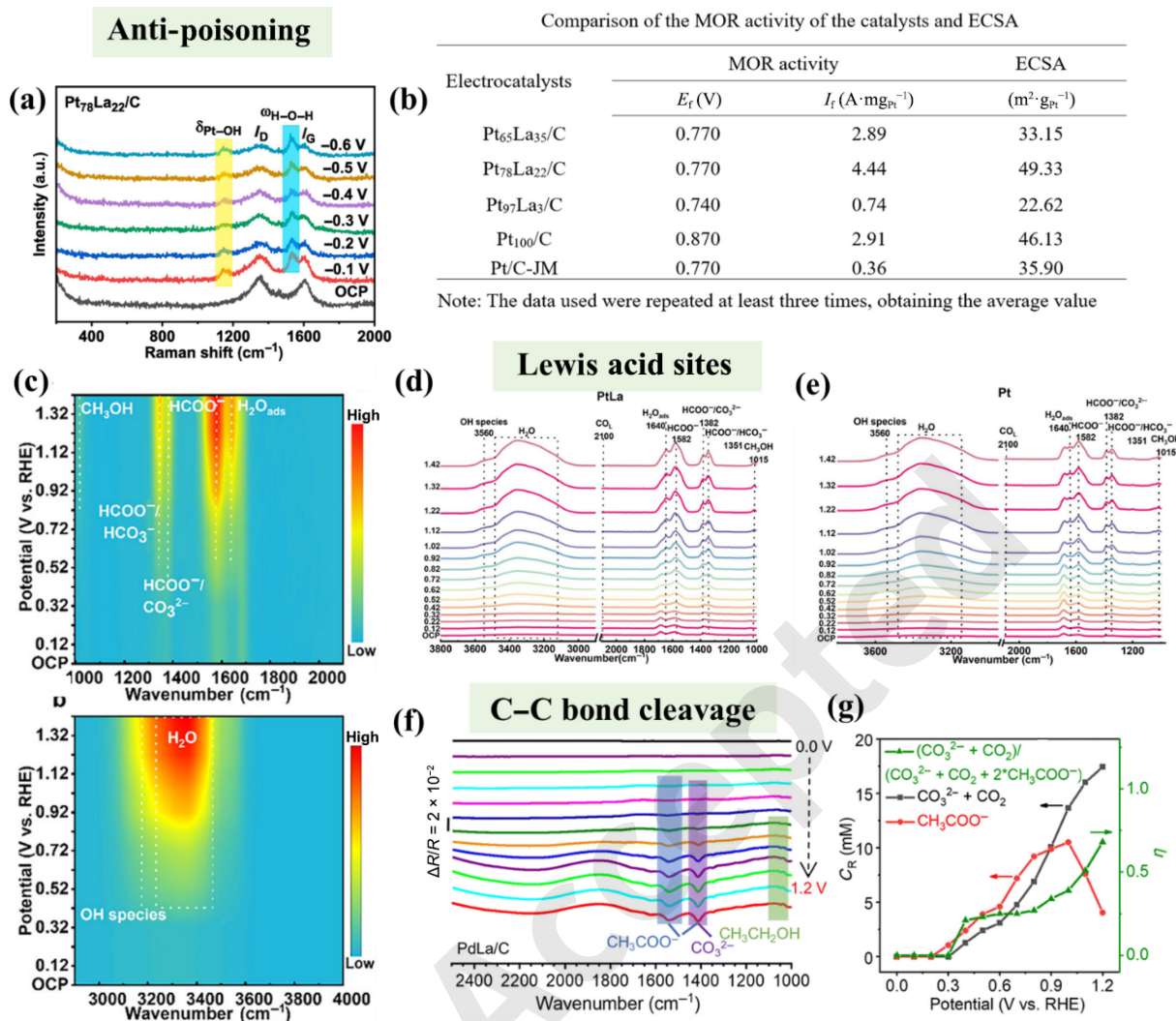
### 3.5.2 Methanol/ethanol oxidation reaction

MOR and EOR are important anodic reactions in direct alcohol fuel cells, which can replace OER to lower the overpotential and enable efficient energy conversion alongside hydrogen production in coupled electrolysis systems. Rare earth elements, such as Ce, La, Yb, Tm, Lu, Nd, and Dy, can optimize the electronic structure of Pt, Pd, and Ni-based active sites through ligand and strain effects, elevate the d-band center, enhance  $\text{OH}^*$  adsorption and  $^*\text{OH}$  species generation, promote C–C bond cleavage and CO anti-poisoning, and accelerate the kinetics of rate-limiting steps, thereby significantly improving the catalytic activity, stability, and selectivity of alcohol oxidation reactions.

In a representative work, Yue et al. [148] loaded nickel selenide with  $\text{CeO}_2$  onto N-doped carbon nanosheets, synthesizing a series of catalysts with both ethanol and urea oxidation performance. Characterizations prove that the co-interaction between  $\text{CeO}_2$  and  $\text{Ni}_{0.85}\text{Se}$ , allows more defects as catalytic sites and promotes fast electron transfer in the N-doped carbon substrate. DFT calculations show that  $\text{CeO}_2$  facilitates  $\text{OH}^*$  and  $\text{OOH}^*$  production and accelerates the reaction between  $\text{OOH}^*$  and methanol and urea. The best-performing  $\text{CeO}_2\text{-Ni}_{0.85}\text{Se-550-NC}$  has a potential of 1.309 V at  $10 \text{ mA}\cdot\text{cm}^{-2}$  and a peak current density of  $200.36 \text{ mA}\cdot\text{cm}^{-2}$  in 1 M KOH + 0.5 M MeOH, while in 1 M KOH + 0.5 M urea, the peak current density is  $178.56 \text{ mA}\cdot\text{cm}^{-2}$  and the potential is 1.294 V at  $10 \text{ mA}\cdot\text{cm}^{-2}$ .

In a noteworthy work, femtosecond laser was utilized to synthesize electrocatalyst for MOR. Feng et al. [149] developed a bifunctional catalyst for both alkaline HER and MOR. The researchers synthesized a series of PtLa alloy catalysts with varying atomic ratios on carbon black using a liquid-phase reduction method. For HER, the doping of La accelerates the water adsorption and activation processes, promotes water dissociation and  $^*\text{OH}$  desorption, and reduces the poisoning of Pt active sites by  $^*\text{OH}$ . For MOR, La promotes C–O bond cleavage and reduces CO adsorption at the Pt sites. Among the series of catalysts, the best-performing  $\text{Pt}_{78}\text{La}_{22}/\text{C}$ , when employed simultaneously as both the anode and cathode, requires only 1.030 V to achieve a current density of  $20 \text{ mA}\cdot\text{cm}^{-2}$  (Figs. 11(a) and 11(b)).

Zhang et al. [150] synthesized ligand-free Pt–La nanoclusters with clean surfaces and uniform La distribution via femtosecond



**Figure 11** (a) *Operando* Raman spectra at various potentials (−0.600 to 0 V) (vs. RHE) with an interval of 0.100 V in 1.0 M KOH for Pt<sub>78</sub>La<sub>22</sub>/C. (b) Comparison of the MOR activity of the catalysts and ECSA. Reproduced with permission from Ref. [149], © Elsevier Inc. 2024. *In situ* characterization of PtLa MOR electrocatalyst under electrochemical working conditions. (c) *In situ* ATR-SEIRAS spectra of PtLa clusters under MOR working conditions. *In situ* ATR-SEIRAS spectra under MOR operation for (d) PtLa clusters and (e) Pt clusters. Reproduced with permission from Ref. [150], © Wiley-VCH GmbH 2025. (f) *In situ* FTIR spectra of PdLa/C. (g) Selectivity plots of PdLa/C. Reproduced with permission from Ref. [153], © The Royal Society of Chemistry 2025.

laser ablation in liquids, a strategy overcoming the phase segregation issue in conventional wet-chemical synthesis of Pt–Ln alloys. *In situ* characterizations confirm HCOO<sup>−</sup> as the key MOR intermediate and reveal that La doping enhances OH<sup>−</sup> adsorption/desorption kinetics at the electrolyte–electrode interface. DFT calculations and ultraviolet photoelectron spectroscopy (UPS) results demonstrate that La elevates the Pt d-band center, strengthens intermediate adsorption, and reduces the kinetic barrier of the rate-limiting step (\*CHO to \*HCOOH). The oxophilic La creates Lewis acid sites to enrich local OH<sup>−</sup>, accelerating intermediate activation and MOR turnover. This femtosecond laser synthesis provides a facile route for preparing metastable rare earth-based alloy nanoclusters, promising for large-scale direct methanol fuel cell (DMFC) applications and other catalytic systems. The as-prepared PtLa/XC-72 catalyst achieves a record-high mass activity of 17.50 A·mg<sub>Pt</sub><sup>−1</sup> and a specific activity of 205 mA·cm<sup>−2</sup> in alkaline MOR, far exceeding commercial Pt/C and PtRu/C catalysts. It also exhibits superior CO-poisoning resistance with a low CO oxidation onset potential of 0.345 V vs. RHE and excellent durability, retaining 76.5% of initial activity after 1000 CV cycles (Figs. 11(c)–11(e)).

In this work, researchers further developed a series of rare earth–Pt alloy catalysts. Zhang et al. [151] combined several lanthanide elements with Pt to develop Pt<sub>3</sub>Tm, Pt<sub>3</sub>Yb, and Pt<sub>3</sub>Lu nanoalloys with a cubic crystal system. Due to the low electronegativity of Ln (Ln = Tm, Yb, and Lu) and the ligand effect in the alloy, the electronic structure of Pt is continuously optimized. DFT calculations indicated that the low-electronegativity Ln-modified Pt sites can accelerate MOR pathways. Besides, compared with Pt, Ln has a high affinity for oxygen, and the adsorbed OH groups can induce higher resistance to CO poisoning. Among these materials, optimized Pt<sub>3</sub>Yb/C shows the highest specific activity of 35.28 mA·cm<sub>Pt</sub><sup>−2</sup> and mass activity of 11.61 A·mg<sub>Pt</sub><sup>−1</sup>.

Unlike the alloys mentioned above, this work synthesized a unique PdLa bimetallic. Shen et al. [152] synthesized PdLa bimetallic with a multi-defect crimped perforated nanostructure via a one-step wet chemical method, with the optimal Pd/La mass ratio of 3:1. DFT calculations reveal that La acts as an electron acceptor, shifting Pd d-band center 0.28 eV away from the Fermi level, weakening hydrogen binding strength, and reducing the EOR energy barrier, thus optimizing intermediate adsorption and

desorption. This work combines rare earth doping with 2D bimetallic design, expanding rare earth applications in electrocatalytic hydrogen production and providing new ideas for high-performance bifunctional catalyst development. The optical sample exhibits excellent EOR activity with a mass activity of  $2.46 \text{ A}\cdot\text{mg}_{\text{Pd}}^{-1}$  and a specific activity of  $3.28 \text{ mA}\cdot\text{cm}^{-2}$ . For HER, it only needs an overpotential of  $67.4 \text{ mV}$  to reach  $10 \text{ mA}\cdot\text{cm}^{-2}$ , with a Tafel slope of  $138 \text{ mV}\cdot\text{dec}^{-1}$ . In the two-electrode EOR&HER coupled system, the catalyst achieves  $100 \text{ mA}\cdot\text{cm}^{-2}$  at just  $0.61 \text{ V}$ , with a hydrogen evolution Faradaic efficiency of nearly  $98.3\%$ . It also shows outstanding stability after 2000 HER cycles and 24 h continuous operation of the coupled system.

Besides Pt, another precious metal, Pd, is also composited with rare earth elements to synthesize bimetallic catalysts. Li et al. [153] synthesized PdRE/C catalysts (RE = La, Nd, and Dy) via liquid-phase chemical reduction with carbon black as the support, targeting electrocatalytic MOR and EOR. Among these, PdLa/C exhibits superior performance. *In situ* tests show that PdLa/C enhanced ethanol adsorption/C–C bond cleavage and improved  $\text{CO}_2$  selectivity. Based on the reaction mechanism, researchers believe that incorporating rare earth elements also improves the distribution of active sites, enhancing catalytic activity. In addition, rare earth elements preferentially combine with oxygen radicals, which greatly increases the catalyst's resistance to poisoning. It achieves a mass activity of  $2.28 \text{ A}\cdot\text{mg}_{\text{Pd}}^{-1}$  for MOR and  $5.67 \text{ A}\cdot\text{mg}_{\text{Pd}}^{-1}$  for EOR, with  $95.6\%$  stability retention after 4000 s for MOR and  $84.3\%$  for EOR (Figs. 11(f) and 11(g)).

### 3.5.3 5-Hydroxymethylfurfural (HMF) oxidation reaction (HMFOR) and other nucleophile oxidation reactions

HMF is a biomass raw material derived from hexose fermentation and can be upgraded and converted into a variety of chemicals. Among them, 2,5-furandicarboxylic acid (FDCA) is one of the most prominent catalytic oxidation products and can be applied to the synthesis of biodegradable plastics. Replacing oxidant-based oxidation with electrocatalytic oxidation serves as an eco-friendly strategy for the conversion of HMF to FDCA. Rare earth elements can regulate the electronic structure of catalysts, facilitate the formation of high-valence active species (such as  $\text{Ni}^{3+}$  and  $\text{Co}^{3+}$ ), introduce oxygen vacancies, optimize the adsorption energy of reaction intermediates, and reduce the Gibbs free energy barrier of the rate-determining step. Consequently, they remarkably enhance the catalytic activity, selectivity, and stability of the electrooxidation reaction of small organic molecules. This chapter also presents several other representative research advances on the application of rare earth elements in the electrocatalytic oxidation of nucleophilic reagents.

Hydroxides are the most common HMFOR catalysts. In this work, the Ce doping strategy was adopted to modify the hydroxide. Ding et al. [154] developed nickel foam-supported CoCrCe-LDH electrocatalysts via a one-step hydrothermal method, aiming to boost the electrooxidation of HMF to high-value FDCA. The optimal CoCrCe(7.5%)-LDH retains a nanosheet structure with uniform distribution of Co, Cr, and Ce. Ce doping modulates the electronic structure of Co and Cr, promoting the formation of high-valence Co and accelerating charge transfer, as confirmed by XPS and XANES. DFT calculations reveal that Ce doping optimizes intermediate adsorption, reduces the Gibbs free energy barrier of the rate-determining step to  $0.78 \text{ eV}$ , and enhances reaction kinetics. It exhibits exceptional catalytic performance at  $1.4 \text{ V}$  vs. RHE with  $99\%$  HMF conversion,  $99\%$  FDCA yield, and  $100\%$  Faradaic

efficiency, and a current density of  $50.5 \text{ mA}\cdot\text{cm}^{-2}$ . The catalyst also shows excellent stability, maintaining  $97\%$  HMF conversion after 10 cycles and stable performance over 2000 CV cycles.

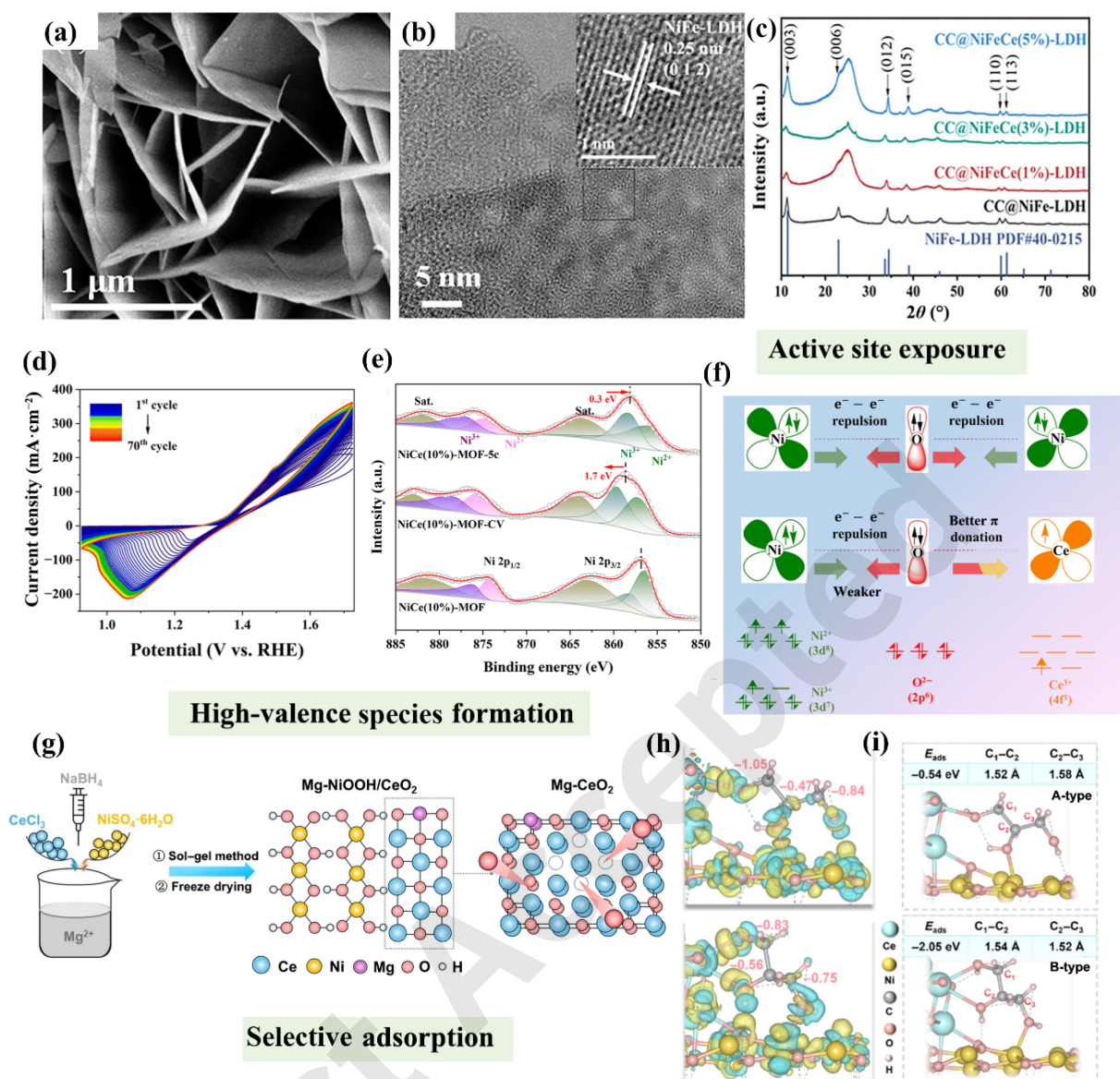
In another piece of work, Ce doping was also applied to modify NiFe-LDH. Zhang et al. [155] systematically explored the effects of Ce doping,  $\text{CeO}_2$  modification, and their synergistic interaction on the electrocatalytic oxidation of HMF over CC-supported NiFe-LDH. Structural characterizations confirm Ce is uniformly doped into the NiFe-LDH lattice, forming vertically aligned nanosheet arrays that enhance electrolyte contact and active site exposure. XAFS and XPS analyses reveal that Ce doping modulates the electronic structure of Ni and Fe, promotes the formation of high-valence  $\text{Ni}^{3+}$  active sites, and increases oxygen vacancies. DFT calculations demonstrate that Ce doping optimizes the adsorption of HMF and reaction intermediates, reduces the energy barrier of the rate-determining step, and accelerates charge transfer. Among the prepared catalysts, CC@NiFeCe(3%)-LDH with only Ce doping outperforms the others, achieving  $95.73\%$  HMF conversion,  $93.31\%$  FDCA yield, and  $99.47\%$  Faradaic efficiency at  $1.44 \text{ V}$  vs. RHE (Figs. 12(a)–12(c)).

In addition to doping, rare earth oxides are also used for the modification of hydroxides in some studies. Ye et al. [156] developed a high-performance electrocatalyst HMFOR via electroactivation-induced transformation of Ce-regulated NiCo-LDH (NCCe5-P) into  $\text{CeO}_2$ -modified NiCoOOH (NCCe5-R). Synthesized by one-step potentiostatic electrodeposition on nickel foam, NCCe5-P undergoes structural reconstruction during electrochemical activation, forming abundant oxygen vacancies and elevating the oxidation states of Ni, Co, and Ce. Characterizations confirm that  $\text{CeO}_2$  modification and  $\text{V}_\text{O}$  synergistically enhance HMF adsorption, accelerate charge transfer, and promote the formation of high-valent metal active sites. DFT calculations reveal NCCe5-R reduces the energy barrier of the rate-determining step to  $1.01 \text{ eV}$ , far lower than NC-R ( $1.58 \text{ eV}$ ). The optimized NCCe5-R exhibits exceptional HMFOR performance:  $100\%$  HMF conversion,  $99.5\%$  FDCA yield, and  $99.1\%$  Faradaic efficiency, with a current density of  $54.2 \text{ mA}\cdot\text{cm}^{-2}$  at  $1.4 \text{ V}$  vs. RHE. When integrated into an HER||HMFOR coupled system, NCCe5-P (cathode) and NCCe5-R (anode) achieve  $10 \text{ mA}\cdot\text{cm}^{-2}$  at  $1.32 \text{ V}$  vs. RHE, outperforming traditional water electrolysis.

In addition to hydroxides, doping with rare earth elements is also expected to be effective in other catalysts used for HMFOR. Dou et al. [157] synthesized nickel foam-supported Ce-doped NiOOH electrocatalysts via electrocatalytic self-reconstruction of Ce-doped Ni-BDC (where BDC stands for a terephthalic acid linker) MOFs (NiCe-MOFs). Structural characterizations confirm that CV activation drives the decomposition of MOF ligands and *in situ* formation of NiOOH, with Ce uniformly doped into the NiOOH lattice. XPS and XANES analyses reveal strong electron interactions between Ce and Ni, promoting the formation of high-valence  $\text{Ni}^{3+}$  active sites. DFT calculations demonstrate that Ce doping enhances the adsorption of HMF and  $\text{OH}^*$  and reduces the energy barrier of the rate-determining step. The catalyst follows both direct and indirect oxidation mechanisms for HMFOR, with competitive adsorption between HMF and  $\text{OH}^*$  optimizing reaction kinetics. The optimal NiCe(10%)-MOF achieves a high current density of  $153.15 \text{ mA}\cdot\text{cm}^{-2}$  at  $1.5 \text{ V}$  vs. RHE for HMFOR and retains  $100\%$  HMF conversion,  $98.6\%$  FDCA yield, and  $99.8\%$  Faradaic efficiency after 20 consecutive cycles at  $1.44 \text{ V}$  vs. RHE (Figs. 12(d)–12(f)).

In addition to the doping strategy, rare earth elements, serving





**Figure 12** (a) Scanning electron microscopy (SEM) image of the CC@NiFeCe(3%)-LDH. (b) TEM and HRTEM (inset) images of the CC@NiFeCe(3%)-LDH. (c) XRD patterns of CC@NiFe-LDH, CC@NiFeCe(1%)-LDH, CC@NiFeCe(3%)-LDH, and CC@NiFeCe(5%)-LDH. Reproduced with permission from Ref. [155], © Wiley-VCH GmbH 2024. (d) CV curves of NiCe(10%)-MOFs and in 50 mM HMF + 1.0 M KOH solution. (e) Ni 2p in the high-resolution XPS spectra of NiCe(10%)-MOFs, NiCe(10%)-MOF-CV, and NiCe(10%)-MOF-5c. (f) Schematics of the electronic interplay among Ni, Ce, and O. Reproduced with permission from Ref. [157], © The Royal Society of Chemistry 2025. (g) Synthetic strategy for Mg-NiOOH/CeO<sub>2</sub>. (h) Charge density difference maps for glycerol adsorption in A-type and B-type configurations, with Bader charges of the corresponding C atoms. (i) Adsorption energy and C-C bond length for glycerol adsorption. Reproduced with permission from Ref. [161], © American Chemical Society 2026.

as substrates, may also exert a modulating effect in the HMFOR catalyst system. Yao et al. [158] prepared oxygen vacancy-enriched Ni(OH)<sub>2</sub>/CeVO<sub>4</sub>@NF electrocatalysts via a one-step hydrothermal *in situ* growth strategy on nickel foam, aiming at electrocatalytic oxidation of HMF to high-value FDCA. Ce and V bimetallic doping realizes electronic coupling that modulates Ni d-band center, optimizes the electronic structure of Ni(OH)<sub>2</sub>, and elevates the catalyst's ability to adsorb and activate HMF molecules. The Ni<sup>2+</sup>/Ni<sup>3+</sup> redox pairs in the catalytic system serve as efficient electron donors for HMF oxidation. Electron paramagnetic resonance (EPR) characterization confirms that V doping increases oxygen vacancy concentration, enhancing charge transport capability. DFT calculations further reveal that the oxidation step from 5-formyl-2-furancarboxylic acid (FFCA) to FDCA is the rate-determining step of the whole conversion

process, and the bimetallic doping effectively reduces the energy barrier of this step. At 1.5 V vs. RHE, this catalyst achieves outstanding performance with 100% HMF conversion, 97.8% FDCA yield, and 97.6% Faradaic efficiency, and maintains high catalytic stability over 9 consecutive cycles.

Rare earth elements are also expected to play a role in the oxidation reactions of some other nucleophiles. Sofian et al. [159] developed a Pd<sub>3</sub>Y<sub>x</sub>/reduced graphene oxide (rGO) for formic acid oxidation reaction by uniformly dispersing small-sized Pd and Y<sub>2</sub>O<sub>3</sub> onto rGO. Through theoretical calculations, the researchers prove that the addition of Y<sub>2</sub>O<sub>3</sub> significantly increased the electrochemically active area. The strong interaction between another rare earth element Pb, Y<sub>2</sub>O<sub>3</sub>, and rGO is the reason for the improvement of the catalyst activity. Moreover, Y also has applications in the field of urea oxidation reaction. Among them,

the Pd<sub>6</sub>Y<sub>4</sub>/rGO with the best performance shows the highest current density (106 mA·cm<sup>-2</sup>) and the lowest onset potential compared with Pd/rGO (28.1 mA·cm<sup>-2</sup>) and the Pd/C (21.7 mA·cm<sup>-2</sup>). At the same time, the catalyst also has good stability and anti-CO pollution performance.

In a noteworthy study, the rare earth element Pr acts as a variable-valence element in the indirect oxidation mechanism with rare earth elements as nucleophiles within the catalyst system. Yang et al. [160] fabricated a Pr/Pr<sub>2</sub>(SeO<sub>3</sub>)<sub>3</sub> Mott-Schottky heterojunction for hydrogen HER and GOR by constructing a rare earth Pr-based composite with selenite. The rare earth element Pr plays a decisive role in regulating electronic structure, forming metal-semiconductor interfaces, and optimizing charge transfer. The strong metal-support interaction between Pr<sup>0</sup>/Pr<sup>3+</sup> and Pr/Pr<sub>2</sub>(SeO<sub>3</sub>)<sub>3</sub> accelerates carrier migration and increases active sites, while the unique 4f orbital of Pr enhances the adsorption and conversion of reaction intermediates. The optimal Pr/Pr<sub>2</sub>(SeO<sub>3</sub>)<sub>3</sub>-1 catalyst exhibits superior electrocatalytic performance with a low HER overpotential of 145 mV at 10 mA·cm<sup>-2</sup> and a GOR overpotential of 291 mV at 10 mA·cm<sup>-2</sup> in alkaline media. The two-electrode cell delivers a low cell voltage of 1.51 V at 10 mA·cm<sup>-2</sup> with excellent long-term stability. This study provides a reference for the use of variable-valence rare earth elements as catalysts in the indirect oxidation mechanism of nucleophilic reagents.

In another study, rare earth oxide CeO<sub>2</sub> is utilized to regulate the microreaction environment during the oxidation process of nucleophiles. Zhang et al. [161] fabricated Mg-doped NiOOH/CeO<sub>2</sub> heterojunction aerogels via a sol-gel method, in which rare earth Ce serves as a key electronic modulator and interfacial promoter to realize highly selective electrocatalytic glycerol oxidation to formate. Ce with partially filled 4f orbitals acts as an electron reservoir through reversible Ce<sup>3+</sup>/Ce<sup>4+</sup> redox, and forms Ni-O-Ce nanoheterointerfaces featuring 3d-2p-4f orbital hybridization with Ni sites, building a fast cross-interface electron transfer pathway to boost reaction kinetics. Mg doping further induces abundant oxygen vacancies in CeO<sub>2</sub>, optimizes adsorption energies of intermediates (\*OH and \*OOH), and stabilizes the defective structure. Such Ce-mediated interfacial effects precisely regulate glycerol adsorption configuration by selectively adsorbing C<sub>2</sub> hydroxyl groups and promoting selective C-C bond cleavage. The optimized catalyst delivers an outstanding formate Faradaic efficiency up to 95.7%. When coupled with HER for glycerol-assisted water electrolysis, the cell voltage is reduced to 1.64 V at 50 mA·cm<sup>-2</sup> (Figs. 12(g)-12(i)).

Since the oxidation reactions of most nucleophiles inevitably involve an indirect oxidation mechanism, which entails cyclic valence transitions of active elements. This leads to drastic structural alterations and reconstruction of catalysts during the oxidation of nucleophiles. Therefore, such catalysts often require more intrinsic modulation methods, which is why rare earth elements stand out prominently.

Rare earth elements are widely used in nucleophilic oxidation reactions. REEs play a crucial role in these reactions by acting as electronic modulators or active site components, optimizing the electronic structure of active sites, accelerating the cleavage of chemical bonds (e.g., C-N and C-O), and suppressing the poisoning of active sites by reaction intermediates (e.g., CO), thereby significantly improving the catalytic activity and stability of the catalysts.

It can be easily found from the above literature that rare earth elements mainly act as regulators to modulate the properties of variable-valence metal sites, such as Ni and Co. Some studies also

investigate variable-valence rare earth elements as active sites, which may represent one of the research directions worthy of attention and exploration in the future.

## 4 Conclusions and outlook

REEs rely on their unique 4f electronic configuration, tunable valence states, strong electronic modulation ability, and large atomic radius, and play important roles in various electrocatalytic reaction systems as electronic modulators, defect inducers, active site components, and structural stabilizers. The core regulatory mechanisms of rare earth elements in electrocatalysts include: optimizing the electronic structure and d-band center of active sites, adjusting the adsorption/desorption energy of reaction intermediates; inducing the formation of defects (oxygen vacancies, lattice defects) and active sites, increasing the number of catalytic active sites; stabilizing the high-valence active sites of transition metals, suppressing the dissolution and oxidation of active sites; constructing heterojunction structures, accelerating electron transfer and reaction kinetics, and suppressing competitive reactions, improving the product selectivity of target reactions.

In different electrocatalytic reaction systems, rare earth elements show targeted optimization effects. In water electrolysis, REEs balance the water dissociation energy and \*H adsorption energy (HER), and optimize the adsorption energy of oxygen-containing intermediates (OER). In CO<sub>2</sub>RR, REEs are the main applied rare earth elements, which realize the high-selectivity conversion of CO<sub>2</sub> to formic acid, CO, methane, and C<sub>2+</sub> products by regulating the adsorption of key intermediates and promoting C-C coupling. In ammonia synthesis reaction, REEs realize the high-efficiency conversion of nitrate/nitrogen to ammonia by providing H\* intermediates, activating N<sub>2</sub>/NO<sub>3</sub><sup>-</sup> molecules, and suppressing HER. In ORR, REEs which optimize the adsorption energy of ORR intermediates and realize the high activity of 4e<sup>-</sup>/2e<sup>-</sup> paths. In nucleophile oxidation reactions, REEs accelerate the cleavage of C-N/C-O bonds and suppress the poisoning of active sites by intermediates. The catalysts involved in the relevant references of Section 3.5 and their performances are shown in Table 6.

This review summarizes representative studies on the application of rare earth elements, excluding Pm and Ho, in the field of electrocatalysis. In these studies, rare earth elements primarily serve structural and electronic modulation roles. By leveraging their abundant outer electrons and large atomic sizes, the valence state ratios, band structures, and electron distributions of catalysts are optimized, while their microstructures are adjusted. This enables rare earth elements to be widely used in the preparation of catalysts for various electrocatalytic reactions. Based on this, the following summaries and prospects are proposed:

(1) In some studies, multiple rare earth elements can produce similar effects, allowing researchers to determine the optimal type and dosage of rare earth elements through extensive experimental screening. In some studies, researchers conduct controlled experiments with various rare earth elements to screen out the optimal doping elements. Similarly, multiple rare earth elements can deliver favorable performance in the same reactions. Rare earth elements within the same series share certain similarities in chemical properties. Nevertheless, it is undeniable that differences in their properties may lead to variations in performance. This issue has not been thoroughly discussed in the literature cited in this review, which merits further consideration and exploration by researchers.

Table 6 Summary of catalyst performances in Section 3.5

| References | Name                                                           | Catalyst    | Electrolyte                                      | Mass loading                                                                                     | Performance                                                                                                                                                                                                                                 | Commercial catalysts                                                                                                                                |
|------------|----------------------------------------------------------------|-------------|--------------------------------------------------|--------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------|
| [141]      | YNi-10                                                         | UOR         | 1.0 M KOH + 0.33 M urea                          | 1.5–1.7 mg·cm <sup>-2</sup>                                                                      | Current density = 127 mA·cm <sup>-2</sup> at 1.5 V; YNi-10  Pt/C: 10 mA·cm <sup>-2</sup> , steady for 22.2 h                                                                                                                                | UOR  HER: 18% energy-saved than RuO <sub>2</sub>                                                                                                    |
| [142]      | YRO-Sm                                                         | UOR         | 1.0 M KOH + 0.34 M urea                          | Three-electrode: 2 mg·cm <sup>-2</sup> ; urea-assisted ZAB system (U-ZAB): 1 mg·cm <sup>-2</sup> | At 100 mA·cm <sup>-2</sup> ; UOR: 1.43 V; overall: 1.65 V, 200 h, 5.8% overpotential increased                                                                                                                                              | RuO <sub>2</sub> : 1.60 V, 10 mA·cm <sup>-2</sup>                                                                                                   |
| [143]      | Ce, N-Ni(OH) <sub>2</sub>                                      | HER UOR     | 1.0 M KOH + 0.34 M urea                          | 5.8 mg·cm <sup>-2</sup>                                                                          | 100 mA·cm <sup>-2</sup> ; UOR: 1.39 V, 10 mA·cm <sup>-2</sup> ; overall: 1.49 V, 700 mA·cm <sup>-2</sup> , 70 h 2000 cycles                                                                                                                 | UOR: better than RuO <sub>2</sub> ; HER: not as good as Pt/C                                                                                        |
| [144]      | Ce-doped Ni <sub>3</sub> P <sub>4</sub>                        | UOR         | 1.0 M KOH + 0.35 M urea                          | 44.8 mg·cm <sup>-2</sup>                                                                         | 500 mA·cm <sup>-2</sup> ; UOR: 1.33 V; 1000 mA·cm <sup>-2</sup> ; overall: 8.8% current decrease after 60 h at 2.37 V                                                                                                                       | 500 mA·cm <sup>-2</sup> ; RuO <sub>2</sub> (1.51 V)                                                                                                 |
| [145]      | Ni <sub>0.2</sub> Mo <sub>0.8</sub> N/CeO <sub>2-0.3</sub> /NF | HER UOR     | 1.0 M KOH/1.0 M KOH + 0.33 M urea                | 0.8 mg·cm <sup>-2</sup>                                                                          | HER: -120 mV, UOR: 1.462 V, overall: 1.672 V, for 100 mA·cm <sup>-2</sup> , steady at 1.5 V overall, 24 h                                                                                                                                   | HER: Pt/C/NF, 100 mA·cm <sup>-2</sup> , 170 mV; UOR: IrO <sub>2</sub> /NF, 1.652 V, 100 mA·cm <sup>-2</sup>                                         |
| [146]      | VCe-FeCoNiP/NF                                                 | HER UOR     | 1.0 M KOH/1.0 M KOH + 0.33 M urea                | ~ 4 mg·cm <sup>-2</sup>                                                                          | HER: $\eta_{100}$ = 173 mV; UOR: 1.308/1.338 V for 10/100 mA·cm <sup>-2</sup> ; overall: 1.56 V, 20 mA·cm <sup>-2</sup> , steady for 225 h                                                                                                  | HER: Pt/C, $\eta_{100}$ = 164 mV; UOR: IrO <sub>2</sub> /NF, 100 mA·cm <sup>-2</sup> , 1.442 V                                                      |
| [147]      | Fe-(CeS <sub>2</sub> /Ni <sub>3</sub> S <sub>2</sub> )         | OER UOR EOR | 1.0 M KOH (+ 0.5 M urea/ 0.5 M EtOH)             | —                                                                                                | OER: $\eta_{100}/\eta_{500}$ = 238/372 mV; UOR/EOR: 1.36/1.32 V for 10 mA·cm <sup>-2</sup> , 30/30 h                                                                                                                                        | RuO <sub>2</sub> /NF: $\eta_{100}$ = 457 mV                                                                                                         |
| [148]      | CeO <sub>2</sub> -Ni <sub>0.85</sub> Se-550-NC                 | UOR MOR     | 1.0 M KOH + 0.5 M urea/ 0.5 M MeOH               | ~ 0.5 mg·cm <sup>-2</sup>                                                                        | UOR/MOR: 1.294/1.309 V for 10 mA·cm <sup>-2</sup> , 5/5 h                                                                                                                                                                                   | —                                                                                                                                                   |
| [149]      | Pt <sub>78</sub> La <sub>22</sub> /C                           | HER MOR     | 1 M KOH (+ 0.5 M MeOH)                           | —                                                                                                | HER: $\eta_{100}$ = 111 mV; 15,000 cycles CV, +31 mV; overall: 1.030 V for 20 mA·cm <sup>-2</sup> , 1.06 V, 15 h                                                                                                                            | Pt/C, HER: $\eta_{100}$ = 153 mV; MOR: 0.36 A·mg <sub>Pt</sub> <sup>-1</sup>                                                                        |
| [150]      | PtLa/XC-72                                                     | MOR         | 1.0 M KOH + 1.0 M MeOH                           | 0.04 mg/working electrode (WE)                                                                   | Specific activity = 205 mA·cm <sub>Pt</sub> <sup>-2</sup> ; mass activity = 17.50 A·mg <sub>Pt</sub> <sup>-1</sup> ; 76.5% retention of the initial current after 1000 CV cycles                                                            | PtRu/C: 5.62 A·mg <sub>Pt</sub> <sup>-1</sup> , 20 wt.%; Pt/C: 3.8 A·mg <sub>Pt</sub> <sup>-1</sup>                                                 |
| [151]      | Pt <sub>3</sub> Yb/C                                           | MOR         | 1.0 M KOH + 1.0 M MeOH                           | 0.04 mg·cm <sup>-2</sup>                                                                         | Specific activity = 35.28 mA·cm <sub>Pt</sub> <sup>-2</sup> ; mass activity = 11.61 A·mg <sub>Pt</sub> <sup>-1</sup> ; 96.0% retention of the initial current after 1000 CV cycles                                                          | Pt/C: mass activity = 2.10 A·mg <sub>Pt</sub> <sup>-1</sup>                                                                                         |
| [152]      | PdLa bimetallic                                                | EOR HER     | 1.0 M KOH (+ 1.0 M EtOH)                         | 0.5 mg·cm <sup>-2</sup>                                                                          | MOR: 2.46 A·mg <sub>Pd</sub> <sup>-1</sup> ; overall: 0.61 V, for 100 mA·cm <sup>-2</sup> ; EOR: 12 cycles; HER: 2000 CV cycles                                                                                                             | RuO <sub>2</sub> -Pt/C, overall: 100 mA·cm <sup>-2</sup> , cell voltage > 1.4 V                                                                     |
| [153]      | PdLa/C                                                         | MOR EOR     | 1.0 M KOH + 1.0 M MeOH/EtOH                      | —                                                                                                | MOR: 2.28 A·mg <sub>Pd</sub> <sup>-1</sup> ; 95.6% retention of the initial current after 4000 s potentiostatic test; EOR: 5.67 A·mg <sub>Pd</sub> <sup>-1</sup> ; 84.23% retention of the initial current after 4000 s potentiostatic test | Pd/C-JM, MOR: 0.19 A·mg <sub>Pd</sub> <sup>-1</sup> ; EOR: 2.46 A·mg <sub>Pd</sub> <sup>-1</sup>                                                    |
| [154]      | CoCrCe(7.5%)-LDH                                               | HMFOR       | 1.0 M KOH + 50 mM HMF                            | —                                                                                                | C: 99%; Y: 99%; FE = 100%, steady for over 10 cycles at 1.4 V vs RHE/10 h potentiostatic test/2000 CV cycles                                                                                                                                | —                                                                                                                                                   |
| [155]      | CC@NiFeCe(3%)-LDH                                              | HMFOR       | 1.0 M KOH + 50 mM HMF                            | —                                                                                                | C: 95.73%; Y: 93.31%; FE = 99.47%, steady for over 5 cycles or 2000 CV cycles                                                                                                                                                               | —                                                                                                                                                   |
| [156]      | NCCe5-R                                                        | HMFOR       | 1.0 M KOH + 10 mM HMF                            | —                                                                                                | C: 100%; Y: 99.5%; FE = 99.1%; > 98% retention of the initial performance over 15 consecutive runs                                                                                                                                          | —                                                                                                                                                   |
| [157]      | NiCe(10%)-MOF-CV                                               | HMFOR       | 1.0 M KOH + 50 mM HMF                            | —                                                                                                | C: 100%; Y: 98.6%; FE = 99.8%, steady for over 20 cycles or 6 days of potentiostatic testing                                                                                                                                                | —                                                                                                                                                   |
| [158]      | Ni(OH) <sub>2</sub> /CeVO <sub>4</sub> @NF                     | HMFOR       | 1.0 M KOH + 10 mM HMF                            | —                                                                                                | C: 100%; Y: 97.8%; FE = 97.6%, 9 cycles                                                                                                                                                                                                     | —                                                                                                                                                   |
| [159]      | Pd <sub>6</sub> Y <sub>4</sub> /rGO                            | HCOOH OR    | 0.5 M H <sub>2</sub> SO <sub>4</sub> + 1 M HCOOH | 0.077 mg <sub>Pt</sub> ·cm <sup>-2</sup>                                                         | Highest current density = 106.6 mA·cm <sup>-2</sup> ; 70% retention of the initial current after 5000 s at 0.4 V                                                                                                                            | Current density: of Pd <sub>6</sub> Y <sub>4</sub> /rGO is 4.9 times as that of Pd/C; mass activity: 4.82 times; $E_{on}$ = 110 mV, lower than Pd/C |
| [160]      | Pr/Pr <sub>2</sub> (SeO <sub>3</sub> ) <sub>3</sub>            | HER GOR     | 1.0 M KOH (+ 0.1 M glucose)                      | 1.41 mg·cm <sup>-2</sup>                                                                         | HER: $\eta_{10}$ = 145 mV; GOR: $\eta_{10}$ = 291 mV; 93.1% retention of the initial current after 40,000 s at 1.4 V                                                                                                                        | HER: Pt/C, $\eta_{10}$ = 142 mV; OER: RuO <sub>2</sub> , $\eta_{10}$ = 408 mV                                                                       |
| [161]      | Mg-doped NiOOH/CeO <sub>2</sub>                                | GOR         | 1.0 M KOH + 0.1 M glucose)                       | 2 mg·cm <sup>-2</sup>                                                                            | FE = 95.7%, GOR: 5% current decrease after 18 h at 1.49 V; HER: 24 h, 100 mA·cm <sup>-2</sup> ; GOR  HER: 50 mA·cm <sup>-2</sup> , 5% performance degradation after 15 h                                                                    | —                                                                                                                                                   |



(2) Precisely because rare earth elements play structural and electronic modulation roles, research on their application in electrocatalysis requires in-depth exploration of reaction mechanisms and microstructures. Advanced characterization techniques, such as *in situ* XAS, *in situ* Raman, and DFT calculations, have become essential tools to clarify the role of rare earth elements in catalysts, helping to reveal the structure–activity relationship and guide the rational design of catalysts.

(3) Greater emphasis should be placed on combining experiments with theory. In some studies, through *in situ* testing and theoretical modeling calculations, researchers have conducted thorough investigations into the role of rare earth elements in catalysts, providing a foundation for a more systematic understanding and screening of rare earth element-based catalysts. For instance, DFT calculations have confirmed that rare earth elements can adjust the d-band center of active sites, optimize the adsorption energy of intermediates, and reduce reaction energy barriers.

(4) The utilization efficiency of rare earth elements should also be considered. As elaborated earlier, there is a contradiction between the uneven global distribution of rare earth resources and their high demand. Currently, the prices of rare earth elements are lower than those of precious metals, and the mining and smelting technologies for some light rare earth elements in particular have become relatively mature. Nevertheless, the ultimate goal of applying rare earth elements in electrocatalysis is to realize industrial production. With the development of emerging markets and the transformation of energy structures, the environmental issues arising from rare earth mining and the supply of rare earth resources are all factors that have to be taken into account. Similar to precious metals, the future trend will involve more efficient and lower-density use of rare earth elements. The development of single-atom rare earth catalysts and the strategy of doping trace rare earth elements to achieve significant performance improvement have become effective ways to improve the utilization efficiency of rare earth elements, which is of great significance for reducing costs and promoting industrial applications.

(5) During the preparation of rare earth element electrocatalysts, attention should be paid to the retention of rare earth elements, especially in strongly acidic electrolyte systems. A typical example is the acidic oxygen evolution reaction. Targeted measures need to be adopted for different catalyst systems. Strategies, including lattice modulation, surface coating, electronic structure regulation, pre-leaching treatment, and high-entropy structure design, can effectively mitigate rare earth leaching of electrocatalysts.

(6) Attention should be paid to the large-scale preparation of rare earth electrocatalysts. Electrocatalysis based on rare earth elements has achieved extensive success in laboratory settings, and the catalysts exhibit excellent performance and stability. Nevertheless, rare earth-based electrocatalysts still face challenges in large-scale production. This requires researchers to focus on the scalability and transferability of catalyst preparation methods during their studies. In addition, considering supply chain, environmental, and cost factors, researchers should also pay more attention to the development of electrocatalysts based on light rare earth elements, so as to mitigate the environmental and economic impacts caused by the extensive use of heavy rare earth elements.

(7) It is advisable to actively integrate the design of rare earth electrocatalysts with machine learning. Combined with the shift rule of the d-band center, machine learning can efficiently guide

the targeted screening of rare earth elements. Research can build datasets based on first-principles calculations and experimental data, and extract key descriptors, such as the electronic structure, ionic radius, and redox properties of rare earths. The model can explore the internal correlation between features and d-band shifts to realize high-throughput prediction and rapid screening. Combined with DFT calculations and experimental verification to form a closed loop, the traditional trial-and-error cycle can be greatly shortened, providing strong support for the rational design of rare earth-based electrocatalysts.

Although issues, such as policies, markets, and environmental protection, still need to be considered to realize the industrial-scale preparation and application of rare earth electrocatalysts, rare earth electrocatalysis remains a vital strategy for the strategic transformation of human energy in the future. In the future, with more rational catalyst design, synthesis, and characterization methods, as well as more systematic summarization and screening, rare earth elements are expected to achieve broader and deeper applications in the field of electrocatalysis.

## Acknowledgements

This work was financially supported by the Natural Science Foundation of Liaoning Province (No. 2024-MSBA-11), Postdoctoral Fellowship of Heilongjiang Province (No. LBH-Z23156), Postdoctoral Fellowship Program of CPSF (No. GZC20233449), and the National Natural Science Foundation of China (No. 22278097).

## 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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