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Recent advances in lanthanide-based materials for oxygen evolution reaction: Challenges and future prospects

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ABSTRACT

Lanthanide-based materials have emerged as highly promising electrocatalysts for the oxygen evolution reaction (OER), a pivotal process in water splitting and energy conversion applications. These materials present a sustainable and cost-effective alternative to noble-metal catalysts, addressing critical challenges of scarcity and cost. Their exceptional catalytic activity and stability are attributed to unique electronic properties, including multiple oxidation states, large ionic radius, and strong spin-orbit coupling. Recent breakthroughs demonstrate significant enhancements in overpotential reduction and long-term stability under extreme electrochemical conditions, positioning lanthanides as a transformative solution for renewable energy systems. This review comprehensively explores various classes of lanthanide-based OER electrocatalysts, including transition metals, metal-organic frameworks (MOFs), perovskites, nanomaterials, and chalcogenides, nitrides, borides, and phosphides. Perovskites, in particular, have achieved remarkable stability and efficiency, underscoring their potential for realworld applications. Tailored strategies such as anionic substitution and heteroatom doping further optimize the electronic structure, active site stabilization, and charge transfer efficiency, driving significant performance improvements. Notably, recent studies report a substantial reduction in overpotential by up to 200 mV for lanthanide-based materials, along with significantly enhanced catalytic durability compared to conventional noble-metal catalysts. Key challenges remain, such as improving electrical conductivity, scalability, and performance longevity. Strategic integration of lanthanides into catalytic frameworks addresses these limitations while reducing reliance on scarce resources. These advancements enable lanthanide-based OER electrocatalysts to revolutionize renewable energy technologies and drive the commercialization of efficient water-splitting and electrochemical processes.

1. Introduction

The two primary challenges facing industrialized society, which are critical to the global economy and social sustainability, are energy and the environment [1]. Globally, over 80 % of primary energy consumption comes from traditional energy sources, such as natural gas, coal, and petroleum, which are non-renewable and environmentally damaging [2–4]. The International Energy Agency (IEA) has emphasized the need to redirect investment away from fossil fuels towards cleaner

energy technologies in order to achieve net zero emissions by 2050 [5]. Moreover, the depletion of limited fossil fuel resources and the climate change associated with energy production and consumption are raising global concerns about the sustainability of energy sources and supply [6,7]. As a result, scientists are exploring alternative methods for generating clean, renewable energy to replace fossil fuels [3,8]. Among these, hydrogen an efficient and environmentally friendly energy carrier can be formed using various methods, including photocatalysis, natural energy, fossil fuels, biomass, and electrocatalysis [9–12]. Thus, the

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Fig. 1. Summary of lanthanide-based materials for OER.

development of a green, cost-effective, and efficient hydrogen production method is essential [13].

Electrolytic water splitting is a favored approach for hydrogen production due to its efficiency, operational simplicity, and ease of recovery, although it remains energy-intensive and faces significant kinetic barriers and overpotentials [14,15]. The efficiency of electrolysis can be improved by the use of catalysts. Water splitting consists of two key reactions: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), with the OER being particularly critical due to its involvement in a complex four-electron process. Developing electrocatalysts with lower overpotentials and improved durability is essential to enhancing OER efficiency. Historically, noble metal electrocatalysts have been employed in water splitting due to their high activity in OER [16,17]. Composites based on noble metals, such as ruthenium (Ru) and iridium (Ir), are the most efficient commercial electrocatalysts for OER, due to their negligible overpotential and superior kinetics [18,19]. However, the poor stability, scarcity, and high cost of these rare metalbased composites pose significant challenges to the large-scale adoption of OER technologies [20,21]. Thus, developing inexpensive, abundant, and highly efficient electrocatalysts for OER is crucial.

In recent years, lanthanides have attracted considerable attention due to their unique physical and chemical properties, which stem from their 4f shell electronic structures [22,23]. Their ability to exhibit multiple coordination numbers and distinctive 4f subshell orbital characteristics makes them valuable for modifying the electronic structures of transition metal-based catalysts [24,25]. The variable valence states of lanthanides facilitate the formation of oxygen vacancies, making these materials effective for electrocatalysis. Lanthanide metal oxides are widely used in oxidation reactions, such as methane (CH₄) and carbon monoxide (CO) oxidation, where the adsorption, activation, transfer, and dissociation of oxygen molecules are critical similar to the oxygen evolution process [26,27]. In the 1970s, LaNi5 became the first lanthanide metal electrocatalyst used in the hydrogen evolution reaction [28]. Since then, lanthanide metals have been extensively studied in electrochemistry, particularly in OER. Their ability to create oxygen vacancies and engage in complex redox processes makes them attractive



Fig. 2. Proposed mechanisms for OER. (a) Acidic AEM, (b) Alkaline AEM, (c) Acidic LOM, and (d) Alkaline LOM.

for improving the efficiency and stability of OER electrocatalysts. Lanthanides regulate the adsorption energy of intermediates, lower the energy barriers controlling reaction rates, and enhance electron transfer in electrocatalytic processes, owing to their strong affinity for oxygen. Additionally, the substantial differences in atomic radius and electronegativity between lanthanide elements and transition metals give lanthanides unique abilities to modulate the electronic structure of catalysts.

For instance, Xia et al. successfully regulated and utilized 4f electrons in lanthanide elements by constructing an electron/ion transport interface composed of copper, ultrathin cerium oxide, and iron chromium nickel hydroxide (Cu@CeO₂@NFC) [29]. The study demonstrated that the inclusion of lanthanide elements enriched the electron distribution near the Fermi level and created a fast *d*-*f* electron transfer pathway for adsorbed species. This indicates that the constructed lanthanide 4f orbital ladder can effectively regulate the adsorption of reaction intermediates. These properties make lanthanides essential or auxiliary metals in electrocatalytic OER. As research in this field continues to progress, a comprehensive review of electrocatalytic OER in energy conversion is timely and valuable. While some reviews have focused on cerium-based catalysts [30,31], our article broadens the scope to include a wider range of lanthanides, offering a more comprehensive understanding of their potential in enhancing OER performance. Currently, no review integrates the various aspects of lanthanide-based catalysts or provides a detailed summary of the critical roles that lanthanides play in these catalysts. This article consolidates recent research efforts and experimental data aimed at improving the activity and stability of lanthanide-based materials in OER, comparing their performance to highlight advancements in the field.

In this review, we focus on recent developments and breakthroughs in both experimental as well as theoretical achievements and underlying mechanisms of electrocatalysts for OER. We begin by introducing the fundamental mechanisms of OER, which serve as a foundation for understanding the catalytic process. Following this, we explore the synthesis strategies and microstructural analysis of lanthanide-based materials (Fig. 1). The catalytic activity and stability of these lanthanide-based materials are critically examined as key factors for OER performance. Additionally, we highlight ongoing challenges and unresolved issues in the field, offering potential research directions to enhance catalytic performance and material design. Finally, we provide recommendations for future studies aimed at improving the design and efficacy of OER catalysts. By consolidating experimental and theoretical advancements, this review seeks to guide future research efforts and foster innovative approaches for the development of high-performance OER electrocatalysts.

2. Fundamentals

The fundamentals and applications of electrocatalysis are closely intertwined, bridging the gap between physical electrochemistry and engineering, and fostering knowledge exchange between industry and academia [32]. Electrocatalytic water splitting is driven by an electric current at the electrode, where charge transfer converts electrical energy into chemical energy. During this process, water is converted into oxygen (O₂) at the anode and hydrogen (protons) at the cathode [33]. Minimizing overpotential is essential for facilitating electrochemical reactions, and this can be achieved through the use of suitable electrocatalysts. Unlike hydrocarbon reforming or cracking, water splitting is considered a simpler, more cost-effective, and environmentally friendly method for hydrogen production. This electrochemical process, which transforms water into gaseous hydrogen and oxygen, is heavily dependent on electrocatalysis. Direct water splitting into hydrogen and oxygen represents a promising technology for hydrogen production. Despite hydrogen's long-standing industrial applications, there remains considerable potential for advancements in water splitting, including improvements in selectivity and stability through the use of electrocatalysts. The four fundamental reactions in electrocatalytic hydrogen evolution, oxygen evolution, oxygen reduction, and chlorine evolution



Fig. 3. Schematic representation of OER mechanisms: (a) AEM, highlighting the sequential steps of adsorption, oxidation, and association of intermediates at the electrolyte-catalyst interface, (b) LOM, depicting the role of lattice oxygen, surface vacancies, and gas-phase oxygen during bulk and surface reactions and (c) illustration of the LOM lattice framework, highlighting oxygen diffusion, vacancy formation, and lattice oxygen replenishment in the catalyst structure.

are historically the most significant [34]. The principles of electrocatalysis in water splitting are rooted in the kinetics and thermodynamics of the reactions occurring at the electrode surface. The OER is pivotal to water splitting, rechargeable metal-air batteries, and other energy conversion technologies. At the anode, this process oxidizes water (H₂O) to produce oxygen gas (O₂), while releasing protons (H⁺) and electrons (e⁻). The OER is kinetically slow due to its complex fourelectron transfer mechanism, which limits the efficiency of energy conversion systems. Two distinct mechanisms underpin the OER: the lattice-oxygen-mediated mechanism (LOM) and the traditional adsorbate evolution mechanism (AEM) [35]. A thorough understanding of these mechanisms and the ability to manipulate the reaction pathways can enable the intrinsic control of catalyst activity. This section focuses on both acidic and alkaline mechanisms and provides a comparative analysis.

2.1. OER Mechanism

The OER typically proceeds via two pathways: the AEM and LOM [36]. The AEM is widely recognized as the standard OER mechanism, characterized by its scaling relationship among reaction intermediates [37]. According to the Sabatier principle, the binding strength of intermediates on the catalyst surface affects the reaction overpotential [38]. While the AEM's scaling relationship enables rapid screening of catalysts, OER activity remains limited. Experimental and theoretical studies on reaction mechanisms and catalyst activity parameters suggest that lattice oxygen, associated with the LOM, may play a key role in improving OER performance [39]. The LOM overcomes the limitations of the AEM by showing that the active sites are not the metal centers themselves. In the LOM, bulk lattice oxygen directly participates in the evolution of intermediate oxygen species and the formation of oxygen [40]. Thus, electrocatalysts operating via the LOM are not constrained by the scaling relationship and frequently demonstrate exceptional performance. The AEM and LOM mechanisms are further explained in detail below.

2.1.1. AEM Mechanism

It is well-established that a catalyst's theoretical OER overpotential is governed by the *Sabatier* principle, which relates to the oxygen adsorption energy on the catalyst surface. An ideal catalyst should interact with intermediates at an optimal strength neither too strong nor too weak while simultaneously minimizing the overpotential as much as possible. The primary source of oxygen in the AEM comes from adsorbed water molecules, and there are scaling correlations among the adsorption energies of oxygenated intermediate species [41,42]. Based on active metal sites, four cooperative proton-electron transfer processes are typically involved in the AEM [43]. As shown in Fig. 2a for acidic AEM, a one-electron oxidation process results in the adsorption of a water molecule onto the metal site, forming an *OH intermediate. This *OH is then converted into an *O species through proton coupling and electron elimination. In the next step, *O reacts with another water molecule to form an O—O bond, yielding *OOH. Finally, a one-electron transfer oxidizes *OOH, releasing O₂ and regenerating the original metal active site.

In the alkaline AEM, hydroxide (OH⁻) reacts with the active sites (* + OH⁻ \rightarrow *OH + e⁻, where * represents the active sites). Initially, OH⁻ is adsorbed onto the coordination-unsaturated metal site, leading to the formation of *OH after electron loss. De-protonation of *OH then results in electron transfer and the formation of *O (*OH + OH⁻ \rightarrow *O + H₂O + e⁻). In the next step, OH⁻ from the electrolyte interacts with *O to facilitate O–O bond formation, generating the intermediate *OOH through another electron transfer (*O + OH⁻ \rightarrow *OOH + e⁻). Finally, de-protonation of *OOH results in O₂ evolution via the reaction *OOH \rightarrow * + O₂(g) + e⁻ + H⁺ (Fig. 2b).

2.1.2. LOM Mechanism

The OER in the AEM is constrained by a scaling relationship among intermediates, which limits the theoretical overpotential to 0.37 V. To overcome this limitation, various strategies have been employed to stabilize *OOH while maintaining the adsorption of *OH. However, recent challenges to this traditional process have led to the introduction of the LOM, which diverges from the conventional approach. The initial stages of acidic LOM, involving the generation of *O, are similar to those in acidic AEM. However, in LOM, an oxygen vacancy forms in the lattice as *O bonds with lattice oxygen, leading to the release of an oxygen molecule. Finally, the migration of OH⁻ from the solution can fill the resulting vacancy (Fig. 2c) [44]. This mechanism circumvents the scaling relationship between *OH and *OOH, as *OOH does not form during the LOM cycle. Additionally, since the oxygen within the catalyst lattice serves as the intermediate, extensive surface coverage of reaction intermediates is unnecessary.

In the alkaline LOM, OH^- groups are initially adsorbed as they fill oxygen vacancies. The adsorbed OH^- groups undergo deprotonation, resulting in the formation of highly electronegative O^{2-} species without electron transfer. The negatively charged O^{2-} is then oxidized to O^- by eliminating electrons from its orbitals. Next, two neighboring O^- atoms hybridize their non-bonding states, facilitating O—O coupling without electron transfer, followed by the release of an oxygen molecule (O_2) through further electron extraction from the oxygen orbitals (Fig. 2d).

The AEM and LOM mechanisms differ fundamentally in several key respects. In AEM, O—O bond formation occurs through the attack of OH⁻ from the electrolyte on adsorbed *O, leading to the production of *OOH. In contrast, LOM achieves O—O coupling by hybridizing the non-bonding states of adjacent lattice oxygen atoms. Moreover, AEM relies on metal redox chemistry, where metal sites serve as active sites for electron transfer, occurring within the lower-Hubbard bands (LHB) and involving adsorbed oxygen-containing intermediates. Conversely, LOM is characterized by an oxygen redox process, with oxygen sites functioning states of oxygen and the reaction intermediates, fundamentally altering the pathway of the OER [45]. The comparison of both AEM and LOM mechanisms is provided in detail below.

2.2. Comparison of AEM and LOM Mechanisms

The AEM is a widely recognized mechanism in the OER. In this mechanism, the formation and transformation of oxygen-containing intermediates adsorbed on the catalyst surface are central to the OER process. The AEM involves a series of proton-coupled electron transfer (PCET) steps, leading to the generation of molecular oxygen [39]. In the first step of AEM mechanism hydroxide adsorption, a hydroxide ion (OH⁻) from the alkaline electrolyte adsorbs onto an active site (M) on the catalyst surface, forming an intermediate metal-hydroxide (M-OH) (Fig. 3a) [46]. The active site is typically a transition metal or metal oxide site, such as Fe, Ni, or Co centers in oxides like Fe₂O₄ or Co₃O₄. This step is energetically favorable due to the strong affinity of OH⁻ ions for these active sites, facilitating the adsorption process. In the second step, the adsorbed hydroxide intermediate (M-OH) undergoes PCET, releasing a proton (H⁺) and an electron (e⁻), resulting in the formation of a highly reactive metal-oxo species (M-O) [47,48]. This process is a crucial step in the OER, as the metal-oxo species serves as a critical intermediate. The electron is transferred to the electrode under an applied potential, while the proton diffuses into the electrolyte. This step, typically the first oxidation in the sequence, requires sufficient energy from the applied voltage to overcome the reaction barrier. In the third step, a hydroxide ion (OH⁻) from the electrolyte interacts with the metal-oxo species (M-O) to form a metal-peroxide intermediate (M-OOH). This process involves a nucleophilic attack by OH⁻ on the metaloxo group, resulting in the formation of a peroxide linkage (O-O) [49,50]. The creation of this bond is a pivotal step in the OER, as it prepares the system for the eventual release of molecular oxygen. The electronic properties of the catalyst play a critical role in facilitating this step by stabilizing the M-OOH intermediate. In the final step, the metalperoxide intermediate (M-OOH) undergoes further oxidation, leading to the release of molecular oxygen (O_2) and the regeneration of the catalyst active site (M). This step involves the breaking of the O-O bond in M-OOH, producing O₂ gas, which desorbs from the surface and is released into the environment [51,52]. The regenerated catalyst site (M) becomes available to participate in subsequent cycles of the OER. Additionally, the electrons produced in this step are transferred to the electrode, contributing to the overall current in the electrochemical process.

The LOM is an advanced pathway for the OER, which is a vital process in energy conversion and storage systems like water splitting and metal-air batteries. Unlike the traditional AEM, where oxygen evolution occurs solely through the adsorption and desorption of reactants on catalyst surfaces, LOM contains the direct participation of lattice oxygen (O^{2-}) in the reaction [53]. In the first step of the LOM, lattice oxygen ions (O^{2-}) at the catalyst surface are oxidized, releasing oxygen gas (O_2) and creating vacancies in the lattice (Figs. 3b-c). This oxidation process disrupts the O-M bonds, where M represents the metal in the lattice. The evolution of oxygen gas occurs at the active site,

Table 1

Comparison table summarizing the differences between the AEM and LOM mechanisms, along with their relevance to industrial OER electrocatalysis.

Characteristic	AEM	LOM
Basic mechanism	Involves adsorption, transformation, and desorption of intermediates such as OH ⁻ and OOH ⁻ on electrocatalyst surface.	Utilizes lattice oxygen (O ^{2–}) directly in oxygen evolution.
Key step	PCET converts the metal- hydroxide intermediate (M- OH) into highly reactive metal-oxo species M-O)	Oxidation of lattice $O^{2-} \rightarrow$ Vacancy formation \rightarrow Bulk oxygen diffusion \rightarrow Lattice regeneration.
Electrocatalysts examples	Transition metal oxide such as, NiO, Fe_2O_4 , Co_3O_4 etc.	High ionic conductive materials such as, perovskites (LaNiO ₃ and SrCoO ₃).
Reaction kinetics	Slowed by the *OH and *OOH scaling relationship.	Faster due to bypassing scaling limitations via lattice oxygen involvement.
Energy requirements	The theoretical minimum overpotential is 0.37 V.	Potentially lower overpotential due to lattice oxygen redox.
Stability	High stability under moderate current densities but prone to degradation at high currents.	Lower stability due to formation of vacancies, risking structural degradation over time.
Electrocatalyst design	Predictable, following the <i>Sabatier principle</i> ; easier to model and optimize.	Complex, requiring strategies to stabilize oxygen vacancies and maintain lattice integrity.
Industrial feasibility	Suitable for scalable industrial applications requiring durability and reliability.	Promising for high-efficiency applications but requires advanced materials engineering.
Efficiency	Limited by scaling relationships, which restrict efficiency gains.	Higher intrinsic activity, ideal for cutting-edge, low- overpotential applications.
Challenges	Durability issues under high current densities; theoretical overpotential limitation.	Catalyst degradation due to vacancy accumulation; complex optimization of lattice properties.
Application	Applications requiring robust and predictable performance (e.g., electrolysis in alkaline media).	Innovative applications prioritizing efficiency, such as advanced water splitting systems.
Industrial impact	Established for commercial water electrolyzers due to ease of scalability and robustness.	Emerging in niche industries aiming for maximum efficiency, especially under low-energy input.

leaving behind an oxygen-deficient lattice [54]. This step is driven by the applied electrochemical potential, which facilitates the oxidation and subsequent release of O2. In the second step, lattice oxygen ions (O^{2-}) are oxidized, leading to the release of oxygen gas (O_2) and the formation of oxygen vacancies in the lattice. This process involves the breaking of O-M bonds, where M represents a metal within the lattice structure, such as Fe, Co, or Ni. Protons (H⁺) and electrons (e⁻) may also participate, depending on the specific reaction conditions, contributing to the overall redox process [55]. This step is crucial for sustaining the reaction cycle by creating reactive sites for subsequent processes. In the third step, lattice oxygen ions (O^{2-}) from the bulk diffuse to the surface to replenish the oxygen that was oxidized and released as O2. This diffusion process is essential for maintaining the reactivity of the catalyst, ensuring a continuous supply of oxygen atoms for further reactions [48,56]. Catalysts with high ionic conductivity, such as perovskites, facilitate this step effectively. This step highlights the importance of oxygen ion mobility in sustaining the catalytic cycle and overall efficiency of the OER. In the final step, the oxygen vacancies created earlier are regenerated as water (H₂O) reacts with the catalyst. This reaction restores the lattice oxygen network by incorporating oxygen ions (O^{2-}) into the structure, while simultaneously releasing protons (H⁺) and electrons (e⁻) [57–59]. These protons and electrons are further utilized



Fig. 4. The schematic diagram of the fabrication method for NiSe₂-Ce₂(CO₃)₂O. (b) SEM, (c) TEM, (d) HR-TEM, and (e) EDS mapping of NiSe₂-Ce₂(CO₃)₂O. Reproduced with permission from ref [63]. Copyright Elsevier Ltd 2024.

in the electrochemical reaction, maintaining the catalytic cycle. This step is essential for ensuring the stability and longevity of the catalyst, enabling sustained catalytic activity throughout the reaction process.

Both AEM and LOM offer distinct advantages and challenges in OER electrocatalysis. The AEM, which follows the Sabatier principle, provides predictability, making it easier to model and tune catalysts [60]. This mechanism benefits from well-established catalyst design principles. However, the intrinsic scaling relationship between the *OH and *OOH intermediates impose a 0.37 V theoretical minimum overpotential in AEM, thereby limiting the potential for efficiency improvements. Additionally, AEM dependence on metal sites can reduce catalyst durability at high current densities [61]. On the other hand, LOM, by circumventing the scaling relationship and directly utilizing lattice oxygen, can significantly lower the overpotential, leading to catalysts with greater intrinsic activity and lower energy requirements. However, LOM complexity poses challenges, as the involvement of lattice oxygen results in the development of oxygen vacancies and potential catalyst degradation over time (Table 1). As a result, optimizing and developing LOMbased catalysts is more difficult due to their unconventional nature. The choice between AEM and LOM largely depends on the specific application. AEM, being more predictable and easier to work with, is suitable for scenarios that require stability and reliability. In contrast, LOM may be more appropriate for applications where minimizing overpotential is critical, although this comes at the potential cost of catalyst stability and lifespan. Therefore, LOM is often considered for cutting-edge applications that prioritize catalytic efficiency over durability. Both mechanisms have distinct roles in industrial OER electrocatalysis. While AEM is the backbone of current hydrogen production technologies, LOM holds the key to future innovations in high-efficiency, low-overpotential applications. Advances in material science and a deeper understanding of lattice dynamics are critical for bridging the gap among lab-scale promise and industrial-scale deployment for LOM-based catalysts. A deeper understanding and optimization of both mechanisms could lead to the progress of more durable and effective OER electrocatalysts in the future.

3. Fabrication methods and microstructural analysis of lanthanide-based materials

Lanthanide-based materials are synthesized using various methods, each offering distinct advantages that influence the composition, structure, and performance of the electrocatalysts. The preparation technique critically impacts the chemical as well as physical properties of these materials, including crystallinity, particle size, surface area, and active site availability, all of which are vital for the efficacy and stability of the OER activity. Research indicates that lanthanide-based materials are becoming increasingly important for sustainable energy solutions. This section examines different fabrication methods and their microstructural analysis, highlighting their advantages and limitations.

3.1. Hydrothermal method

Hydrothermal synthesis crystallizes materials from aqueous solutions under elevated temperature and pressure in a sealed autoclave. This technique provides precise control over crystal growth, ensures phase purity, and facilitates the formation of nanostructures, thereby enhancing the catalytic efficiency of lanthanide-based materials [62]. For instance, our group developed a NiSe₂-Ce₂(CO₃)₂O heterojunction homogeneously grown on carbon cloth (CC) as a self-supported electrode for highly efficient OER. This electrode was fabricated using a straightforward two-step hydrothermal method (Fig. 4a). The NiSe2-Ce₂(CO₃)₂O exhibits a rice-granular structure, with protuberant nanoparticles securely anchored to the CC, enhancing its stability (Fig. 4b). Transmission electron microscopy (TEM) images support the scanning electron microscopy (SEM) findings, confirming the rice-granular morphology of NiSe₂-Ce₂(CO₃)₂O (Fig. 4c). High-resolution TEM (HR-TEM) images (Fig. 4d) further confirm that the NiSe₂-Ce₂(CO₃)₂O heterostructure was successfully prepared, showing distinct lattice fringes corresponding to the cubic NiSe₂ (200) plane, orthorhombic NiSe₂ (020) plane, and $Ce_2(CO_3)_2O$ (011) plane with interplanar distances of 0.298 nm, 0.308 nm, and 0.576 nm, respectively. High-angle annular darkfield scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) elemental mapping images (Fig. 4e) demonstrate that Ni, Ce, Se, O, and C are uniformly dispersed



Fig. 5. (a) The schematic diagram of the fabrication process for Co-CeO₂/C aerogels. (b) SEM, (c) TEM, and (d-e) HR-TEM images of Co-CeO₂/C aerogels. (f) HAADF-STEM and elemental mapping images of Co-CeO₂/C aerogels. Reproduced with permission from Ref. [68]. Copyright 2022 Royal Society of Chemistry.

throughout the heterostructure [63].

Similarly, *Alharbi et al.* synthesized Er_2O_3 -NiO nanocomposites using the hydrothermal method, which revealed a nanoflake-like morphology [64]. *Liao et al.* utilized a one-step hydrothermal process to form 2D Gddecorated CeO₂/Ce(OH)CO₃ nanohybrids, pioneering their use as stable as well as effective catalysts for OER activity [65]. The resulting CeO₂/ Ce(OH)CO₃ displayed a nanoflower structure composed of nanosheets. TEM analysis revealed that the prepared nanohybrid featured a homogeneous nanosheet structures. The uniform grain attachment and morphological changes suggest that Gd plays a pivotal role in controlling crystal growth. Furthermore, *Hussain et al.* fabricated a Samariumdoped SnFe₂O₄ electrocatalyst to improve OER activity. The incorporation of Sm ions into the lattice significantly altered the morphology of SnFe₂O₄, resulting in less dense, well-shaped nanoparticles that formed interconnected structures, which greatly improved OER performance [66].

These examples demonstrate the versatility of the hydrothermal method in fabricating lanthanide-based materials with optimized microstructures for enhanced OER performance. However, the method's reliance on high temperatures and pressures, along with its relatively long processing times, can be seen as limitations that may affect scalability and cost-effectiveness in large-scale applications.

3.2. Sol-gel method

The sol-gel technique includes via metal salts and metal ester precursors that are combined with various organic ligands and reacted at controlled temperatures for the formation of a gel. This gel is then processed through calcination and drying to produce oxide materials. In the synthesis of lanthanide-based materials, metal nitrates are commonly used as precursors, along with ligands such as polyvinylpyrrolidone (PVP) and citrate. The sol-gel method facilitates homogeneous doping of various elements under relatively mild reaction conditions, making it particularly effective for synthesizing multicomponent lanthanide-based materials. The resulting products typically exhibit high-surface area, thereby advantageous for catalytic applications [67].

In another study, Liu et al. prepared a new of Co-CeO2 heteronanoparticles (NPs) uniformly dispersed within three dimension (3D) porous carbon aerogels (Co-CeO2/C). The Co-CeO2/C aerogels were produced via the sol-gel technique by polymerizing chitosan, CeCl₃, as well as K₃Co(CN)₆, followed by freeze-drying and pyrolysis (Fig. 5a). The resulting Co-CeO₂/C aerogels displayed a porous three-dimensional nanostructure composed of nanoparticles and interconnected carbon (Fig. 5b). TEM images (Fig. 5c) confirmed the SEM findings, showing a uniform distribution of Co and CeO2 nanoparticles throughout the carbon matrix with minimal aggregation. A histogram of particle diameters indicated that the Co and CeO2 nanoparticles were relatively small, ranging from 6 to 12 nm, as measured from 100 nanoparticles in random regions (inset of Fig. 5c). The nonappearance of isolated particles in the TEM recommends effective interactions between the chitosan and metal ions. HR-TEM magnification (Fig. 5d, marked by orange grid lines) showed two types of grating boundaries: one with a spacing of 0.309 nm, matching to the (111) plane of the fcc phase of CeO_2 , and the other with a spacing of 0.205 nm, corresponding to the (111) plane of the fcc phase of Co (Fig. 5e). Furthermore, Fig. 5f shows the HAADF-STEM with elemental mappings, revealing that Ce, O, C, and Co are uniformly distributed in the aerogels [68].

In another example, *Munawar* et al. used the sol-gel process to synthesize Nd-doped CeO₂ (CeNdO₂) nanostructures co-doped with lanthanide metals [69]. The synthesized material exhibited a contiguous paternoster-like structure. *Huang* et al. applied the sol-gel process to investigate the electrocatalytic properties of 214-type encapsulated crystalline oxide LnSrCoO₄ (where Ln stands for La, Pr, Sm, Eu, or Ga), which demonstrated semiconductor-like activity. Among these, PrSrCoO₄ exhibited a slightly smaller particle size but formed irregular,



Fig. 6. (a) The schematic diagram of synthesis process, (b) crystal structure of CeO₂ (c-d) SEM and (e-f) TEM images of 2 % Gd doped CeO₂ nanostructures. Reproduce with permission from ref. [71]. Copyright Elsevier Ltd. 2024.

small bulk structures prone to aggregation [70].

The sol-gel method offers several advantages, including the capability to control the composition as well as structure at the nanoscales, producing materials with high surface area and homogeneous doping. However, it also has some limitations, such as the tendency for particle aggregation in some systems and the need for subsequent hightemperature treatments to achieve crystallization, which can lead to sintering and loss of surface area. Despite these challenges, the sol-gel method remains a versatile as well as extensively used technique for fabrications of lanthanide-based materials.

3.3. Co-precipitate method

Co-precipitation is another extensively used approach for preparing lanthanide-based materials. This approach contains precipitating metal ions from a solution, often resulting in the simultaneous deposition of multiple components. However, the equilibrium transition during coprecipitation can lead to the formation of impurities or contaminants. The efficiency of the precipitation reaction depends on several aspects, like temperature, pH, dielectric constant, as well as other reaction conditions. Despite these challenges, co-precipitation is valued for its low reaction temperature and ease of operation, making it an effective method for producing large quantities of catalysts. Consistent agitation during synthesis is essential to ensure the homogeneity of the final products.

In a study by *Swathi* and colleagues, Gd-doped CeO₂ was prepared using a simple co-precipitation approach (Fig. 6a). Fig. 6b illustrates the cubic crystal structure of CeO₂. The SEM images (Figs. 6c-d) reveal a uniform dispersal of spherical nanoparticles on the surface. The incorporation of Gd ions into the CeO₂ crystal lattice caused slight morphological distortions, with feather-like structures emerging due to the doping. TEM images (Figs. 6e-f) further illustrate the well-dispersed, agglomerated crystallite particles with a spherical shape. The Gd dopant was crucial for promoting crystal formation, enhancing the material's structure [71].

Yu et al., synthesized RuO₂ supported on CeO₂ using a coprecipitation method. EDS analysis demonstrated a uniform distribution of Ru as well as Ce along the scanning line, indicating the even dispersion of RuO₂ particles on the CeO₂ support. Interestingly, smaller grains were observed surrounding the CeO₂ particles, which contrasted with the TEM images of pure defective CeO₂, highlighting the role of RuO₂ in modifying the morphology [72]. Similarly, *Kutlusoy* et al., prepared La-based perovskites using the co-precipitation method. The resulting particles displayed an isometric shape, without a preferred surface orientation, indicating that the synthesis process allowed for random crystallographic growth [73].

The co-precipitation method is both simple and scalable, rendering it a perfect choice for the large-scale production of electrocatalysts. Nevertheless, the process requires careful control of reaction conditions to avoid contamination and ensure homogeneous product formation. Additionally, optimizing variables such as temperature, pH, and stirring rates is critical to achieving consistent results.

3.4. Method of MOFs pyrolysis

MOFs are widely utilized in the development and production of earth-abundant metal electrocatalysts due to their ability to serve as carbon skeletons and sources of heteroatoms, which enhance the protection of active metal sites and improve charge transport. MOFs offer adjustable composition, high porosity, and large specific surface areas, making them ideal precursors for electrocatalyst production. Pyrolysis of MOFs facilitates the production of lanthanide-based materials incorporating carbon and heteroatoms, which can be combined with additional metal catalysts. Preserving the large surface area of MOF-derived materials while forming porous oxide structures during pyrolysis requires careful control of the conditions to maximize catalyst



Fig. 7. (a) Fabrication process, (b) SEM of CoCe@ZIF-8, and (c) Co/Ce@NC. (d) TEM and (e) HR-TEM of Co/Ce@NC. (f-k) HAADF and elemental mapping of Co/Ce@NC. Reproduced with permission from Ref. [74]. Copyright © 2024, American Chemical Society.

performance and atomic efficiency.

For example, *Wu* et al. prepared an electrocatalyst featuring atomic distributions of Ce and Co on a NC substrate via incorporating the lanthanide element Ce and Co into a MOF precursor. The preparation process for Co/Ce@NC is shown in Fig. 7a. Initially, ZIF-8 is synthesized by adding a calculated amount of $Zn^{2+/}Ce^{3+}$ to a solution containing 2methyl imidazole as an organic ligand, resulting in a white precipitate. After continuous stirring, a Co²⁺ ion solution is added dropwise, producing a purple solution and forming ZIF-8 doped with Co^{2+}/Ce^{3+} . This mixture is stirred for 24 h, followed by centrifugation, washing, and drying. The Co²⁺/Ce³⁺-doped ZIF-8 precursor is then carbonized at 1000 °C in an argon atmosphere, yielding the Co/Ce@NC catalyst. As presented in Figs. 6b-c, the SEM image of Fig. 7b representing the CoCe@ZIF-8 precursor shows a well-defined regular dodecahedral structure, which is comparable to the structure of the ZIF-8 precursor. As illustrated in Fig. 7c, the hollow polyhedra collapsed and formed porous structures after carbonization. Furthermore, CNTs were formed and protruded from the surface of Co/Ce@NC catalyst. The development of CNTs is further verified through the TEM (Fig. 7d), which shows that the carbon scaffolds and CNTs are interconnected to form a threedimensional structure. In the HR-TEM image of Co/Ce@NC (Fig. 7e), distinct Co nanoparticle lattice fringes with interlayer distances of 0.2, 0.18, and 0.125 nm, which is corresponding to the (111), (200), and (220) planes of Co metal. Additionally, the 0.34 nm separation match the (002) plane of graphitic carbon. Figs. 7f-k presents the HAADF images along with the corresponding EDS mapping of Co/Ce@NC. The EDS maps reveal that Co, Ce, N, and C are uniformly distributed in the carbon matrix. The energy spectrum reveals that Co and Ce are positioned in

close proximity, and their distribution appears scattered. Additionally, the images indicate that both Co and Ce exist predominantly in a singleatom form [74].

In another example, *Zhang* et al. developed a new acetylene black (AB)-supported La_2O_3 -Co/AB electrocatalyst, derived from a La-doped ZIF-67 via a composite synthesis approach. The pyrolysis product was stabilized by La_2O_3 , and the coordination between lanthanum as well as cobalt prevented the formation of La-ZIF-67 crystals, enhancing the contact of active sites thus improving catalytic performance [75].

Additionally, *Munawar* et al., used pyrolysis and hydrothermal approaches to produce Nd₂O₃@C and V₂O₅@C materials derived from MOFs. The internal structure of the V₂O₅@C nanocomposite was characterized by the embedding of V₂O₅ nanoparticles within amorphous carbon layers, which served as a bridge connecting the V₂O₅ nanoparticles. After pyrolysis, the nanocomposite exhibited irregular spherical nanoparticles, highlighting the structural transformation and carbonization effects [76].

MOF pyrolysis provides multiple benefits, such as generating porous materials high-surface area as well as incorporating heteroatoms to enhance the catalytic properties of the resulting materials. However, careful control of pyrolysis conditions is necessary to preserve the structural integrity and optimize the performance of the catalysts. By fine-tuning these parameters, MOF-derived materials can achieve excellent performance in the field of OER.

3.5. Microwave method

The microwave technique has gained popularity as a rapid, efficient,



Fig. 8. (a) The schematic diagram of the preparation process. Defect models of (b) intrinsic CeO₂, (c) Fe/CeO₂–400, (d) Fe/CeO₂–500, and (e) Fe/CeO₂–600. SEM of, (f) CeO₂, (g) Fe/CeO₂–400, (h) Fe/CeO₂–500, and (i) Fe/CeO₂–600. TEM images of (j-k) Fe/CeO₂–400, (l-m) Fe/CeO₂–500, (n-o) Fe/CeO₂–600. Reproduced with permission from ref. [77]. Copyright Elsevier Ltd. 2022.

and highly controllable method for synthesizing lanthanide-based materials, particularly for applications in OER electrocatalysis. This method uses microwave radiation to uniformly heat reactants, significantly reducing reaction times and energy consumption compared to conventional methods. Microwave synthesis is an attractive approach for tailoring nanostructured catalysts because as it facilitates accurate manipulation of the size, morphology, and defect formation of the resultant materials.

Furthermore, *Zhang* et al. used microwave approach to fabricate a defect-rich OER catalyst, Fe/CeO₂–400, with oxygen vacancies (O_v), calcined at 400 °C. The process used K₃[Fe(C₂O₄)₃]·3H₂O as both the iron and C₂O₄^{2–} sources, resulting in Fe-doped cerium oxalate within 30 min (Fig. 8a). Furthermore, defect models (containing O_v defects) of CeO₂, Fe/CeO₂–400, Fe/CeO₂–500, and Fe/CeO₂–600 (Figs. 8b-e). SEM images revealed the flake-like structure of the calcined materials (Figs. 8f–i). When the calcination temperature increase, the size of the nanosheets (NSs) steadily decrease from 100 µm in the precursors to 2 µm in Fe/CeO₂–600. TEM images of Fe/CeO₂–400, Fe/CeO₂–500, and Fe/CeO₂–500, and Fe/CeO₂–600 (Fig. 8j, l, and n, respectively) supported the SEM findings, showing that size reduction occurred with increasing temperature. Additionally, Fig. 8k, m, and o revealed microscopic dumps on the NSs, indicating that calcination at high temperature disrupted the basal plane, leading to defect formation [77].

Using microwave-assisted hydrothermal methods, *Kashinath and Byrappa* synthesized highly crystalline hexagonal CeO₂ nanoparticles on the multilayer surface of nitrogen-doped graphene oxide (NGO). This technique enhances the formation of high-density active sites on CeO₂@NGO composites while reducing the presence of oxygen

structures in ultrafine Ce—O particles, thus improving the composites' charge transfer capabilities. Microstructural analysis revealed that the wrinkled or distorted sheets were decorated with nanoparticles, and nitrogen doping led to twisted sheets, increasing their surface area [78].

Xian et al. developed a microwave shock technique that enables the rapid one-step preparation of two-dimension porous $Gd_{0.8}Sr_{0.2}FeO_3$ (GSFO) perovskite. This method uses a transiently adjustable highenergy microwave shock heating and cooling process to replace Sr at the GdFeO₃ A-site and create a 2D porous morphology. The resulting GSFO-0.2 nanosheets, with transverse dimensions of up to 10 μ m, exhibited a curly and flexible structure, demonstrating exceptional homogeneity. Microstructural analysis indicated that the lattice streaks of GFO and GSFO-0.2 had spacings of 2.81 Å and 2.85 Å, individually, corresponding to the (020) planes. The incorporation of Sr expanded the lattice spacing of GSFO-0.2 due to crystal distortion, and the Sr cations improved structural adaptability and functionality via electronic interactions. [79].

The microwave method offers several advantages, including rapid synthesis, reduced energy consumption, and precise control over material properties. However, the high-energy input and rapid heating/ cooling cycles can introduce defects, which may either enhance or degrade the performance of the catalyst depending on the application. With continued optimization, microwave-assisted synthesis holds great promise for producing high-performance lanthanide-based materials catalysts for OER and other electrocatalytic applications.



Fig. 9. (a) Illustration of the preparation process of CeO_2 -CoO nanofibers. SEM and TEM images of (b-c) 10 % CeO_2 -Co₃O₄ NFs and (d-e) 10 % CeO_2 -CoO NFs. (f) TEM image of 10 % CeO_2 -CoO NFs. (g) HR-TEM image of 10 % CeO_2 -CoO nanofibers (inset: large magnification of the HRTEM image). (h) HAADF-STEM image and (i-k) the corresponding EDX elemental mappings of O, Co, and Ce of 10 % CeO_2 -CoO NFs. Reproduced with permission from ref. [81]. Copyright © 2021, American Chemical Society. (l) Fabrication diagram of PNC electrocatalyst on graphite. (m) TEM of PNC and inset demonstrate the SEM image of PNC along with the size distribution of Pt and CeO_2 nanoparticles. (n) HR-TEM image of PNC. Reproduced with permission from ref. [83]. Creative Commons Attribution License 4.0 (CC BY 4.0). Copyright © 2020 Linghang Wang et al. Exclusive licensee Science and Technology Review Publishing House.

3.6. Other methods

Electrospinning is a simple yet powerful technique for producing nanofibers using a high-voltage electric field. Over the decades, it has evolved significantly, especially with the advancement of nanotechnology in the 1990s, becoming a key method for fabricating onedimensional (1D) nanomaterials [80]. Electrospinning creates ultrathin fibers with porosity and through high surface area applying high voltage to a polymer solution containing lanthanide precursors. The characteristics of porosity and high surface area are critical for growing the contact of active sites, further enhances the electrocatalytic performance of lanthanide materials in oxygen evolution reactions (OER). Moreover, electrospun nanofibers improve ion and electron transport, which is crucial for OER performance. For instance, Zhao, et al. developed a novel nanofibrous hybrid structure using electrospinning, calcination, and reduction techniques to combine CeO2/CoO surfaces into an excellent performance of OER. The synthesis of CeO2-CoO nanofibers (NFs) involved three key steps: electrospinning a precursor solution including PVP, ethanol, DMF, Co(NO3)2, and Ce(NO3)3, followed through calcination at 550 °C under air flow to prepare CeO₂-Co₃O₄ nanofibers (Figs. 9a-c). The resulting CeO2-CoO nanofibers exhibited a rough surface with diameters ranging from 95 to 135 nm (Figs. 9d-e), ascribed to the decomposition of Co₃O₄ and carbon during the two-step calcination approach. The magnified TEM image in Fig. 9f of the CeO₂-CoO nanofibers reveals a coarse surface that enhances the exposure of active sites, facilitating better interact with electrolytes throughout the catalytic process. Furthermore, HR-TEM indicates well-defined crystalline phases of CeO₂/CoO, verifying the effective integration of these two materials (Fig. 9g). Additionally, a unique interface is observed, in parallel to the (111) surface of CeO₂ and forms an angle of approximately 35° with the (111) surface of CoO. This interfacial structure is believed to contribute to the formation of additional active site, thereby boosting catalytic performance. Furthermore, HAADF-STEM and EDX indicate a even distribution of Ce, Co, and O, suggesting the homogeneous development of CeO2/CoO within the nanofibrous structures (Figs. 9h-k) [81].

Table 2

Comparison of various methods with their advantages and disadvantages.

Fabrication Method	Suitability for OER	Advantages	Disadvantages	Scalability and industrial relevance
Hydrothermal	High-performance, well-defined, pure materials.	Excellent control over size/ morphology, high purity, scalable.	High cost, long reaction time, high temp/pressure.	Scalable; suitable for industries needing pure, crystalline materials.
Sol-gel	Thin films/coatings with large surface area but require modification.	High surface area, homogeneous materials, versatile.	Limited scalability, long processing, post-heat required.	Suited for lab/small industrial scale; scalability improvements needed.
Co-precipitate	Bulk materials with uniform composition; needs extra treatments for optimization.	Fast, simple, cost-effective, uniform composition.	Difficult size/morphology control, agglomeration risk.	Scalable for bulk production; needs control for high-performance use.
MOFs Pyrolysis	High-surface-area catalysts with active metal sites via MOF pyrolysis.	High activity, dispersed nanoparticles, versatile precursors.	Complex optimization, high temp, potential by-products.	Promising for high-value catalysts; requires MOF/pyrolysis advancements.
Microwave	Quick synthesis with improved characteristics; scalability limited.	Energy-efficient, rapid synthesis, small uniform particles.	High cost, non-uniform heating, scalability issues.	Limited scalability; suited for prototyping/niche applications.
Electrospinning	Nanofiber-based materials with high surface area and active sites.	High porosity, controlled nanofiber diameters.	Small-scale, limited to fibers, precise control needed.	Specialized applications; scalability improvements required.
Electrodeposit- ion	Thin films/coatings with excellent material property control.	High purity, substrate adhesion, precise composition.	Ineffective for bulk materials, requires conductive substrates.	Highly scalable for thin films; ideal for targeted high-performance OER.

Electrodeposition is another promising method, offering several advantages, including precise control over the size and quantity of deposits through the modification of plating parameters such as electrolyte concentration, voltage, and deposition time. This method provides a rapid, efficient approach for producing uniformly distributed electrocatalysts without requiring capping agents or reductants. Moreover, it operates under ambient conditions and is highly scalable. Electrodeposition also allows for regulated, patterned, and faceted crystallization of nanostructures, making it an ideal method for advanced material development [82].

Liu et al. utilized electrodeposition to prepared ultrafine Pt NPs decorated on Ni(OH)₂/CeO₂ nanosheet. This process involved a two-step cathodic electrodeposition procedure (Fig. 91). First, a graphite substrate was positively charged to insert nitrate ions into the graphite layers, improving the interface between the electrocatalyst as well as the substrate. Then, the potential was inverted to facilitate the cathodic coelectrodeposition of CeO2 and Ni(OH)2 onto the graphite. Pt nanoparticles were subsequently deposited onto the Ni(OH)2/CeO2 nanosheets to form the PNC hybrid electrode. This approach reduced Pt loading while maximizing Pt exposure, thereby enhancing its utilization. TEM images (Fig. 9m) revealed a uniform distribution of Pt nanoparticles over the hydroxide substrate, with an average size of 3.1 nm, smaller than those in Pt nanoparticles (3.4 nm) as well as Pt graphite (13.2 nm). High-resolution TEM (HR-TEM) analysis indicated lattice spacings of 0.314 nm and 0.227 nm, conforming the (111) plane of fcc CeO₂ and Pt, respectively (Fig. 9n) [83].

Both electrospinning and electrodeposition offer unique advantages for the fabrication of nanostructured electrocatalysts (Table 2). Electrospinning excels at producing high-surface-area nanofibers with enhanced ion and electron transport, while electrodeposition provides precise control over nanostructure formation, allowing for optimized catalyst design and performance. These methods, combined with others, offer significant potential for driving progress in the field of OER electrocatalysis.

4. Critical role of lanthanide-based materials for enhancing OER performance

Lanthanide-based materials have attracted significant interest for their ability to improve OER activity, a critical step in water splitting. The unique electronic structure of lanthanides, characterized by partially filled 4*f* orbitals, allows them to stabilize multiple oxidation states and interact effectively with oxygen species. These properties are vital for improving the efficiency as well as durability of OER electrocatalysts. Additionally, the broad ionic radii and high coordination numbers of lanthanides facilitate their incorporation into various material matrices, allowing for fine-tuning of the electronic configuration near active sites. This versatility enables the creation of hybrid materials that combine the strengths of lanthanides with other elements, improving catalytic activity and stability under operational conditions. Lanthanide-based materials also exhibit high thermal and chemical resilience, making them ideal for harsh OER environments, particularly at high temperatures and in corrosive media. Advanced synthesis methods allow for the incorporation of lanthanides at the nanoscale, optimizing the distribution of active sites and improving catalytic efficacy. By integrating lanthanides into catalytic frameworks, researchers have enhanced OER catalyst activity, selectivity, and durability, bringing these materials closer to practical applications in renewable energy. This section explores the role of lanthanide-based materials, including transition metals, MOFs, perovskites, nanomaterials, and other compounds including chalcogenides, nitrides, borides, and phosphides, advancing OER performance in alkaline and in acidic media.

4.1. Lanthanide-based transition metal

Recent studies have focused on developing earth-abundant metal catalysts have potential to match the competence of noble metals while using inexpensive and abundant materials. Transition metals catalysts are seen as promising for its alternatives because of their low overpotential and remarkable stability [84,85]. Transition metals (TMs) are classified by their valence electronic configuration in the d-orbitals, and their interaction with oxygen-containing species facilitates electron transport at the catalyst surface. However, challenges such as poor conductivity, limited accessibility to active sites, and high activation energy barriers hinder the performance of TMs catalyst. Numerous approaches have been employed to modify their optimize intermediate adsorption/desorption, electronic structures, and improve electron transfer, but most approaches that focus on a single aspect have yet to meet the criteria for high-performance OER catalysts [86]. The introduction of lanthanides, such as cerium (Ce), into transition metal-based catalysts has proven beneficial in enhancing OER performance. Ce, known for its outstanding redox features, crystal stability, and electronic/ionic conductivity, can significantly improve the OER activity of transition metals by altering their microstructure and electronic states [87,88]. For example, our group synthesized a NiSe₂-Ce₂(CO₃)₂O heterostructure using a hydrothermal method. This structure demonstrated enhanced OER performance, with NiSe2-Ce2(CO3)2O requiring only 268 mV to reach 50 mA cm⁻², outclassing other catalysts. Furthermore, corresponding Tafel slope was lowest as 86.2 mV dec^{-1} , demonstrating improved OER kinetics (Figs. 10a-b). Additionally, the electrochemical C_{dl} value was 2.2 mF cm⁻², further confirming the superior performance of prepared material. This heterostructure also showed stable



Fig. 10. (a) LSV curves, (b) corresponding Tafel slopes, (c) C_{dl} plots, (d) CP at 50 mA cm⁻² (the inset shows the contact angle measurements for both catalysts), and (e) illustration of the OER mechanism for NiSe-Ce₂(CO₃)₂O. (f) Simulated oxygen production rate and (g) surface tension of oxygen bubbles on the anodic NiSe₂-Ce₂(CO₃)₂O. (h) Potentials and current density of the electrolyte and (i) Current density distribution contour map for NiSe₂-Ce₂(CO₃)₂O. (j) DOS plots of NiOOH and NiOOH/Ce₂(CO₃)₂O. (k) Gibbs free energy profiles for NiOOH and NiOOH/Ce₂(CO₃)₂O. Reproduced with permission from ref. [63]. Copyright Elsevier Ltd. 2024. (l) LSV curves and, (m) Tafel slope of SnFe₂O₄ and Sm-doped SnFe₂O₄ catalysts. (n) C_{dl} of Sm-doped SnFe₂O₄ catalysts. (o) Chronoamperometry test of Sm-doped SnFe₂O₄ catalysts. Reproduced with permission from ref. [66]. Copyright Elsevier Ltd. 2024. (p) LSV polarization curves and (q) Tafel slopes of Co₄N@CeO₂/NF, Co₄N/NF, CCH@CeO₂/NF, and CCH/NF. (r-s) Bode plots at different potentials in 1 M KOH. Atomic structure models for (t.i-ii) Co₄N and (t.iii-iv) Co₄N @ CeO₂. (u) Charge density difference profile at the Co₄N@CeO₂/NF interface. (v) TDOS of Co₄N/NF and Co₄N@CeO₂/NF. (w) Free energy change during the OER process. Reproduced with permission from ref. [89]. Copyright Elsevier Ltd. 2024.

performance over 120 h with no detectable decline in activity at 50 mA cm⁻² (Figs. 10c-d). Enhanced hydrophilicity, as demonstrated by the reduced contact angle of 16.4°, improved electrolyte wettability and transport, further is boosting OER performance (Figs. 10e-f). Incorporating lanthanides like Ce into catalytic structures optimizes the electronic environment and improves the adsorption of OER intermediates, resulting better electrocatalytic efficiency. For instance, computational studies revealed that NiOOH/Ce₂(CO₃)₂O exhibited a lower Gibbs free energy for the rate-determining step (RDS) of *O to *OOH transformation (1.41 eV) compared to NiOOH (1.88 eV), confirming that the incorporation of Ce₂(CO₃)₂O significantly improves the electronic structure and catalytic activity of the material (Figs. 10f-i). The density of states (DOS) analysis revealed increased electron density close to the Fermi level, signifying improved electrical conductivity as a result of Ce incorporation (Figs. 10j-k) [63].

Lanthanide-based transition metal catalysts can be broadly classified into two categories based on how the lanthanide metal is integrated into the catalyst, doping into the crystal structure of the transition metal catalyst or incorporating the lanthanide metal or its oxide to form a composite. These two strategies lead to distinct structural and electronic properties, which, in turn, influence the catalytic performance in reactions such as the OER. Doping involves introducing lanthanide ions directly into the crystal lattice of a transition metal catalyst. This substitution modifies the electronic structure and can enhance properties like electrical conductivity and catalytic activity. For instance, Hussain et al. synthesized a samarium (Sm)-doped SnFe2O4 electrocatalyst via a hydrothermal method, which demonstrated enhanced OER performance. At 10 mA cm⁻² the overpotential was reduced to 179 mV for Smdoped SnFe₂O₄, compared to 239 mV for undoped SnFe₂O₄ (Fig. 10l). The corresponding Tafel slope of was 32 mV dec⁻¹ for Sm-doped SnFe₂O₄ indicated excellent reaction kinetics outperforming other prepared electrocatalysts (Fig. 10m). The Sm-doped catalyst also exhibited a higher C_{dl} of 4.46 mF cm⁻², demonstrating its improved surface area and stability over 50 h of operation (Figs. 10n-o) [66]. The Sm-doped SnFe₂O₄ catalyst incorporates Sm directly into the crystal structure of SnFe₂O₄, which modifies the electronic structure of the prepared electrocatalyst. This alteration leads to enhanced conductivity, increased surface area, and faster reaction kinetics. The lowest overpotential as well as Tafel slope observed for the Sm-doped catalyst indicate its improved efficiency and faster electron transfer during OER. The catalyst also demonstrated high stability of continuous operation, suggesting that doping with Sm not only improves catalytic performance but also enhances the durability of the catalyst.

Another strategy is combining lanthanide metals or their oxides with transition metal catalysts to form heterostructures. The components interact at the interface, leading to synergistic effects that enhance catalytic performance. For example, Zhou et al. successfully synthesized a Co₄N@CeO₂ heterostructure supported by nickel foam (NF/Co₄N@-CeO₂) using a hydrothermal-impregnation-nitridation process. In the Co₄N@CeO₂ system, CeO₂ functions as an "electron pump", effectively drawing electrons from Co₄N and facilitating charge redistribution at the heterointerface. This modification facilitated the catalyst to attain 10 mA cm⁻² with a lower overpotential of 263 mV for OER in alkaline media (Fig. 10p). Similarly, NF/Co₄N@CeO₂ shows the fastest OER kinetics, with the lowest Tafel slopes of $60.9 \,\mathrm{mV} \,\mathrm{dec}^{-1}$ compare to other prepared catalysts (Fig. 10q). The operando EIS measurements were conducted on Co₄N/NF and Co₄N@CeO₂/NF to investigate the effect of CeO₂ on electrode-electrolyte interactions during OER. As the potential reaches $1.5 \, V_{\text{RHE}}$, the phase angle in the low frequency area of Bode plots (Figs. 10r-s) indicates charge transfer at the electrode-electrolyte interface. OER onset occurs between 1.45 and 1.50 V_{RHE} , consistent with both NF/Co₄N and NF/Co₄N@CeO₂ onset potentials. When the potential range is 1.50 to 1.60 $V_{\text{RHE}}, \text{NF/Co}_4\text{N} @\,\text{CeO}_2$ exhibits a lower peak phase angle than NF/Co₄N, indicating that CeO₂ enhances charge transfer during OER. The reaction mechanism was investigated in detail using DFT calculations. The optimized structural models of Co₄N and

Co₄N@CeO₂ are shown in Figs. 10t-(i-iv), respectively. Further differential charge densities were calculated to analyze the electronic interactions at the Co₄N@CeO₂ heterointerface. As depicted in Fig. 10u, electrons are clustered on the CeO₂ side of the interface, confirming electron transfer from Co₄N to CeO₂. The DOS of Co₄N and Co₄N@CeO₂ are shown in Fig. 10v, reveal continuous electronic states across the Fermi level, representing metal-like electron transport characteristics. Notably, Co₄N@CeO₂ exhibits a higher number of electronic states at the Fermi level compared to Co₄N, highlighting that the introduction of CeO₂ significantly improves the electronic conductivity of the electrocatalyst. Fig. 10w reveals that for U = 0 V, Co₄N@CeO₂ has a lower OH⁻ adsorption barrier of 0.93 eV than Co₄N (0.97 eV), suggesting a more suitable heterointerface for OH⁻ adsorption. After adding CeO₂, the OER RDS on Co₄N shifts from *OOH production with a barrier of 1.69eV to O₂ formation with a reduced barrier of 1.53 eV. Thus, theoretically proves that the Co₄N@CeO₂ heterointerface development facilitates the OER process [89]. The Co₄N@CeO₂ composite catalyst works through the synergistic interaction between Co₄N and CeO₂, where CeO₂ functions as an electron pump to enable electron transfer among two components. This composite approach improves the electronic conductivity of the catalyst and improves charge transfer during the OER process. The operando EIS and DFT studies revealed that CeO2 not only accelerates charge transfer at the electrode-electrolyte interface but also lowers the OH⁻ adsorption barrier, making it more effective at the OER potentialdetermining step. The combination of fast reaction kinetics and increased catalytic efficiency makes the Co₄N @ CeO₂ composite catalyst a promising material for OER applications.

Incorporating lanthanide elements into transition metal catalysts can be achieved through doping or composite formation, each offering distinct advantages and challenges. Doping involves substituting lanthanide ions into the crystal lattice of the host catalyst, which can enhance electronic conductivity and modify the electronic structure to improve catalytic activity. However, this method is often constrained by the limited solubility of dopants and the potential introduction of defects that may adversely affect performance. On the other hand, composite formation entails physically combining lanthanide compounds with transition metal catalysts to create heterostructures. This approach leverages synergistic interactions between the components, potentially leading to enhanced catalytic properties and the ability to fine-tune characteristics by adjusting component ratios. Nevertheless, challenges such as achieving uniform distribution, ensuring strong interfacial interactions, and preventing phase separation over time can complicate the synthesis and stability of these composites. Therefore, the selection between doping and composite formation should consider factors such as the desired electronic properties, structural stability, and the specific operational conditions of the OER electrocatalytic application.

In another study, Wang et al. developed ternary NiFeM (M: La, Mo) electrocatalysts along with asymmetrical M-NiFe units to optimize dorbital and electronic structures for enhanced OER activity. The introduction of La improved *d*-orbital and O 2*p* hybridization, strengthening oxygen intermediate adsorption and lowering the RDS energy barrier. The 5d-La incorporation NiFeLa catalyst displayed an lower overpotential of 190 mV at 10 mA $\rm cm^{-2}$ and demonstrated long stability at 100 mA cm^{-2} for 600 h in alkaline media [90]. Lanthanide-based materials offer unique advantages in OER electrocatalysis, including enhanced redox features, high thermal and chemical resilience, and the ability to optimize the electronic environment around active sites. By incorporating lanthanides into transition metal-based catalysts, researchers can significantly improve the performance of OER catalysts, making them more efficient and durable for practical applications in renewable energy systems. Through advanced synthesis techniques and careful tuning of material properties, lanthanide-based materials are poised to play a vital role in the future of energy conversion technologies.

Most OER catalysts exhibit inferior activity and stability in acidic media compared to alkaline media, with even noble metals like RuO₂



Fig. 11. (a) *iR*-corrected CV curves and (b) Tafel plots for both catalysts. (c) ECSA-normalized CV curves with the inset showing J_{ECSA-normalized} at 450 mV overpotential. (d) Co K-edge XANES spectra showing absorption edge shifts after OER testing. (e) Average Co oxidation states and I_{oct}/I_{tet} ratios. (f) k^3 -weighted Co K-edge EXAFS Fourier transforms before and after OER. (g) Schematic bonding changes in Co₃O₄ and electronic modifications in Co₃O₄/CeO₂ post-OER. Reproduced from ref. [91]. (CC BY 4.0), Nature Portfolio 2021. (h) LSV curves, (i) Tafel plots, and (j) fitted plots showing the C_{dl} values for 4 % Er-Co₃O₄, ErCoO₃, and Co₃O₄. (f) Chronopotentiograms of 4 % Er-Co₃O₄ and Co₃O₄ at 10 mA cm⁻². (l) Calculated 1D surface Pourbaix diagram. (m) Calculated 2D surface Pourbaix diagram. (n) Microkinetic volcano model for OER. Reproduced from ref. [92]. (CC BY 4.0), American Chemical Society @ 2024.

and IrO2 facing dissolution issues. The activity-stability tradeoff in acidic OER complicates catalyst design, limiting the availability of earthabundant, highly efficient catalysts, though cobalt-based materials show promise. However, mechanistic insights for these emerging catalysts in acidic conditions remain scarce. For example, Huang et al. developed a Co₃O₄/CeO₂ nanocomposites directly on fluorine-doped tin oxide (FTO) electrodes by electrodeposition, where nanocrystalline CeO2 modifies the redox properties of Co₃O₄, enhancing its intrinsic OER activity in acidic conditions. Co₃O₄/CeO₂ effectively regulates the redox properties of Co₃O₄, significantly enhancing its acidic OER performance. The Co₃O4/CeO₂ catalyst with 10 at.% Ce exhibited an 84-mV reduction in overpotential (423 \pm 8 mV vs. 507 \pm 5 mV for Co₃O₄) at 10 mA cm⁻² and a lower Tafel slope of 88.1 mV dec^{-1} , indicating faster OER kinetics (Figs. 11a-b). The introduction of CeO₂ eliminates charge accumulation, leading to improved catalytic efficiency compared to pure Co₃O₄. After normalizing the catalytic current density by the ECSA derived from C_{dl}, Co₃O₄/CeO₂ exhibited a significantly lower OER onset potential and a higher ECSA-normalized catalytic current density of 23.7 µA cm⁻² at 450 mV overpotential, double that of Co₃O₄ (Fig. 11c). These results confirm that Co₃O₄/CeO₂ has enhanced intrinsic OER activity in acidic media compared to Co₃O₄. The Co K-edge X-ray absorption near-edge spectra revealed that Co₃O₄/CeO₂ exhibited a slightly higher Co oxidation state than Co₃O₄ before OER testing, with both catalysts reaching similar higher oxidation states after testing. The average Co oxidation states were calculated to be 2.43 and 2.54 for as-synthesized Co₃O₄ and Co₃O₄/CeO₂, respectively, and increased to 2.63 and 2.64 after OER testing (Figs. 11d-e). This indicates that while CeO₂ slightly altered the Co oxidation state, this difference did not persist after OER, suggesting that the distinct electrochemical properties of Co₃O₄/CeO₂ cannot be solely attributed to the Co oxidation state change. Besides the higher Co oxidation state, significant changes in the local bonding environment of Co₃O₄ were induced by CeO₂, as revealed by extended Xray absorption fine structure (EXAFS) analysis. Fourier transforms of k³weighted Co K-edge EXAFS spectra for both Co₃O₄ and Co₃O₄/CeO₂ catalysts displayed three major signals associated with the Co-O, Co-

Cooct (octahedral site), and Co-Cotet (tetrahedral site) scattering paths. Compared to the as-synthesized Co₃O₄, a shorter Co-O bond distance was observed in Co₃O₄/CeO₂, likely due to the higher positive charge density at the Co centers after electron redistribution from Co₃O₄ to CeO₂. This redistribution leads to a higher Co oxidation state in $Co_3O_4/$ CeO2, which facilitates the OER process. After OER testing, the bond distances in Co3O4/CeO2 remained unchanged, as indicated by the identical intensity ratio of Co-Co_{oct} and Co-Co_{tet} scattering paths before and after the reaction, suggesting that the crystal structure of Co₃O₄/ CeO₂ remained stable during OER. In contrast, Co₃O₄ exhibited distinct changes in bonding distances after OER testing, including shortening of the Co-O and Co-Co_{tet} bonds and elongation of the Co-Co_{oct} bond. These changes are reflected in the altered intensity ratio of Co-Co_{oct} to Co-Co_{tet} (I_{oct}/I_{tet}), which increased from 1.44 to 1.52 after OER testing, indicating that the crystal structure of Co₃O₄ underwent dynamic changes during the reaction (Figs. 11f-g). These structural modifications in Co₃O₄ may be related to the formation of active structural motifs, similar to those observed in OER reactions in alkaline or neutral media, suggesting that CeO2-induced structural stability in Co3O4/CeO2 contributes to its enhanced OER performance [91].

Pan et al. proposed a strategy to enhance the catalytic activity and stability of Co_3O_4 for acidic OER through Er doping, demonstrating that 4 % Er-doped Co_3O_4 exhibited an overpotential of 321 mV at 10 mA cm⁻² (Fig. 11 h). As shown in Fig. 11i, the 4 % Er- Co_3O_4 electrocatalyst exhibited a lower Tafel slope of 75.9 mV dec⁻¹ compared to Co_3O_4 (102.5 mV dec⁻¹) and ErCoO₃ (159 mV dec⁻¹), indicating superior reaction kinetics for the 4 % Er- Co_3O_4 . In terms of ECSA, 4 % Er- Co_3O_4 demonstrated the highest double-layer capacitance (C_{dl}) of 511.8 mF cm⁻² (Fig. 11j), significantly outperforming Co_3O_4 (372.3 mF cm⁻²) and ErCoO₃ (3.2 mF cm⁻²), suggesting greater exposure of catalytic active sites. The CP curve in Fig. 11 k further illustrates the excellent stability of 4 % Er- Co_3O_4 , showing only a slight increase of 92.5 mV in overpotential after 250 h of operation. Notably, the voltage increase rate was just 0.37 mV/h, indicating remarkable durability in acidic electrolytes, with no significant loss in catalytic performance. This is consistent with

the high Faradaic efficiency of 98.43 %. In contrast, Co₃O₄ showed significant deactivation after only 50 h (Fig. 11 k). The surface Pourbaix diagram was used to determine the most thermodynamically stable state of Co₃O₄ (311). Figs. 111-m present the 1D and 2D surface Pourbaix diagrams of Co₃O₄ (311) under experimental conditions. The 11/12 ML O* coverage was identified as the lowest-energy configuration under OER operating conditions, indicating that this coverage on Co₃O₄ (311) is the most favorable surface configuration for OER, compared to the pristine Co₃O₄ (311). Further theoretical investigations were conducted on the Er-doped Co₃O₄ (311) with 11/12 ML O* coverage to assess its OER performance. Ab initio molecular dynamics (AIMD) simulations showed that Er-doped Co₃O₄ maintains high stability without significant structural deformation. To better understand the enhanced OER activity of Er-doped Co₃O₄, advanced microkinetic volcano modeling was employed to analyze the OER activity as a function of GO-GHO, considering both the kinetics and thermodynamics of the essential OER steps. The OER activities of Er-doped Co₃O₄ (311), along with other highperformance OER catalysts, were predicted by the volcano model at 10 mA cm^{-2} (Fig. 11n). The results suggest that introducing a small amount of Er into Co₃O₄ (311) significantly enhances the OER activity of the surface [92]. The strategic doping of Er into Co_3O_4 significantly improves its catalytic activity, stability, and durability for acidic OER, demonstrating its potential as an effective and long-lasting electrocatalyst for water-splitting applications.

Lanthanide-based transition metal catalysts have shown tremendous promise for improving the OER in both alkaline and acidic media, offering enhanced performance and stability. In alkaline media, lanthanides play a pivotal role in enhancing the electronic structure and conductivity of catalysts, facilitating faster reaction kinetics and lowering overpotentials. Their ability to increase ionic conductivity, promote the formation of oxygen vacancies, and optimize the adsorption of reaction intermediates are key factors contributing to their enhanced catalytic efficiency. Additionally, lanthanide incorporation stabilizes catalytic structures, ensuring long-term durability under harsh operating conditions. These advantages make lanthanide-based materials excellent candidates for large-scale, sustainable energy conversion technologies, particularly in alkaline water splitting applications.

In acidic media, lanthanides continue to exhibit transformative effects by addressing the challenges of poor stability and high dissolution rates that typically limit many OER catalysts in such environments. Lanthanides enhance the redox properties and local bonding environment of transition metal catalysts, improving their resistance to degradation. This modification leads to a more favorable electron transfer process, reduced activation energy barriers, and accelerated reaction kinetics, resulting in higher catalytic activity. By preventing charge accumulation and mitigating the dissolution of catalysts, lanthanide incorporation ensures a more stable and efficient OER performance in acidic conditions, where noble metals like RuO₂ and IrO₂ often face issues of degradation. This makes lanthanide-based catalysts highly promising for OER in acidic electrolytes, further advancing the potential of water-splitting technologies.

Overall, lanthanides, play a crucial role in enhancing the efficiency and stability of OER catalysts in both alkaline and acidic media. In alkaline conditions, they improve conductivity, oxygen vacancy formation, and intermediate adsorption, leading to better catalytic performance and durability. In acidic conditions, lanthanides help stabilize the catalyst, enhance electron transfer, and reduce activation energy barriers, ensuring a more efficient and stable OER process. By modifying the electronic environment around active sites and preventing catalyst dissolution, lanthanides offer a dual benefit, making them valuable for OER in both media. With continued research and optimization, lanthanide-based materials are poised to play a key role in the development of cost-effective, efficient, and durable electrocatalysts for nextgeneration water-splitting technologies.

4.1.1. Practical implications of integrating lanthanides

Integrating lanthanides into transition metal-based catalysts for OER electrocatalysis presents both opportunities and challenges, particularly regarding cost and synthesis challenges.

- (i) Enhanced catalytic performance: Lanthanides introduce unique and transformative properties to transition metal-based catalytic systems by modulating electronic structures, enhancing synergistic interactions, and accelerating OER kinetics. The ability of lanthanides *f*-orbitals to interact effectively with the *d*-orbitals of transition metals plays a critical role in stabilizing reaction intermediates and lowering overpotentials. This interaction not only improves catalytic efficiency but also enhances durability, making lanthanide-doped systems a promising choice for advanced catalytic applications [93–95]. These attributes underline their potential in developing highperformance, long-lasting catalysts for energy conversion and chemical transformation processes.
- (ii) Cost implications: Lanthanides have demonstrated the potential to enhance catalyst performance significantly. However, their integration into catalytic systems raises critical concerns regarding cost. Although certain lanthanides, such as cerium and neodymium, are relatively abundant, their extraction and processing remain expensive due to complex supply chains and limited sources. This perception of rarity often inflates market prices compared to more commonly used transition metals. The economic implications are particularly pronounced in large-scale industrial applications, where cost-effectiveness is a primary consideration. While some lanthanides, like cerium, are more affordable, others, such as terbium and dysprosium, are less common, resulting in higher material costs [96-99]. These challenges necessitate careful evaluation of the trade-offs between performance benefits and economic viability. To address these concerns, minimizing the amount of lanthanide used while maximizing its catalytic impact is essential for the commercialization of lanthanide-enhanced catalysts.
- (iii) Synthesis challenges: Incorporating lanthanides into transition metal catalysts presents significant synthesis challenges. Achieving uniform dispersion of lanthanide elements and precise control over doping levels is complex due to variations in ionic radii and reactivity. Advanced synthesis techniques, such as hydrothermal methods, sol-gel processes, co-precipitation, or MOF pyrolysis, are often required to address these issues. These techniques, however, can be time-consuming, energy-intensive, and difficult to scale for industrial applications [100-102]. Additionally, maintaining phase purity and avoiding the formation of undesirable secondary phases during synthesis is critical for ensuring optimal catalytic performance. Precise control of stoichiometry in such multi-component systems further complicates the process, making reproducibility and scalability challenging. These complexities underscore the need for innovative approaches to balance performance with practical production constraints.
- (iv) Industrial relevance: Integrating lanthanides into transition metal catalysts requires a careful balance between performance enhancements and the complexities and costs associated with their synthesis. Scalable and cost-effective methods, such as coprecipitation and electrodeposition, offer potential pathways for industrial adoption. However, further research is essential to streamline synthesis protocols, minimize the dependency on costly lanthanides, and develop efficient recycling strategies for recovering lanthanide elements from spent catalysts [103,104]. These advancements are crucial for enhancing the sustainability and economic viability of lanthanide-based catalytic systems.

Lanthanide integration into transition metal-based catalysts offers



Fig. 12. The OER performance in 1.0 M KOH. (a) LSV curves and (b) Tafel slopes. (c) LSV curves before and after 1000 cycles (the inset CP at 10 and 100 mA cm⁻²). (d) Contact angles. (e) Calculated DOS and (f) PDOS of Ni 3*d* and O 2*p* for Dy₂O₃/NiOOH and NiOOH. (g-h) OER mechanism and Gibbs free energy diagrams for Dy₂O₃/NiOOH and NiOOH. Reproduced with permission from ref. [111]. Copyright Elsevier Ltd. 2024 (i) LSV curves and (j) Tafel slope of Fe₂O₃, Pr-MOF and Pr-MOF/Fe₂O₃. (k) C_{dl} curve and (l) Chronoamperometry of Pr-MOF/Fe₂O₃. Reproduced with permission from ref. [112]. Copyright Elsevier Ltd. 2023. (m) LSV and (n) Tafel plots. (o) C_{dl} curves. (p) I–t curve of CoCe-MOF/CP for OER. (q) Charge densities of CoCe-MOF/CP. (r) DOS around the doping site in Co-MOF/CP. (s) DOS around the doping site in CoCe-MOF/CP. (t) Gibbs free energy changes during the OER process. Reproduced with permission from ref. [113]. Copyright Wiley-VCH 2024.

transformative potential for OER electrocatalysis, enhancing performance and long-term stability. However, cost and synthesis challenges remain significant hurdles. Addressing these issues through innovative synthesis strategies, process optimization, and the use of abundant lanthanides will be key to realizing the industrial-scale application of these advanced catalysts.

4.2. Lanthanide-based MOFs

MOFs have garnered significant attention as electrocatalysts for batteries and supercapacitors due to their unique properties, such as high surface area, tunable pore sizes, low density, thermal stability, and organized crystal structures. These properties also contribute to favorable OER performance. However, the low electrical conductivity and poor durability of MOFs limit their efficiency in energy storage and conversion [105–109]. Addressing these challenges requires strategies such as photo-induced lattice strain, pore-space partitioning, heterointerface engineering, and heteroatom doping [110]. Heteroatom doping modifies the electronic structure of pure MOFs, enhancing surface characteristics, charge transfer, and lowering the OER reaction energy barrier, which improves catalytic activity. Additionally, the incorporation of a second metal into pristine MOFs alters the electronic structure of the metal center, further boosting electrical conductivity.

Lanthanides, which typically exhibit a stable +3 valence state, can form stable compounds and, due to their filled 5*s* and 5*p* orbitals, shield their 4*f* orbitals from the chemical environment. This shielding effect

allows lanthanide-based materials to display strong performance in electrocatalytic processes such as the OER and oxygen reduction reaction (ORR). Our group has explored an innovative approach using dysprosium (Dy) doping to enhance the electrocatalytic activity of MOFs. This approach involves fabricating Dy-doped Ni-MOF (Dy@Ni-MOF) nanoneedles on carbon cloth (CC) through a Dy-induced valence electronic perturbation technique. The OER performance of the synthesized electrocatalysts was tested in a 1.0 M KOH solution [111].

As shown in Fig. 12a, the linear sweep voltammetry (LSV) curves reveal that Dy@Ni-MOF exhibits superior OER activity, requiring overpotential of only 246 mV to achieve 10 mA cm⁻², outperforming Ni-MOF and RuO₂. The Tafel slope of Dy@Ni-MOF (96.5 mV dec⁻¹) is notably lower than that of Ni-MOF (129.4 mV dec⁻¹) and comparable to RuO₂ (94.6 mV dec⁻¹), indicating improved OER kinetics due to Dy doping (Fig. 12b). After 1000 cycles, the polarization curves remained nearly unchanged (Fig. 12c), demonstrating the excellent cycling stability of Dy@Ni-MOF. Furthermore, Dy@Ni-MOF maintained stable performance at current densities of 10 and 100 mA cm⁻² for over 80 h without noticeable degradation, confirming its long-term stability (Fig. 10c, inset). The incorporation of Dy also significantly enhanced hydrophilicity, as reflected in the reduction of the contact angle from 21° (Ni-MOF) to 0° (Dy@Ni-MOF), which improves electrolyte interaction and mass transfer (Fig. 12d).

Density functional theory (DFT) calculations were conducted to assess the effect of Dy doping on the electronic structure of Dy@Ni-MOF after the OER process. The density of states (DOS) analysis (Fig. 12e) revealed a substantial DOS at the Fermi energy level (E_f) for Dy₂O₃/NiOOH, indicating enhanced electrical conductivity and charge transfer efficiency. The partial density of states (PDOS) analysis showed significant orbital overlap between Ni and adsorbed oxygen intermediates near E_f , suggesting strong electron coupling between Ni 3d orbitals in Dy₂O₃/NiOOH and O 2*p* orbitals of the adsorbed oxygen intermediates (Fig. 12f). The OER mechanism and optimal adsorption configurations of OER intermediates for Dy₂O₃/NiOOH and NiOOH are depicted in Fig. 12g, showing that the rate-determining step (RDS) for Dy₂O₃/NiOOH involves the conversion of *O to *OOH. The ΔG_3 value for Dy₂O₃/NiOOH is 1.56 eV, significantly lower than the 1.85 eV for NiOOH, suggesting improved OER kinetics for Dy₂O₃/NiOOH (Fig. 12h). This highlights how Dy doping optimizes the electronic structure of Ni active sites, improving electron interactions, optimizing oxygen intermediate adsorption, and accelerating OER kinetics [111].

In another study, Shabbir et al. synthesized Pr-MOF/Fe₂O₃ using a hydrothermal approach. The polarization curves (Fig. 12i) showed that Pr-MOF/Fe₂O₃ exhibited an overpotential of 238 mV, which was lower than those of Pr-MOF (265 mV) and Fe₂O₃ (304 mV), indicating superior OER performance. The Tafel slope of Pr-MOF/Fe₂O₃ (37 mV dec⁻¹) was also lower compared to Fe₂O₃ (39 mV dec⁻¹) and Pr-MOF (47 mV dec^{-1}), indicating faster OER kinetics (Fig. 12j). The double-layer capacitance (C_{dl}) of Pr-MOF/Fe₂O₃ was measured at 9.5 mF cm⁻², further supporting its enhanced catalytic activity (Fig. 12k). Chronoamperometry tests over 40 h in a 1.0 M alkaline solution showed that the material maintained a relatively constant activity level throughout the electrolysis process, with only minor decreases in current density over time (Fig. 12l) [112]. Furthermore, Liao et al. developed a Co-MOF nanoflower on carbon paper (CoCe-MOF/CP) using cerium doping via a solvothermal method to enhance OER performance. The CoCe-MOF/CP exhibited a low overpotential of 267 mV at 10 mA cm⁻² (Fig. 12m). The Tafel slope, derived from LSV curves, was used to evaluate OER reaction kinetics (Fig. 12n). For Co-MOF/CP without Ce doping, the Tafel slope was 132.5 mV dec $^{-1}$, indicating that the first electron transfer step of the OH⁻ group was RDS. With Ce doping, the Tafel slope decreased to 96.1 mV dec $^{-1}$, suggesting a mixed rate-determining step involving both the first and second electron transfer steps, highlighting that Ce doping promotes the first electron transfer in the OER process. Notably, CoCe-MOF/CP exhibits the largest C_{dl} (29.7 mF cm⁻²) compared to other catalysts (Fig. 12o), indicating a higher number of electrochemically active sites and increased surface area exposed in the electrolyte solution. The stability and durability of CoCe-MOF/CP were assessed by performing a 100 h I-t-test and LSV measurements after 3000 cycles (Fig. 12p). After 100 h of continuous electrolysis at a constant potential of 1.74 V versus RHE, the current density only slightly dropped from 71.61 to 71.23 mA \cdot cm⁻², indicating excellent stability with minimal change. The charge difference density slice of CoCe-MOF/CP in Fig. 12q shows that the introduction of Ce atoms significantly redistributes the charge density, particularly around the Co atoms near the Ce atoms. This redistribution is due to the different charge densities of the doped Ce atoms compared to the original Co atoms in Co-MOF/CP. The electronic structure of Co-MOF/CP is tailored by charge redistribution near the Ce atoms, attributed to the interaction through Co-O-Ce bonds. The introduction of Ce atoms in CoCe-MOF/CP notably redistributes the charge density, particularly around the Co atoms near the Ce sites. The DOS plots in Figs. 12r-s show that Ce doping leads to the formation of ghost states near the Fermi level, due to the interaction between Co 3d, O 2p, and Ce 4f orbitals, forming Co-O-Ce bonds. The Gibbs free energy change (Fig. 12t) reveals that the RDS for both CoCe-MOF/CP and Co-MOF/CP is the transformation from *OH to *O, with Ce doping reducing the energy barrier for this step and thus improving OER performance. The high electrocatalytic activity of CoCe-MOF/CP is attributed to its interlaced sheet structure, the strong Co 3d-O 2p-Ce 4f orbital coupling, and the reduced energy barrier for oxygen intermediates [113].

In another study, K. Shrestha et al. developed a Ce-doped MIL-88B

(Ni)/NF anode using a solvothermal method to induce site-selective crystalline/amorphous heterostructures in the MIL-88B(Ni) framework. The optimized Ce-doped MIL-88B(Ni)/NF exhibited outstanding OER performance with overpotentials of 205, 290, 410, and 450 mV at current densities of 10, 100, 1000, and 2000 mA cm⁻², respectively, and a Tafel slope of 46.09 mV dec $^{-1}$. Supported by DFT calculations, Ce doping enhanced the OER activity by inducing crystal disorder [114]. This study highlights the significant role of lanthanides like Ce in improving the electrocatalytic performance and durability of materials for advanced energy conversion processes. Additionally, Ma et al. synthesized Fe-MOF nanosheet arrays on nickel foam through erbium doping (Er_{0.4} Fe-MOF/NF) using a solvothermal method and applied them as OER electrocatalysts. The Er_{0.4} Fe-MOF/NF demonstrated excellent OER performance, achieving a current density of 100 mA cm^{-2} at an overpotential of 248 mV and maintaining outstanding electrochemical durability for over 100 h. Even at large current densities of 500 and 1000 mA cm⁻², overpotentials of only 297 mV and 326 mV were observed, showcasing its industrial potential. The enhancement was attributed to synergistic effects between Fe and Er, with Er optimizing the electronic states of Fe sites to boost OER activity. This approach highlights the potential of lanthanide metal ion doping in designing MOF-based catalysts for industrial OER applications [115].

The above studies demonstrate that lanthanide doping in MOFs significantly improves their OER performance by enhancing conductivity, stability, and reaction kinetics. Incorporating lanthanides into MOF-based electrocatalysts can thus pave the way for more efficient and durable OER systems, contributing to advancements in renewable energy technologies.

Lanthanides in MOFs significantly enhance catalytic activity, stability, and reaction kinetics, making them ideal candidates for OER electrocatalysis. Their unique electronic configurations optimize the electronic structure of MOFs, facilitating charge transfer during OER by reducing energy barriers, which makes the reaction more energetically favorable and improves overall catalytic efficiency. The incorporation of lanthanides creates or modifies active sites, improving the interaction between the catalyst and oxygen-containing intermediates, thereby accelerating reaction rates.

Moreover, lanthanide-based MOFs exhibit enhanced structural stability, crucial for maintaining long-term catalytic efficiency under harsh electrochemical conditions. Lanthanides can also alter the morphology of MOFs, improving accessibility to reactants and facilitating better mass transfer. These attributes position lanthanide-based MOFs as promising alternatives to noble metal-based catalysts for energy conversion technologies. As research advances, these materials are emerging as sustainable and cost-effective solutions in clean energy applications, representing both a scientific frontier and a practical approach to addressing global energy challenges.

4.3. Lanthanide-based perovskite

Perovskites are a broad class of materials with the general formula ABX₃, where A represents an alkaline or lanthanide element, B represents transition metals (TMs), and X is typically oxygen or sulfur. In traditional single-perovskite oxides, B-site metals form octahedral [BO₆] structures, while A-site elements form cuboctahedral structures. Lanthanide-based perovskites have garnered significant interest in energy electrocatalysis due to their structural flexibility and potential for enhanced OER performance. To optimize their catalytic efficiency, researchers have employed strategies such as elemental doping and defect engineering, which improve oxygen vacancies and cation substitution in these materials.

These modulation techniques adjust the O 2*p* band center, influencing the binding strength of B—O bonds and surface oxygen exchange rates [116–118]. This fine-tuning leads to a universal design strategy for high-performance lanthanide-based perovskites, as surface oxygen exchange produces lattice oxygen, directly enhancing oxygen



Fig. 13. (a) LSV curves of GSFO based catalyst. (b) Tafel plots. (c) C_{dl} plot. (d) The durability tests of GSFO-0.2. (e) The *E*-t plot of GSFO at the current density of 10 mA cm⁻². Reproduced with permission from ref. [79]. Copyright Elsevier Ltd. 2024. Electrochemical OER properties of the double perovskite M_2 NiMnO₆ (M = Eu, Gd, Tb), catalysts measured in 1 M KOH electrolyte. (f) iR-corrected OER polarization curves recorded at a scan rate of 5 mVs⁻¹, along with the LSV for a benchmark RuO₂/NF catalyst. (g) Tafel slopes. (h) C_{dl} plot. (i) Chronoamperometric stability curves measured at 10 and 100 mA cm⁻² over 100 h. Reproduced with permission from ref. [122]. Copyright MDPI 2023. OER performance of LnSrCoO₄ (Ln = La, Pr, Sm, Eu, and Gd) catalysts in 1 M KOH. (j) LSV curves. Inset: LSV curves in the range of 1.55–1.65 (V vs. RHE). (k) Tafel slope. (l) C_{dl} plot. (m) Chronopotentiometry test of LnSrCoO₄ at 10 mA cm⁻². (n) Calculated Gibbs free energy (Δ G) diagrams for four steps of OER on LaSrCoO₄, PrSrCoO₄, and EuSrCoO₄. DOS of (o) LaSrCoO₄, (p) PrSrCoO₄, and (q) EuSrCoO₄. Reproduced with permission from ref. [70]. Copyright © 2024, American Chemical Society.

electrocatalysis. The OER activity of perovskites is often linked to the occupancy of B-site transition metals, as it affects the d-band center, leading to increased orbital overlap with adsorbed oxygen intermediates and altering the covalent binding between B-site cations and these intermediates [119].

While A-site lanthanide cations do not directly participate in electrocatalysis, they indirectly influence the electronic structure and conductivity of perovskites, thereby impacting electrocatalytic performance. A-site substitution of lanthanides realigns bent B-O-B bonds in perovskite oxides to a linear 180° configuration, improving B—O hybridization, electron transport between B-site ions, and oxygen vacancy formation in bulk perovskite oxides. This realignment elevates the B—O bonding band closer to the Fermi level, enhancing the e_g orbital occupancy of B-site cations and balancing the adsorption/desorption strength of intermediates [120,121]. Consequently, A-site lanthanide cations serve as excellent indirect enhancers of electrocatalysis. Lanthanide-based perovskites also exhibit high electronic density due to the modulation effects of lanthanide species, as shown by Hirshfeld charge population analysis. This redistribution of charge density enhances the electronic conductivity of lanthanide-based

perovskites, indicating their potential for energy-related electrocatalysis applications.

For example, Xian et al. developed a two-dimensional (2D) porous GdFeO₃ (GFO) perovskite using A-site strontium (Sr) substitution via a microwave shock technique. The resulting Gd_{0.8}Sr_{0.2}FeO₃ (GSFO) electrocatalyst demonstrated an impressive overpotential of 294 mV at a current density of 10 mA $\rm cm^{-2}$ and a minimal Tafel slope of 55.85 mV dec⁻¹ in alkaline electrolytes (Figs. 13a-b). Additionally, GSFO-0.2 exhibited a high C_{dl} value of 14.66 mF cm⁻², significantly higher than that of GFO and other GSFO variations (Fig. 13c). GSFO-0.2 showed exceptional stability during an accelerated durability test, maintaining excellent OER performance after 3000 cycles of cyclic voltammetry (Figs. 14d-e) [79]. Similarly, Shinde et al. synthesized lanthanide-doped double perovskites, specifically M_2NiMnO_6 (where M = Eu, Gd, Tb), using a solid-state reaction approach. Among the catalysts studied, Tb₂NiMnO₆ exhibited outstanding OER characteristics, with a low overpotential of 288 mV to achieve a current density of 10 mA cm⁻² ² and a reduced Tafel slope of 38.76 mV dec⁻¹ (Figs. 13f-g). The C_{dl} value for Tb_2NiMnO_6 was also high at 11.36 mF cm⁻², indicating an increased electrochemically active surface area compared to Eu2NiMnO6 (6.36 mF



Fig. 14. (a) Polarization curves and (b) Tafel slopes of R_2NiRuO_6 following 30 cycles of the OER. (c) Evolution of the potential at 10 mA cm⁻² as a function of the Ru—O distances in R_2NiRuO_6 . (d) Schematics of the processes occurring on the catalyst surface during the OER. Reproduce from ref. [124]. (e) The positions of B-site substitution on LPOs (B—Mn, Fe, and Co). (f) Free energy diagram of 4e⁻ OER of LaMnO₃, LaFeO₃, and LaCoO₃ at the different potentials: 0 V, equilibrium potential (1.23 V), and limiting potential (V_L) are presented by blue, black, and red line, respectively. The volcano plots of (g) and (h) OER on LPO surfaces. Reproduced with permission from ref. [126]. Copyright Wiley-VCH 2024. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cm⁻²) and Gd₂NiMnO₆ (2.22 mF cm⁻²) (Fig. 13h). During chronopotentiometry tests conducted at 10 and 100 mA cm⁻² over 100 h, Tb₂NiMnO₆ demonstrated stable performance with vigorous gas production at both the cathode and anode, even under higher current densities, where minor fluctuations occurred due to bubble formation (Fig. 13i) [122].

Furthermore, Huang et al. investigated the electrocatalytic effect of $LnSrCoO_4$ (Ln = La, Pr, Sm, Eu, and Ga), 214-type perovskite oxides with semiconductor like behavior synthesized using the sol-gel method. The overpotentials of LaSrCoO₄, SrCoO₄, GdSrCoO₄, PrSrCoO₄, SmSrCoO₄, and Eu catalysts were 405, 375, 397, 394, and 386 mV at 10 mA cm⁻². respectively, and the lowest overpotential was observed for PrSrCoO₄ (Fig. 13j). In addition, the Tafel slope values describing the reactive kinetics of these five catalysts (Fig. 13k) were 79.1, 83.4, 86.0, 90.3, and 79.9 mV dec $^{-1}$, respectively. The smallest value of the Tafel slope for LaSrCoO₄ represents the fastest kinetic process, while it has the largest value of the perovskite potential, which indicates that the reactive kinetics is only one of the important factors affecting the magnitude of the perovskite potential. Furthermore, (Fig. 13l) shows the C_{dl} of the five catalysts. PrSrCoO₄ has the highest value of 4.25 mF cm⁻² compare to other catalysts. Moreover, PrSrCoO₄ has a very high stability compared with other catalysts (Fig. 13m). DFT was then used to calculate the fourelectron processes of OER reaction in LaSrCoO₄, PrSrCoO₄ and EuSrCoO₄ oxide catalysts as shown in (Figs. 13n-q). The ratedetermining steps of these three catalysts include all the processes of O₂ generation from OOH*, and the calculated Gibbs free energy changes (Δ G) are 4.10, 2.68, and 3.37 eV, respectively. PrSrCoO₄ has lower Δ G and larger DOS, which reduces the energetic barrier of the OER reaction process and improves the electrocatalytic performance [70]. In another study, Kumar et al. reported the synthesis of double perovskite oxide materials LnBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O₆ (LnBSCF, Ln = Pr, Nd, Sm, Gd) using

a citrate-nitrate-based sol-gel method. Among these, GdBSCF exhibited the best catalytic performance in 0.1 M KOH, with a Tafel slope of 83 mV dec^{-1} [123].

These studies demonstrate that lanthanide-doped perovskites can enhance OER performance by improving conductivity, stability, and reaction kinetics. The flexibility in modulating the electronic and structural properties of perovskites through lanthanide doping makes them promising candidates for next-generation energy conversion technologies, providing a sustainable alternative to noble metal-based catalysts.

Perovskite materials have garnered significant attention in the field of acidic OER electrocatalysis due to their unique structural and electronic properties, which enhance their catalytic performance in acidic electrolytes. Their tunable crystal structure, high conductivity, and the ability to incorporate various metal or lanthanide elements make perovskites highly effective in promoting acidic OER. For example, García et al. developed Ru-based perovskites, specifically Dy2NiRuO6, which exhibited the highest OER activity (1.507 V at 10 mA cm^{-2}), using the citrate method (Fig. 14a). Fig. 14b shows the Tafel plots for each catalyst, calculated from the 30th voltammogram. Dy₂NiRuO₆ exhibits a slope of just 58 mV dec $^{-1}$, while the other catalysts have slopes exceeding 128 mV dec⁻¹, with Nd and Pr catalysts showing slopes over 200 mV dec⁻¹. These findings suggest that the type of rare earth element influences not only the catalytic activity of the perovskites but also the underlying OER mechanism. To understand why Dy-containing perovskite exhibits the highest activity, crystallographic parameters were correlated with catalytic performance. Fig. 14c shows that as the Ru-O distances in R₂NiRuO₆ decrease, the activity improves, indicating that shorter Ru-O bonds favor OER. Shorter Ru-O distances are linked to higher Ru oxidation states, which enhance OER activity, as seen in Dy_2NiRuO_6 with a calculated valence of +3.9. This demonstrates a



Fig. 15. (a) Crystal structure of Gd₄-MOF, viewed along the c-axis. (b) The spatially connected pattern of Gd₄-MOF with $[Gd_4(\mu_4-O) (\mu_3H)_3(INA)_3(G)_3]^+$ as the unit, viewed along the a-axis. (c) Interplanar distance and $\pi - \pi$ overlap between 1D chains along the c-axis. Reproduced with permission from ref. [138]. Copyright © 2023, American Chemical Society. Typical crystal structures of different types of perovskite oxides: (d) Cubic (ABO₃), (e) Quadruple (AA₃B4O₁₂), (f) A-site ordered (AAB₂O₆) and B-site ordered (A₂BBO₆), and (g) RP (A_{n+1}BnO_{3n+1}, *n* = 1, 2 and 3) perovskite oxides. Reproduced with permission from ref. [148]. Copyright 2024 Springer (CC Attribution 4.0 International License).

consistent correlation between shorter Ru—O distances and increased OER activity across the entire family of compounds. The Fig. 14d illustrates how the electrolyte interacts with the Dy_2NiRuO_6 structure, facilitating the adsorption of water molecules (H₂O) and O₂ intermediates, ultimately promoting the OER process. The presence of Dy in the perovskite structure enhances the catalytic activity by stabilizing key intermediates and optimizing the adsorption of oxygen species, which is crucial for efficient OER [124].

Furthermore, *Morales* et al. developed Ir-based double perovskites, Ba₂MIrO₆ (M = Y, La, Ce, Pr, Nd, and Tb), which demonstrate tunable performance for acidic OER. In 0.1 M HClO₄, the OER activity of these double perovskites varies based on the B-site cation, following the order Ce \approx Tb \approx Y < La \approx Pr < Nd. Despite containing 32 wt% less Ir than IrO₂, all Ba₂MIrO₆ perovskites exhibit more than threefold higher OER activity compared to IrO₂. Among them, Ba₂PrIrO₆ and Ba₂YIrO₆ showed remarkable stability under acidic OER conditions, outperforming IrO₂, while La, Nd, and Tb-based perovskites lost activity within 1 h of testing. Ba₂PrIrO₆ emerged as the best-performing catalyst, surpassing IrO₂ in both activity and stability. The superior performance of these perovskites is attributed to their 3D network of corner-shared octahedra, which optimizes orbital interactions, adjusts bond distances, and accommodates local charge changes. Further improvements in performance could be achieved by tailoring the A, B, and B' cations and optimizing the synthesis process to reduce particle size [125].

The development of efficient OER electrocatalysts is crucial for reducing overpotentials and improving reaction kinetics, ultimately leading to more cost-effective clean energy production. While progress has been made in OER catalyst development, a deeper understanding of the active site mechanism is still needed [127,128]. Theoretical approaches, particularly DFT, have become essential in exploring potential catalyst materials, accelerating the development process and reducing research costs [129–131]. DFT allows for precise analysis of electronic structures, helping to establish composition-structure-function relationships and predict high-performance catalysts. With advancements in computer technology, DFT offers valuable insights into electrocatalytic active sites and mechanisms at the atomic level [132,133]. For

example, Somdee et al., theoretical study investigates the effect of B-site substitution in La-based perovskite oxides (LPOs) on electrocatalytic OER activity. DFT calculations reveal that Co-terminated LaMn_{0.25-} Co_{0.75}O₃ (LM25C75O) shows excellent OER performance, with Co acting as the active site for OER. The positions of the B-site substitutions on the LPOs are shown in Fig. 14e. These electrocatalysts were chosen to have the stable structures with the lowest Ef. The role of the A-site, La, is closely linked to the electrocatalytic properties of the OER. La provides a stable framework and supports the inclusion crystal structure allowing flexible substitution of the B-site with transition metals such as Mn, Fe and Co. The presence of La contributes to the structural stability of the perovskite oxides under OER conditions, which is important for maintaining the catalytic performance over a long period of time. In addition, the larger ionic radius of La helps to accommodate various B-site ions and realize tunable electronic structures, which directly affects the binding energy of OER intermediates.

As shown in Fig. 14f, the free energy diagrams of LaMnO₃, LaFeO₃, and LaCoO₃ reveal how the inclusion of La in these oxides interacts with different B-site substituents, thereby affecting the reaction energies. The La framework supports the most favorable catalytic behavior at the B-site when paired with Co, and the lower limiting potential of LaCoO₃ (V_L) and improved energy profile as evidenced by the lower limit potential (V_L) of LaCoO₃, indicating that less energy is required for its OER.

Table 3

Comparison	of	lanthanide	-based	MOFs	and	perovskites.
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Characteristics	MOFs	Perovskites
Structure and Compositions	Porous crystalline structures formed by aligning lanthanide metal centers with organic ligands, offering tunable pore sizes.	Crystalline oxides with diverse structures (e.g., cubic, double, RP), offering flexible B-site and A-site cation arrangements.
Surface area	High specific surface area and tunable porosity provide abundant active sites.	Moderate surface area but sufficient for catalysis, often enhanced by doping or structural modifications.
Conductivity	Limited by insulating organic ligands; enhanced by incorporating π - π stacked aromatic rings or conductive substrates.	Inherently high conductivity due to efficient charge transfer in the crystalline lattice.
Stability	Moderate; sensitive to structural degradation unless supported on conductive substrates or encapsulated.	High activity but prone to moisture sensitivity and thermal instability; stability improved with encapsulation or hybridization.
Synthesis complexity	Complex and costly synthesis processes; challenging for large-scale industrial applications.	Comparatively easier synthesis but still requires precise control over co-metal compositions and processing conditions.
Scalability	Limited due to synthesis complexity and cost of lanthanide metals.	More scalable, widely used in industrial OER systems due to lower cost and established manufacturing processes.
Hybrid strategies	Combined with conductive materials or encapsulated to overcome conductivity and stability issues.	Encapsulation in MOFs improves stability, protecting against moisture and increasing active site exposure.
Industrial potential	Promising for specialized applications requiring high surface area; limited by conductivity and stability.	Widely applicable in industrial OER systems, particularly in water-splitting and fuel-cell technologies.
Challenges	Poor conductivity and costly synthesis hinder practical use; stability issues under harsh conditions.	Moisture sensitivity and thermal degradation limit durability; encapsulation or doping strategies are needed.
Future direction	Focus on enhancing conductivity (e.g., π - π stacking, conductive substrates) and improving scalability.	Development of hybrid systems combining perovskites and MOFs for optimal performance and durability.

In Figs. 14g-h, the volcano plots show the perovskite overpotentials (η_{OER}) associated with the difference in the Gibbs free energies, suggesting that, due to the efficient binding of La to Co, LaCoO₃ consistently exhibits a lower (η_{OER}). The synergistic interaction between La at the A-site and Co at the B-site makes LaCoO₃ particularly efficient for OER because La stabilizes the structure while Co optimally facilitates the reaction. This study emphasizes that the combination of La as the structural backbone with appropriate B-site substitutions, especially Co, is very important for the design of effective LPO for OER electrocatalysis. These findings provide valuable insights for designing superior electrocatalysts through strategic B-site substitution [126].

Studies show that elemental doping and defect engineering significantly enhance the performance of lanthanide-based perovskites by lowering overpotential, reducing Tafel slopes, and improving operational stability. These advancements greatly boost OER efficiency, positioning lanthanide-based perovskites as durable and highperformance electrocatalysts for both alkaline and acidic media. Their long-term effectiveness in harsh alkaline environments, as well as their stability in acidic electrolytes, is attributed to their structural integrity and resistance to degradation, making them ideal for practical applications requiring continuous, reliable performance. To further optimize their electrocatalytic efficiency, a combination of experimental and DFT studies provides crucial insights into catalyst behavior. Theoretical energy estimations and DFT calculations offer molecular-level understanding of energy barriers, active sites, and reaction mechanisms, while experimental data provide practical insights into perovskite potentials, stability, and reaction kinetics. This combined approach enhances the prediction and optimization of electrocatalytic efficiency in advanced materials, improving performance in both alkaline and acidic OER conditions. The durability of these catalysts is crucial for their application in energy conversion and storage technologies, where sustained operation is essential. The progress in lanthanide-based perovskite technology highlights their potential as outstanding candidates for sustainable and efficient energy conversion, offering promising solutions for enhancing the efficiency and sustainability of clean energy systems. As research continues, these materials are expected to play a pivotal role in renewable energy applications, such as water splitting and other electrochemical processes.

4.4. Comparative analysis of lanthanide-based MOFs and perovskites

A comparison of lanthanide-based MOFs and perovskites as electrocatalysts for OER reveals significant differences in structural properties, catalytic performance, stability and overall suitability for practical applications. Lanthanide-based MOFs are formed by aligning lanthanide metal centers with organic ligands to form porous crystalline structures. These materials can exhibit high specific surface areas and tunable pore sizes for electrocatalytic application such as OER [134–136]. For instance, Wang et al. developed a heterojunction structure, such as CoMnLa_{0.2}-MOF/CF synthesized via a one-pot solvothermal process, significantly enhances OER performance by reducing charge-transfer resistance and increasing the activated surface area. The catalyst achieves overpotential of only 201 mV at 10 mA $\rm cm^{-2}$ in 1 M KOH, with stable performance over 25 h [137]. Although lanthanidecontaining MOFs demonstrate exceptional performance, challenges such as limited conductivity and stability persist. Recent advances have led to the development of electrically conductive lanthanide-based MOFs by incorporating π - π stacked aromatic rings into the framework of the lanthanide-MOFs, a modification that significantly improves the electronic conductivity and makes these MOFs more suitable for electrocatalytic processes. The crystal structure of Gd₄-MOF has significant implications in catalysis. In the Gd₄-MOF structure (Figs. 15a-c), the interconnected Gd₄ units and $\pi - \pi$ overlap along the c-axis can facilitate electron transport, essential for enhancing OER activity by improving conductivity and providing active sites for oxygen species adsorption and evolution [138]. Thus, Gd₄-MOF provides a porous structure



Fig. 16. (a) Polarization curves of LSV, (b) Tafel plots, and (c) CP stability test of CeO_2 -NiCo P_x /NCF (the inset is LSV curves before and after CV cycles). (d) Atomistic crystal models, (e) Calculated DOS, and (f) Gibbs free-energy evolution in the OER reaction steps of CeO_2 -NiCo P_x /NCF. Reproduced with permission from ref. [156] Copyright Elsevier Ltd. 2022. (g) LSV curves, (h) Tafel plots, and (i) CP curves for Ce-NiCo-LDH/CNT. Reproduced with permission from ref. [157] Copyright Elsevier Ltd. 2020. (j) LSV, (k) Tafel plots, and (l) CP stability test of $Co_{10}Ce_1/C$ HFs. (m) Model of the Co_3O_4 (311)/CeO₂ (111) interface. (n) Charge-density difference of the Co_3O_4 -CeO₂ interface. (o) Total DOS of the Co_3O_4 -CeO₂ interface system. Reproduced with permission from ref. [158] Copyright Elsevier Ltd. 2024. (p) Polarization curves and (q) Tafel slopes of $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$, $W_{0.2}Ru_{0.8}O_{2-\delta}$, $RuO_{2-\delta}$, and C-RuO₂ nanosheets. (r) The CP stability of $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ nanosheets. (s) Calculated energy barriers diagram for $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta-1}$. Reproduced from ref. [161]. (CC BY 4.0), Nature Portfolio 2020.

beneficial for surface area and gas diffusion, making advantageous for efficient OER electrocatalysis. Conventional MOFs often suffer from poor conductivity, but recent studies have shown that lanthanide-based MOFs can achieve enhanced OER activity if properly engineered [139–141]. For example, combining conductive materials or nanoconductive strategies can reduce the overpotential and improve the current density [142–144]. Despite the advances, many lanthanidebased MOFs suffer from inherently low conductivity due to the insulating nature of the organic ligands. This limits their performance unless combined with a conductive substrate or material [145–147]. The complex and costly synthesis of lanthanide-based MOFs may hinder their large-scale application compared to more established materials such as perovskites.

On the other hand, the unique crystalline structure of perovskites facilitates efficient charge transfer, making them inherently more conductive than many MOFs. This property is favorable for electrocatalytic reactions such as OER. Studies have shown that perovskites have excellent catalytic activity for OER, often outperforming many conventional catalysts [149–151]. For perovskite oxides (Figs. 15d-g), the diverse arrangements in cubic, quadruple, double (A- and B-site ordered), and Ruddlesden-Popper (RP) structures offer varied B-site cations and oxygen coordination, which can adjust electronic structures and increase OER activity. Therefore, perovskites offer stability and tunable electronic properties, making it beneficial for efficient OER electrocatalysis [148]. Their activity can be further enhanced by doping with different metals or modifying the A or B sites in the perovskite structure. For instance, *Jo* et al., prepared perovskite oxides, such as $PrBa_{0.5}Sr_{0.5}Co_{2\cdot x}Fe_xO_{5+\delta}$ (PBSCF), achieving an overpotential of 290 mV at 10 mA cm⁻² and demonstrating remarkable stability in OER, maintaining performance at 100 mA cm⁻² for over 2000 h. This enhanced stability and activity are attributed to Fe doping at the B-site, which alters the intrinsic properties of Co-based perovskites and optimizes their electronic structures [152]. While perovskites can achieve high activity, they often face challenges such as moisture sensitivity and thermal instability, leading to degradation during OER processes. To address these issues, strategies like encapsulating perovskite crystals in MOFs have been developed, which protect them from environmental factors and increase the number of active sites, enhancing both stability and performance [153,154].

Both MOFs and perovskites are promising approaches to improve OER electrocatalysis. While MOFs offer significant advantages in terms of design flexibility and surface area, their conductivity and stability issues remain serious challenges (Table 3). Although, perovskites can provide excellent catalytic performance, but strategies such as encapsulation within MOFs are needed to improve their performance. Future research may focus on hybrid systems that combine the advantages of both materials to develop more efficient and stable electrocatalysts for renewable energy applications.

4.5. Lanthanide-based nanomaterials

Nanomaterials are materials with structural components at the nanometer scale, offering unique properties like increased surface area, enhanced reactivity, and quantum effects. Recently, nanomaterials have attracted significant interest as electrode materials for OER due to their ability to reduce energy barriers and lower charge transfer resistance [155]. Their high surface-to-volume ratio exposes more active sites, optimizing the adsorption and desorption of oxygen intermediates, which enhances catalytic efficiency. Additionally, nanomaterials enable fine-tuning of the electronic structure, improving electron transfer at the electrode surfaces and further boosting OER performance. For example, Wen et al. engineered a hybrid nanowire-nanosheet structure of CeO2-NiCoP_x on Ni-Co foam (CeO₂-NiCoP_x/NCF) for enhanced OER performance, achieving an overpotential of 260 mV at a current density of 10 mA cm⁻² (Fig. 16a). Fig. 16b illustrates the Tafel slope of CeO₂-NiCoP_x/ NCF, which demonstrates a significant improvement with a value of 72 mV dec⁻¹, compared to other catalysts. Fig. 16c shows the long-term I-t curve of the CeO₂-NiCoP_x/NCF catalyst at a current density of 100 mA cm^{-2} in 1 M KOH, with the current density remaining nearly unchanged after 100 h, retaining over 94 % of its initial value. The inset displays the polarization curve after 104 CV cycles, nearly overlapping with the original, confirming the excellent electrochemical stability of the CeO₂-NiCoP_x/NCF electrode. Furthermore, DFT calculations were performed to understand how CeO₂ interacts with NiCoP and Co₂P interfaces, revealing the underlying catalytic mechanism of CeO₂-NiCoP_x/NCF (Fig. 16d). The DOS diagram in Fig. 16e shows that the electronic states of CeO2-NiCoP, CeO2-Co2P, NiCoP, and Co2P all intersect the Fermi level, highlighting the metallic nature of the catalysts. Notably, the DOS of CeO₂-NiCoP and CeO₂-Co₂P heterojunctions exhibits a higher DOS crossing the Fermi level compared to the single NiCoP and Co₂P structures, suggesting enhanced electron transfer. Fig. 16f reveals that the transition from *O to *OOH species involves a significant energy gradient, marking it as the rate-limiting step in the OER process. The energy barriers for CeO₂-NiCoP and CeO₂-Co₂P are 0.06 eV and 1.28 eV, respectively, both considerably lower than those for NiCoP (2.53 eV) and Co₂P (1.67 eV). These calculated energy barriers suggest that the Ni atoms in CeO2-NiCoP nanosheets are the primary active sites for the OER [156].

In another study, Dinari et al. developed a cerium-doped nickel-cobalt layered double hydroxide (Ce-doped NiCo-LDH) nanohybrid grown on carbon nanotubes (CNT), which demonstrated exceptional electrocatalytic activity for the OER. The Ce-doped NiCo-LDH/CNT nanohybrid achieved an overpotential of 236 mV at 10 mA cm^{-2} and a Tafel slope of 56 mV dec⁻¹ in 1 M KOH (Figs. 16g-h). Additionally, chronoamperometric stability tests were conducted to assess the longterm durability of Ce-NiCo-LDHs at various potentials (Fig. 16i). The electrodes exhibited excellent stability, maintaining high performance for over 16 h in the alkaline solution [157]. Furthermore, Ma et al. developed a Co₃O₄/CeO₂/C heterostructure nanoflower (CoCe/C HFs) catalyst with 2D nanostructures using a simple one-step hydrothermal method, which enhanced the electronic conductivity and increased active metal sites. The $Co_{10}Ce_1/C$ HFs (Co:Ce = 10:1) exhibited excellent OER performance, achieving a low overpotential of 274 mV at 10 mA cm^{-2} and a Tafel slope of 82.6 mV dec⁻¹ in 1 M KOH, surpassing other catalysts (Figs. 16j-k). The CP curve in Fig. 16l shows only a slight increase of 21 mV in overpotential after 12 h of testing, underscoring the catalyst outstanding stability. The DFT calculations were performed to investigate the origin of the enhanced conductivity and the synergistic effects that improve catalytic performance. In Fig. 16m, a Co₃O₄ (311)/ CeO₂ (111) p-n heterojunction nanointerface was designed. As shown in Fig. 16n, a strong electron coupling effect is observed at the Co₃O₄ and CeO₂ interface. Fig. 160 presents the DOS for the Co₃O₄ (311)/CeO₂ (111) interface. Compared to pristine Co₃O₄, the heterojunction interface has a narrower band gap at the Fermi level, indicating an enhanced metallic character that facilitates charge transfer during the OER [158]. Wang et al. developed a self-supported Ce-CoFe-LDH/NF electrode by growing Ce-doped CoFe LDHs directly on nickel foam via a one-step hydrothermal method, achieving a nanoneedle morphology that enhances electrocatalytic performance for the oxygen evolution reaction. The catalyst exhibited impressive performance with an optimized

overpotential of 225 mV at 10 mA cm⁻², a Tafel slope of 34.34 mV dec⁻¹ [159]. *Guo* et al. explored the effects of Al ion control and Ce doping on the morphology and OER performance of CoOOH, finding that Al ions induced a morphology change from nanosphere to nanosheet and back, while Ce doping significantly enhanced OER activity. The Ce-doped CoOOH catalyst exhibited an overpotential of 263 mV at 50 mA cm⁻² and a low Tafel slope of 53.74 mV dec cm⁻¹, with the Ce ion serving as the active center, reducing the potential barrier and optimizing the adsorption of oxygen species during the OER process [160].

The OER in acidic electrolytes is a crucial process for energy conversion technologies such as water splitting. However, challenges such as high overpotentials, catalyst instability, and dissolution under acidic conditions have driven the search for efficient and durable electrocatalysts to improve the OER performance in acidic environments. Therefore, Hao et al. demonstrated the rational tuning of RuO₂ electronic structure by introducing W and Er, significantly increasing oxygen vacancy formation energy. The $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ nanosheets exhibited a super-low overpotential of 168 mV (10 mA cm^{-2}) in 0.5M H₂SO₄ (Fig. 16p). In addition, W_{0.2}Er_{0.1}Ru_{0.7}O_{2-δ} demonstrated the highest reaction rate among the prepared catalysts, featuring a low Tafel slope of 66.8 mV dec⁻¹ (Fig. 16q). The stability of $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ was evaluated by calculating the gap between the final and initial overpotential ($\Delta \eta = \eta_{\text{final}} - \eta_{\text{initial}}$) from a chronopotentiometric test at 10 mA cm⁻². As shown in Fig. 16r, the catalyst exhibited excellent durability with a small increase of $\Delta \eta = 83$ mV over 250 h, and from 250 to 500 h, the overpotential increased by only 5 mV, further confirming the long-term stability of W_{0.2}Er_{0.1}Ru_{0.7}O_{2-δ} in acidic electrolyte. The potential-determining steps (PDS) for the designed catalysts occurred between OOH* and O*, with the calculated ΔG for PDS following the order: $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta-1}$ (0.53 eV) $< W_{0.2}Ru_{0.8}O_{2-\delta-1}$ (0.6 eV) < $Er_{0.1}Ru_{0.9}O_{2-\delta-1}$ (0.72 eV) < RuO $_2$ (0.79 eV), indicating that co-doping with W and Er reduces energy barriers and enhances activity. The upshift in the Ru 4d band centers, along with the formation of neighboring intermediates, further tunes the adsorption energy of oxygen intermediates and lowers the energy barriers for OER. Additionally, the calculated ΔG_2 for $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta-1}$ (1.01 eV) aligns with the theoretical value (1.23 eV), suggesting optimal activity and stability for acidic OER (Fig. 16s). These findings demonstrate that co-doping W and Er into RuO₂ effectively enhances both the stability and catalytic performance of the material by reducing V_O formation and suppressing the dissolution of soluble $\operatorname{Ru}^{x>4}$ [161].

Lanthanide-based nanomaterials, including nanosheets, heterostructure nanoflowers, and hybrid nanocomposites, have demonstrated significant potential as efficient OER electrocatalysts in both alkaline and acidic media. The introduction of lanthanide ions into these structures creates unique electronic environments, such as p-n heterojunctions, which enhance charge transfer and lower the energy barriers for OER process. These modifications similarly increase the sum of active sites, further improving catalytic performance. Additionally, the nanoflower morphology promotes high surface area and improved charge distribution in alkaline media, while nanosheet structures in acidic environments offer excellent performance because of its highsurface-area as well as enhanced electron transport properties. In alkaline conditions, lanthanide-based nanomaterials exhibit exceptional long-term stability and high performance, making them viable alternatives to precious metal catalysts. In acidic media, lanthanide-doped nanosheets help to overcome challenges such as catalyst instability and dissolution, maintaining high catalytic performance over extended periods. As a result, lanthanide-based nanomaterials, especially those in nanoflower and nanosheet forms, offer a cost-effective and durable solution for OER, making them highly suitable for renewable energy applications in both alkaline and acidic environments.

4.6. Other lanthanide-containing catalysts

Lanthanide-based chalcogenides, nitrides, borides, and phosphides



Fig. 17. (a) LSV, (b) Tafel slope, and (c) C_{dl} plot of CeO_2 catalysts. (d) LSV polarization curves before and after CP test. (e) Electrochemical measurements and OER mechanism. (f) Chronopotentiometry analysis of S-CeO₂ at 10 mA cm⁻². Reproduced with permission from ref. [165]. Copyright Elsevier Ltd. 2021. (g) 95 % iR-correction LSV curves and, (h) Corresponding Tafel plots of $CoS_{1.97}$, CeO_2 - $CoS_{1.97}$, $CoS_{1.97}$ - CeO_2 , commercial Ir/C catalyst. (i) Capacitive currents plotted against scan rates to determine ECSA. (j) CP analysis at 10 mA cm⁻² in 1.0 M KOH. 3D contour plot illustrating the electronic distribution around the Fermi level of (k) CeO_2 - $CoS_{1.97}$ and (l) $CoS_{1.97}$ -CeO₂. The PDOS of (m) $CoS_{1.97}$ -CeO₂. (n) OER energy pathway and (o) OER energy pathway at an applied potential of 1.23 V in an alkaline environment. Reproduced with permission from ref. [166]. Copyright Elsevier Ltd. 2021.

present a promising avenue for improving OER efficiency through anionic substitution. This approach is less explored compared to cationic modification, but it has the potential to significantly alter the electronic environment of lanthanide centers. The incorporation of sulfur, nitrogen, boron, or phosphorus anions and other materials can directly influence the electronic properties of the material by altering metal-anion bonds, which is more impactful than cationic substitution that typically changes the composition without affecting these critical bonds.

Anionic substitution preserves or enhances catalytic efficiency by maintaining the number of catalytically active metal centers. In contrast, cationic substitution may inadvertently replace active sites with inactive species, which can reduce catalytic activity [162–164]. Therefore, anionic substitution in lanthanide-based materials can improve the electronic structure, surface characteristics, and overall OER catalytic performance in alkaline and acidic media.

For example, *Rajapriya, Keerthana*, et al., synthesized heteroatomdoped CeO_2 using a hydrothermal method, demonstrating the effect of anionic doping on OER performance. Incorporating heteroatom into the CeO₂ framework enhances electronic conductivity, creates active sites, and boosts electrochemical catalytic performance, facilitating the water oxidation process. The OER activity of S-CeO₂ exhibits the lowest overpotential of 190 mV compared to other prepared electrocatalysts (Fig. 17a). The kinetic study indicates a Tafel slope of 83 mV dec⁻¹ for S-CeO₂ is (Fig. 17b). The S-CeO₂ catalyst, in particular, exhibited the highest catalytic activity and a higher electrochemical C_{dl}, improving access to active sites and enhancing OER performance (Fig. 17c).

During the OER, intermediates like M-OH, M-OOH, and M-O are formed, which act as catalytic sites. These intermediates facilitate oxygen release ($M + O_2$) by reducing energy barriers and enhancing the reaction efficiency. These intermediates play crucial part in proton and electron transport, influencing the catalytic performance of the OER. To evaluate the CP stability test of S-CeO₂, LSV curves were obtained before and after 10,000 s (Fig. 17d). Fig. 17e illustrates the electrochemical assessments and the underlying mechanism of OER activity for the S-CeO₂ catalyst. The catalyst maintained 97 % of its activity, demonstrating excellent stability after this prolonged assessment. Further



Fig. 18. (a) LSV polarization curves and (b) Tafel slopes of CeO₂, Nd₂CeO₇ and RE₂Ce₂O₇. (c) ECSA shown in black and roughness factor (RF) presented in green. (d) Nyquist plots. (e) CP stability of RE₂Ce₂O₇ at10 mA cm⁻², with inset showing OER polarization plots of RE₂Ce₂O₇ before and after the CP test. Reproduced with permission from ref. [168]. Copyright Wiley-VCH 2024. (f) Co K-edge EXAFS of LaCo films. Electrochemical activity of 0–17 % LaCo films was evaluated at pH 2 in 10 mM H₂SO₄ with 200 mM K₂SO₄ as the supporting electrolyte. (g) Cyclic voltammograms at 100 mV s⁻¹ show increasing cathodic current for the Co^{3+/2+} redox feature with higher La concentration (inset). (h) Overpotential for OER at 1 mA cm⁻² and (i) Tafel slopes were measured, with errors determined from three independent films. (j) *Operando* Co K-edge EXAFS spectra of 0 % LaCo and 17 % LaCo films collected after 30 min of OER at 2.08 V vs. NHE in 10 mM H₂SO₄ with 200 mM K₂SO₄ (pH 2). Reproduced with permission from ref. [169]. Copyright © 2024 American Chemical Society. (k) *iR*-corrected (95 %) OER curves and (l) Tafel plots of synthesized RuO₂, Er-RuO_x, and commercial RuO₂. (m) CP at 10 mA cm⁻². (n) Calculated PDOS of Ru *d*, O *p*, and Er *f* orbitals in Er-RuO_x. (o) Calculated PDOS of the Ru *d*_{z2} orbital in RuO₂ and Er-RuO_x. Reproduced from ref. [170]. (CC BY 4.0), Nature Portfolio 2024. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

stability tests using chronopotentiometry for 20 h at 10 mA cm⁻², (Fig. 17f) showed minimal variation, confirming the exceptional durability of S-CeO₂. This prolonged stability is attributed to the petal-like structure of S-CeO₂, which increases the number of active sites accessible for oxygen evolution, thus ensuring long-term efficiency in OER performance [165].

In another study, Dai et al. explored two materials, CeO2-CoS1.97 and CoS_{1.97}-CeO₂ for surface decoration to explore the role of spatial structure in the enhanced OER activity. Their results show that CeO₂-CoS_{1.97} has lowest overpotential of 264 mV at 10 mA cm⁻², which is attributed to the stable heterostructure and efficient mass transfer (Fig. 17g). In comparison, $CoS_{1.97}$ -CeO₂ has 49 mV dec⁻¹ Tafel slope as compare to other catalyst, showing better OH⁻ adsorption as well as faster electron transport (Fig. 17h). The C_{dl} study show that $\text{CeO}_2\text{-}\text{CoS}_{1.97}$ has the largest C_{dl} value (8.96 mF cm⁻²) compared to other prepared catalysts, which suggests that CeO2-CoS1.97 possesses more reactive sites, which is attributed to the high degree of disorder in the lattice (Fig. 17i). In addition to high activity, long term durability is also necessary for practical applications. Fig. 17j shows that the heterostructure can maintain a lowest overpotential at current density of 10 mA cm⁻² for more than 50 h with no significant increase observed in overpotential, whereas $CoS_{1.97}$ shows a detectable decay within 24 h.

Moreover, theoretical calculations show that the spatial structure efficiently modifies electronic structure to facilitate the transition from sulfide to hydroxide in favor of higher oxidation states. The elevated surface electroactivity promotes efficient electron transfer between $CeO_2-CoS_{1.97}$ and the adsorbate (Fig. 17k). In contrast, $CoS_{1.97}$ -CeO₂ exhibits a unique electronic structure. Due to the strong interaction with CeO₂, the interfacial region shows electron-rich characteristics, this

enhances electron transfer during the OER, with surface oxygen vacancies of CeO₂ actively facilitating *OH adsorption. Additionally, the presence of CeO₂ on the surface helps prevent the oxidation of CoS_{1.97} and minimizes Co leakage during OER. (Fig. 17l). The PDOS analysis reveals that the Co 3*d* peak of CoS_{1.97}-CeO₂ is positioned near the Fermi level (E_F) at EV-1.29 eV (with EV defined as 0 eV), indicating a higher Co³⁺ concentration. The *s* and *p* orbitals of the S site extend broadly, even crossing the E_F, demonstrating excellent conductivity. Meanwhile, the *s* and *p* orbitals of the O site are situated below the Co 3*d* orbitals, ranging from EV 0.60–4.90 eV. Additionally, the overlap between the Ce 4*f* and Co 3*d* orbitals facilitates electron transfer at the interface (Fig. 17m).

Reaction pathway and overpotential studies shows that CoS_{1.97}-CeO₂ as well as CeO2-CoS1.97 both face the largest energy barriers (1.46 and 1.47 eV) in the alteration from $[O^* + H_2O + 2OH^- + 2e^-]$ to $[OOH^* +$ $H_2O + OH^- + e^-$]. CeO₂-CoS_{1.97} has a stronger desorption capacity in the final OER step due to a smaller energy barrier (Fig. 17n). CoS_{1.97}-CeO₂ has stronger *OH adsorption capacity, while CeO₂-CoS_{1.97} allows spontaneous conversion of *OH to O*. The high performance of the OER is supported by the fact that neither of these structures appears to be a barrier in the last reaction of $[O_2 + 2H_2O]$. CoS_{1.97}-CeO₂ has a calculated overpotential of 0.24 eV and CeO2-CoS1.97. The calculated value of overpotential for is 0.23 eV and the mass transfer advantage is in favor of CeO₂-CoS_{1.97} (Fig. 17o) [166]. DFT calculations reveal that CeO₂ significantly enhances the OER performance of CoS_{1.97} by stabilizing its oxidation state and preventing Co leakage. The strong interaction between CeO₂ and CoS_{1.97} creates an electron-rich interfacial region, which facilitates electron transfer and supports *OH adsorption on CeO₂ in alkaline media. This CeO_2 -CoS_{1.97} interface, with overlapping Ce 4f

Table 4

Lanthanide-based materials for OER electrocatalysis.

Transition metals							
Electrocatalyst	Fabrication method	Electrolyte	Current density (mA cm ⁻²)	Overpotential (mV)	Tafel slope (mV dec^{-1})	Stability (h)	Ref.
NiFeCe oxyhydroxide	Sol-gel	1.0 M KOH	50	284	61.5	8.3	[94]
Nd ₂ Ce ₂ O ₇	Evaporation-induced self-assembly (EISA)	1.0 M KOH	10	243	47.9	16	[171]
CeLaCoNiFe	Co-precipitate	1.0 M KOH	10	175	79.5	120	[172]
Sm-doped AgNbO3	Sonication technique	1.0 M KOH	10	203	35.22	50	[173]
SmFeO ₃ /rGO	Sonication technique	1.0 M KOH	10	180	34	55	[174]
Ni,Co,Yb–FeOOH	Hydrothermal	1.0 M KOH	10	230.9	22.7	26	[175]
Ni ₃ Fe LDH/NiFe ₂ O ₄ /Pt–Tm	Chemical Reduction and Hydrothermal	1.0 M KOH	10	224	54.81		[176]
Gd _{1-x} FeO ₃	Sol-gel	1.0 M KOH	10	413	88	8	[177]
CeO ₂ /NiO-2	Solvothermal	0.1 M KOH	10	320	69.9	5	[178]
20-NiO@CeO ₂	Co-precipitation	1.0 M KOH	50	390	156	6	[179]
Fe-Ni ₂ P/CeO ₂	Hydrothermal	1.0 M KOH	20	190	31.42	120	[180]
NdNi-Co ₃ O ₄	Hydrothermal	0.1 M KOH	10	269	54	50	[181]
DyNiO ₃	Hydrothermal	1.0 M KOH	10	265	78	49	[182]
α-CoGd(OH) ₂ /FIO P-Gd SAs@MnO ₂	Ar-plasma assisted anchoring	1.0 M KOH 1.0 M KOH	100	327 281	84.6 161.9	24 25	[183]
MOE							
Fr-MOF/Fe-O-	Hydrothermal	1.0 M KOH	10	216	47	25	[185]
Dva - Fe-MOF	Solvothermal	1.0 M KOH	10	210	47 82	30	[186]
FeDv@MOF-Ni/CC	Hydrothermal	1.0 M KOH	10	250	52 1	80	[187]
CoMpLa-MOF	Solvothermal	1.0 M KOH	10	201	95	25	[137]
Ce-MOF-NH ₂ /NF	Hydrothermal	1.0 M KOH	10	328	68	10	[188]
Dy ₂ O ₃ /rGO	Hydrothermal	1.0 M KOH	10	251	36	50	[189]
Sm ₂ O ₃ @PPy	Hydrothermal	1.0 M KOH	10	272	34	24	[190]
CeO ₂ /C	Hydrothermal	1.0 M KOH	10	297	46	15	[191]
CoCe-MOF/CP	Solvothermal	1.0 M KOH	10	267	96.1	100	[113]
MXene@Ce-MOF	Hydrothermal	1.0 M KOH	10	270	163.3	12	[192]
Ce-doped-MIL-88B(Ni)/NF	Solvothermal	1.0 M KOH	10	205	46.09	146	[114]
Er _{0.4} Fe-MOF/NF	Solvothermal	1.0 M KOH	100	248	73	100	[115]
Pr-MOF/Fe ₂ O ₃	Solvothermal	1.0 M KOH	10	238	37	40	[112]
NH ₂ functionalized Sm- MOF)	Hydrothermal	1.0 M KOH	10	443	95.1	12	[140]
Perovskites							
La _{0.6} Sr _{0.4} Co _x Ni _{1-x} O _{3-δ}	Electro-spinning	1.0 M KOH	20	363	149.87	50	[193]
LaFe0.8Co0.2O3/Ni(OH)2	Sol-gel	1.0 M KOH	10	329	95	24	[194]
La _{1-x} Pr _x CoO ₃	Sol-gel	1.0 M KOH	10	312	80.6	12	[195]
La _{0.2} Sr _{0.8} FeO ₃	Microwave	1.0 M KOH	10	339	56.84	16	[196]
NdFe _{1-x} Ni _x O ₃	Sol-gel	1.0 M KOH	10	310	149	60	[197]
GdFe _{1-x} Cu _x O ₃	Sol-gel	1.0 M KOH	10	367	105	8	[198]
LaFe _{0.75} Cr _{0.15} Mo _{0.10} O ₃ /NF	Sol-gel combustion	1.0 M KOH	10	263	97	10	[199]
LaFexNi _{1-x} O ₃ NRs	Hydrothermal	1.0 M KOH	10	302	50	20	[200]
La _{0.7} Sr _{0.3} MnO ₃ /Co-Pi	Solid-state reaction method	1.0 M NaOH	10	220	62	16	[201]
$LaSr_{3}Co_{1.5}Fe_{1.5}O_{10\cdot\delta}$	Sol-gel	0.1 M KOH	10	324	58	2.78	[202]
Nanomaterials	** 1 .1 1	1.0.1	10	000		05	[000]
La-CoAg/NF	Hydrothermal	1.0 M KOH	10	233	44.3	35	[203]
NiFeLa-LDH/v-MXene/NF	Electrodeposition	1.0 M KOH	100	255	40	1200	[204]
Ce LDH	Electrodeposition	1.0 M KOH	10	207	37.3	200	[205]
$Ce-m-NI(OH)_2@NI-MOF$	Electrodeposition	1.0 M KOH	100	2/2	42.2	30	[206]
$(CO(OH)_2)_4$ -@-La(OH)_3	Flectrospinning	1.0 M KOH	10	233	76.78	130	[207]
$P_{-Ce} SAs@CoO$	Dlasma_(D)_assisted strategy	1.0 M KOH	10	250	70.78	25	[208]
ProIroOz	Sol-gel	0.1 m HClO	10	201	75	25	[200]
$C_0C_{e-600} N_2$	Pyrolysis	0.1 M KOH	10	274	- 58.3	12	[210]
Ce-doped IrO ₂	Hydrothermal	0.5 M H ₂ SO ₄	10	240	57	50	[211]
Ce _{0.2} -IrO ₂ @NPC	Pyrolysis	0.5 M H ₂ SO ₄	10	224	55.9	100	[212]
Others							
CoP ₂ /CeO ₂ /C	Hydrothermal	1.0 M KOH	10	339.2	80	30	[213]
Ni ₃ N–CeO ₂ /NF	Hydrothermal	1.0 M KOH	50	341	64.44	40	[214]
Ni/CeO2@N-CNFs	Electrospinning	1.0 M KOH	10	230	54.2	55	[215]
CeO ₂ - Ni ₃ S ₂	Hydrothermal	1.0 M KOH	10	251	60	50	[216]
Ni ₅ P ₄ /CePO ₄ NPs	Hydrothermal	1.0 M KOH	10	191	39.26	10	[217]
Gd-CoB	Electrodeposition	1.0 M KOH	10	230	42	35	[218]
NiSe ₂ /CeO ₂	Hydrothermal	1.0 M KOH	10	250	66	7	[219]
Eu-Ni(PO ₃) ₂	Hydrothermal	1.0 M KOH	10	273	39.4	27	[220]
CeO _x /TbCoP	Hydrothermal	1.0 M KOH	50	358	43	40	[221]

(continued on next page)

Table 4 (continued)

Transition metals							
Electrocatalyst	Fabrication method	Electrolyte	Current density (mA cm ⁻²)	Overpotential (mV)	Tafel slope (mV dec ⁻¹)	Stability (h)	Ref.
N-CoP/CeO2	Hydrothermal	1.0 M KOH	10	215	1008	42	[222]
S-Ni(OH) ₂ /CeO ₂ /NF	Hydrothermal	1.0 M KOH	10	196	85	150	[223]
CeO ₂ -GO-3	Pyrolysis	1.0 M KOH	10	240	176	10	[224]
La-doped-FeNi-Se/NF	Co-precipitation	1.0 M KOH	10	158	35.6	20	[225]
Pt _{0.1} La _{0.1} -IrO ₂ @NC	Pyrolysis	$0.5MH_2SO_4$	10	205	50.9	135	[226]

and Co 3*d* orbitals, improves conductivity and electron mobility. Additionally, DFT insights indicate favorable mass transfer and a reduced energy barrier in the final OER step for CeO₂-CoS_{1.97}, highlighting it as a highly efficient electrocatalyst. Furthermore, *Mishra* et al. synthesized phase-pure rare-earth oxyselenides RE₄Ga₂Se₇O₂ (RE = Pr, Nd) using the sealed-tube solid-state reaction method at 950 °C. These compounds adopted a novel orthorhombic structure and exhibit an almost direct optical band gap of 1.70 eV. The Pr-based material demonstrated superior OER performance in 1 M KOH, achieved a lower overpotential of 257 mV at 10 mA cm⁻² as well as exceptional stability, greater mass activity of 70.1 A g⁻¹, and a TOF of 0.0234 s⁻¹, making it highly efficient for electrocatalytic applications [167].

Moreover, Paladugu et al. used the evaporation-induced self-assembly (EISA) technique to prepare highly porous cerate-based fluorite nanocatalysts, demonstrating that substituting Ce with rare earth (RE) cations enhances OER performance in alkaline media. The novel compositionally complex fluorite catalyst, (La_{0.2}Pr_{0.2}Nd_{0.2}Tb_{0.2}Dy_{0.2})₂. $Ce_2O_7,$ exhibited lower overpotential of 210 mV at 10 mA \mbox{cm}^{-2} (Fig. 18a), as ascribed to its increased oxygen Frenkel defects and enhanced compositional complexity. Tafel plots derived from LSV curves were utilized to evaluate the OER reaction kinetics of the electrocatalysts. Fig. 18b demonstrates that RE₂Ce₂O₇ achieved the lowest Tafel slope of 43.1 mV dec $^{-1}$, reflecting its enhanced OER performance. The ECSA and roughness factor revealed that RE₂Ce₂O₇ exhibited the largest ECSA (Fig. 18c), attributed to its nanocrystalline nature, while CeO₂ had the lowest due to its crystalline morphology. The high ECSA of RE₂Ce₂O₇ emphasizes the importance of morphology in OER activity, as a larger ECSA increases the number of active sites, enhances electrolyte infiltration, as well as enhances catalyst-electrolyte interactions, leading to superior OER performance. The EIS spectra revealed that RE₂Ce₂O₇ exhibited lower R_{ct} of 3.02 Ω at 1.55 V versus RHE, compared to other prepared catalysts, indicating superior charge transfer kinetics (Fig. 18d). This highlights the enhanced electrokinetic performance of RE2Ce2O7 for OER, enabling efficient interaction among electrolyte and catalyst surface. The long-term chronoamperometric stability tests showed robust performance for RE₂Ce₂O₇ (60 h) under constant potentials of 1.65 V (Fig. 18e). The OER polarization plot of RE₂Ce₂O₇ remained unchanged after the stability study (inset in Fig. 18e), highlighting its excellent mass transfer properties and mechanical durability in alkaline environments [168].

In another study, *Hartnett* et al. demonstrated that incorporating La³⁺ into Co₃O₄ using the sol-gel method enhances OER performance in acidic media by promoting lattice deconstruction and amorphization. The overpotential for OER decreased with increasing La³⁺ concentration, achieving maximum activity at 17 % La incorporation. The enhanced catalytic performance is ascribed to the increased number of active edge sites formed upon Co₃O₄ lattice deconstruction. EXAFS analysis of as-synthesized LaCo films reveals a loss of structural order with increasing La composition. The Co K-edge EXAFS (Fig. 18f) show reduced peak intensities at all radial distances, particularly at 3.35 Å (O_h…T_d distance) and 5.06 Å (Co³⁺(O_h) in cubane-cubane subunits), indicating that La incorporation disproportionately affects T_d Co sites. The cyclic voltammograms (Fig. 18g) of 0–17 % LaCo films in acidic solution (pH 2) show the Co³⁺/²⁺ redox feature, with 100 % faradaic efficiency confirmed by gas chromatography. The 17 % LaCo catalyst

exhibited the lowest OER overpotential (Fig. 18h) and highest exchange current density (Fig. 18i), although compositions above 17 % showed increased overpotential, indicating a decline in catalytic activity. The Tafel slopes remained consistent across all compositions (76-88 mV dec^{-1}), suggesting that La^{3+} incorporation does not alter the OER mechanism. Operando EXAFS measurements revealed increased catalyst disorder with La incorporation, providing insights into the evolution of the active phase during OER (Fig. 18j). Spectra collected before and during OER at 2.08 V vs. NHE showed pronounced structural disorder with increasing La content, including a loss of T_d Co sites reflected by decreased peak intensity at 3.35 Å. The 17 % LaCo catalyst exhibited additional features, such as a shoulder at 4.8 Å and increased intensity at 5.6 Å, consistent with interlayer Co distances in layered $CoO_x(OH)_y$ and La_{0.3}CoO₂ structures. These results suggest that La³⁺ incorporation deconstructs the Co_3O_4 lattice, forming an amorphous layered $CoO_x(OH)_v$ phase with La^{3+} residing at particle interfaces [169].

Furthermore, Li et al. demonstrated that introducing lanthanides with gradually changing electronic configurations enables precise modulation of Ru–O covalency in RuO_x. The OER activity of Er-RuO_x was assessed in 0.5 M H₂SO₄, showing superior activity compared to commercial and synthesized RuO2. Er-RuOx needed an overpotential of only 200 \pm 8 mV at 10 mA cm⁻², significantly lower compared to other catalysts (Fig. 18k). It also exhibited a lower Tafel slope of $45 \,\mathrm{mV} \,\mathrm{dec}^{-1}$, demonstrating improved reaction kinetics (Fig. 181). The catalytic durability of Er-RuO_x was assessed via chronopotentiometry at $10 \,\mathrm{mA\,cm^{-2}}$ (Fig. 18m), indicating significantly greater stability compared to commercial RuO2. After 73 h, the overpotential of commercial RuO₂ rose by 674 mV, which is about 35.5 times greater than that of Er-RuO_x, emphasizing the positive effect of Er in enhancing catalytic stability. The enhance OER activity of Er-RuOx was investigated by analyzing the adsorption behavior of oxygen intermediates. Er-RuO_x shows lowest Ru d-band center (-1.945eV) compared to RuO₂ (-1.900 eV), suggesting that 4f-2p-4d orbital hybridization alters the electronic environment of Ru d orbitals. Additionally, the Ru d_{z2} -state energy level of Er-RuO_x (-0.855 eV) is nearer to the Fermi level compare to RuO₂ (-2.171 eV), reducing antibonding state occupancy and stronger *OH adsorption (Figs. 18n-o) [170]. These findings highlight that the hybridization of orbitals in Er-RuOx efficiently tunes the electronic structure, enhancing *OH adsorption and ultimately driving superior OER performance. Lanthanide incorporation demonstrates significant potential for optimizing electronic structures to achieve improved OER performance as well as stability in acidic media.

Lanthanide-based materials offer significant advantages in enhancing OER electrocatalysts for energy conversion processes like water splitting. Their exceptional catalytic activity and stability are rooted in their unique electronic properties, including multiple oxidation states, large ionic radii, and strong spin-orbit coupling. These attributes enable lanthanides to modify the electronic structures of catalytic systems, stabilize active sites, and improve overall OER efficiency. Under OER conditions, lanthanide-based transition metal compounds synergize with the catalytic activity of transition metals, leveraging lanthanides unique electronic properties to enhance performance in alkaline and acidic media.

Lanthanide-based MOFs, with their large surface areas and tunable porosity, facilitate mass transport and access to active sites, while perovskites among the most stable and catalytically effective lanthanide-based materials offer distinctive characteristics that boost system efficiency. Lanthanide-containing chalcogenides, nitrides, borides, and phosphides further optimize electronic structures, delivering promising OER performance. These materials harness the unique properties of lanthanides to improve renewable energy applications, showing superior catalytic performance, durability, and resistance to degradation under extreme electrochemical conditions, as evidenced in recent studies (Table 4).

One of the most critical aspects of lanthanide-based materials is their ability to reduce reliance on rare noble metals like Pt and Ir, making them crucial for developing cost-effective and sustainable energy solutions. The strategic integration of lanthanides into catalytic frameworks is expected to advance renewable energy options, driving the commercialization of water-splitting technology and related applications. As research progresses, lanthanide-based materials are poised to play a vital role in the global transition to sustainable energy.

Incorporating heteroatoms such as sulfur, nitrogen, boron, phosphorus, and other materials into lanthanide-based materials enhances their catalytic performance and stability. These materials have the potential to become inexpensive as well as durable alternatives for advanced energy conversion technologies, further solidifying their role in the future of renewable energy.

5. Conclusion and future directions

Lanthanide-based materials have emerged as highly effective electrocatalysts for the OER, showcasing exceptional catalytic activity, stability, and efficiency in energy conversion processes such as water splitting. The distinctive electronic properties of lanthanides, including multiple oxidation states, large ionic radii, and strong spin-orbit coupling, allow these elements to significantly enhance catalytic activity by modifying electronic structure of catalytic systems, stabilizing active sites, and improving charge transfer. Lanthanide-based transition metal compounds, metal-organic frameworks (MOFs), perovskites, and chalcogenides, nitrides, borides, and phosphides all demonstrate remarkable promise as OER catalysts, due to their tunable porosity, high surface areas, optimized electronic structures, and durability in extreme electrochemical conditions. Among these materials, lanthanide-based perovskites stand out due to their stability and unique catalytic properties, establishing them as some of the most compelling choices for OER applications Moreover, lanthanide-containing chalcogenides, nitrides, borides, and phosphides offer an alternative approach through anionic substitution, further optimizing the electronic properties and catalytic efficiency. Incorporating heteroatoms including S, N, B, and P into lanthanide-containing materials has also been shown to improve catalytic activity and durability, making these materials potential substitutes for noble metals including platinum as well as iridium in OER catalysis. As the worldwide demand for sustainable and cost-effective energy solutions grows, lanthanide-based materials are well-positioned to play a critical part in advancing renewable energy technologies. Their ability to reduce the reliance on rare and expensive noble metals while maintaining superior performance underscores their potential for large-scale implementation in energy storage as well as conversion systems. To further advance the application of lanthanide-based materials in OER catalysis, the following research directions are critical.

- 1. Enhancing conductivity: Many lanthanide-based materials, especially MOFs, suffer from low electrical conductivity, which limits their catalytic efficiency. Future studies should investigate novel methods for improving the electronic conductivity of these materials, such as heteroatom doping, hybridization with conductive materials, or defect engineering.
- 2. Exploring new lanthanide-based compounds: Beyond the commonly studied lanthanides, researchers should explore underutilized lanthanide elements and their combinations with

different transition metals or anions (e.g., nitrides, borides, and chalcogenides) to uncover new materials with enhanced catalytic properties.

- 3. Improving durability and long-term stability: While lanthanidebased materials have shown remarkable stability under OER conditions, further studies are needed to ensure their durability over extended periods, especially in real-world applications. Strategies such as protective coatings, surface passivation, or structural reinforcement could be explored to prolong catalyst life.
- 4. Commercial scalability: Scaling up the production of lanthanidebased OER catalysts for commercial applications is a key future direction. Researchers should concentration on emerging inexpensive, sustainable preparation approaches that enable the mass production of these electrocatalysts without compromising their catalytic activity.
- 5. Integration with renewable energy systems: Incorporating lanthanide-based OER electrocatalysts into comprehensive energy conversion and storage systems, including batteries, fuel cells, and electrolyzers, will be critical for their practical implementation. Future studies should explore the synergy between lanthanide-based materials and other components in renewable energy devices to maximize efficiency and performance.
- 6. Catalysts with multi-metals synergistic effects: Design and development of novel electrocatalysts with multi-metal synergistic effects involve studying the interactions between different lanthanide elements and between lanthanides and other transition metals. By exploring these synergistic effects, catalysts with multi-metal centers can be developed. By carefully controlling the proportion and distribution of metal ions, the electronic structure can be optimized, active sites enhanced, and catalytic performance significantly improved. This approach allows for fine-tuning of the catalyst properties to achieve superior efficiency and stability in OER applications.
- 7. Theoretical calculation assistance: Combining theoretical calculation methods such as DFT, simulating the electronic structure, adsorption performance, and reaction pathway of electrocatalysts, predicting the performance of catalysts, and explaining experimental phenomena. Theoretical calculations can help screen potential catalyst structures and provide directions and ideas for experimental research.
- 8. In-depth understanding of catalytic mechanisms: Advanced characterization techniques such as in-situ XAS, in-situ Raman, and in-situ FTIR spectroscopies are used to monitor the structural changes, electronic state changes, and the formation of intermediates of the catalyst in real-time during the reaction process, offering a comprehensive insight into the mechanisms and pathways involved in catalytic reactions. This will help reveal the active sites of the catalyst and key steps in the reaction process, providing theoretical guidance for the design and optimization of catalysts.
- 9. Catalysts based on nanostructures: Using nanotechnology to prepare lanthanides OER catalysts with special morphologies and sizes, such as nanoparticles, nanowires, nanosheets, etc., can provide more active sites, higher specific surface area, and better electron transfer performance, thereby improving the activity and efficiency of the catalyst.
- 10. Substrate: Graphite or carbon substrates face challenges in lanthanides catalysts due to weak interaction with the catalyst, leading to poor adhesion and reduced stability under harsh reaction conditions. Additionally, surface passivation can occur, diminishing catalytic activity over time. To address these issues, carbon surfaces might be functionalized by doping with heteroatoms (such as N, B) or introducing defects to improve the interaction between the lanthanide catalyst and the substrate. Another solution is designing hybrid structures by combining



Fig. 19. Challenges and future directions.

carbon substrates with conductive polymers or MOFs, which can enhance stability, conductivity as well as the density of active sites, thus boosting overall catalytic performance.

- 11. Other challenges: Lanthanide-based OER electrocatalysis faces significant challenges, including difficulties in mass production, high raw material costs, low surface area, poor utilization of active sites, slow reaction kinetics, and high-cost, complex, and time-consuming synthesis methods (Fig. 19). To address these issues, future research should focus on developing scalable as well as inexpensive synthesis techniques, including sol-gel processes, hydrothermal methods, or 3D printing, to streamline production. Incorporating abundant and inexpensive dopants or combining lanthanides with transition metals to form hybrid catalysts can reduce material costs. Enhancing surface area and active site exposure through nanostructuring and porous architecture design is crucial. Strategies like interface engineering, electronic structure tuning, and optimizing reaction conditions can improve active site utilization and accelerate reaction kinetics. Furthermore, leveraging computational modeling and machine learning can guide the efficient design of highperformance lanthanide-based materials, ensuring economic and technical viability for OER applications.
- 12. Collaborative efforts between academia and industry: Collaborative initiatives among academic institutions and industries are crucial for bridging the divide between research innovations and their practical commercialization. Joint R&D programs can accelerate the translation of laboratory discoveries into

commercial products, while industry-focused research addresses real-world challenges like scaling production and integrating catalysts into renewable energy systems. Establishing standardized protocols for evaluating catalyst performance and durability under industrial conditions will further ensure practical applicability and reliability.

13. Integration with broader energy solutions: Lanthanide-based OER catalysts should be integrated into broader renewable energy systems to maximize their impact. Hybrid systems combining lanthanide-based materials with technologies like solar photovoltaics and wind energy can create efficient, interconnected energy solutions. Additionally, adopting circular economy approaches, such as recycling spent catalysts to recover valuable lanthanides, will enhance sustainability and reduce resource dependency.

In conclusion, by addressing the challenges of conductivity, stability, and scalability, lanthanide-based materials hold immense potential for revolutionizing OER and renewable energy applications. Advancing research through computational modeling, synergistic doping, and integration with renewable systems, while fostering collaboration among academia and industry, will accelerate the progress of inexpensive, high-performance electrocatalysts. These efforts will play a key role in driving the global shift to a sustainable energy future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

References

- [1] C. Liu, D. Wang, Appl. Surf. Sci. 627 (2023) 157318.
- [2] D. Wang, L. Jin, M. Liu, T.G. Lee, S.G. Peera, C. Liu, Mol. Cata. 535 (2023) 112879.
- [3] A. Vojdani Saghir, S. Mollazadeh Beidokhti, J. Vahdati Khaki, Ceram. Int. 50 (2024) 24070–24087.
- [4] Y. Wu, Z. Xiao, Z. Jin, X. Li, Y. Chen, J. Colloid Interface Sci. 590 (2021) 321-329.
- [5] S.K.M. Balgehshiri, B. Zohuri, J. Econom. Manag. Res. 4 (2023) 2–7.
- [6] G. Barati Darband, M. Aliofkhazraei, A.S. Rouhaghdam, J. Colloid Interface Sci. 547 (2019) 407–420.
- [7] G.B. Darband, M. Aliofkhazraei, S. Shanmugam, Renew. Sust. Energ. Rev. 114 (2019) 109300.
- [8] Q. Fu, T. Xu, D. Wang, C. Liu, Carbon 223 (2024) 119045.
- [9] N. Elsayed, M.M. El-Rabiei, M. Negem, F.E.-T. Heakal, Electrochim. Acta 404 (2022) 139783.
- [10] H. Hu, X. Zhang, K. Zhang, Y. Ma, H. Wang, H. Li, H. Huang, X. Sun, T. Ma, Adv. Energy Mater. 14 (2024) 2303638.
- [11] T. Zhang, K. Yang, C. Wang, S. Li, Q. Zhang, X. Chang, J. Li, S. Li, S. Jia, J. Wang, Adv. Energy Mater. 8 (2018) 1801690.
- [12] J. Ran, Z. Zhang, H. Feng, H. Zhao, D.-F. Chai, X. Huang, W. Zhang, M. Zhao, G. Dong, Y. Zang, Int. J. Hydrog. Energy 64 (2024) 935–946.
- [13] P.R. Chowdhury, H. Medhi, K.G. Bhattacharyya, C.M. Hussain, Coord. Chem. Rev. 501 (2024) 215547.
- [14] S.H. Chang, M.F. Rajuli, Int. J. Hydrog. Energy 84 (2024) 521-538.
- [15] A. Lahrichi, Y. El Issmaeli, S.S. Kalanur, B.G. Pollet, J. Energy Chem. 94 (2024) 688–715.
- [16] Y. Nam, D. Jin, S. Choi, D.H. Hong, H.R. Moon, Y. Lee, Appl. Surf. Sci. 644 (2024) 158741.
- [17] J. Cao, D. Zhang, B. Ren, P. Song, W. Xu, Chin. Chem. Lett. 35 (2024) 109863.
- [18] T. Xu, D. Wang, Q. Fu, C. Liu, Langmuir 40 (2024) 16463–16472.
- [19] Y. Liu, M. Liao, Y. Hu, T.-G. Lee, R. Koutavarapu, S.G. Peera, C. Liu, Batteries 9 (2023) 175.
- [20] D. Wang, K. Wu, T. Xu, S.G. Peera, C. Liu, Mol. Cata. 550 (2023) 113537.
- [21] S. Aralekallu, K.S. Lokesh, V. Singh, Fuel 357 (2024) 129753.
- [22] T. Xu, D. Wang, Q. Fu, K. Wu, C. Liu, Mol. Cata. 559 (2024) 114053.
- [23] S.G. Peera, T.G. Lee, A.K. Sahu, Sustain. Energy Fuel 3 (2019) 1866–1891.
- [24] Q. Fu, T. Xu, D. Wang, C. Liu, J. Phys. Chem. C 128 (2024) 11210–11218.
- [25] W. Zhao, F. Xu, J. Yang, X. Hu, B. Weng, Inorg. Chem. 63 (2024) 1947–1953.
- [26] D. Wang, M. Liao, L. Jin, K. Wu, S.G. Peera, C. Liu, Inorg. Chem. 62 (2023) 20390–20400.
- [27] D. Duan, C. Hao, W. Shi, H. Wang, C. Ma, X. Song, Z. Sun, Appl. Surf. Sci. 484 (2019) 354–364.
- [28] M.H. Miles, J. Electroanal. Chem. 60 (1975) 89-96.
- [29] J. Xia, H. Zhao, B. Huang, L. Xu, M. Luo, J. Wang, F. Luo, Y. Du, C.-H. Yan, Adv. Funct. Mater. 30 (2020) 1908367.
- [30] H. Zhang, Y. Wang, D. Song, L. Wang, Y. Zhang, Y. Wang, Nanomaterials 13 (2023) 1921.
- [31] Q. Li, L. Song, Z. Liang, M. Sun, T. Wu, B. Huang, F. Luo, Y. Du, C.-H. Yan, Adv. Energy Sust. Res. 2 (2021) 2000063.
- [32] H. Sun, X. Xu, H. Kim, W. Jung, W. Zhou, Z. Shao, Energy Environ. Mater. 6 (2023) e12441.
- [33] L. Peng, Z. Wei, Engineering 6 (2020) 653–679.
- [34] D. Likius, A. Rahman, C. Zivayi, V. Uahengo, Catal. Lett. 150 (2020) 1942–1956.
 [35] H. Zhong, Q. Zhang, J. Yu, X. Zhang, C. Wu, Y. Ma, H. An, H. Wang, J. Zhang,
- X. Wang, J. Xue, Adv. Energy Mater. 13 (2023) 2301391. [36] L. Chen, W. Zhao, J. Zhang, M. Liu, Y. Jia, R. Wang, M. Chai, Small 20 (2024)
- 2403845.
- [37] Z.-F. Huang, J. Song, S. Dou, X. Li, J. Wang, X. Wang, Matter 1 (2019) 1494–1518.
- [38] D.-Y. Kuo, H. Paik, J. Kloppenburg, B. Faeth, K.M. Shen, D.G. Schlom, G. Hautier, J. Suntivich, J. Am. Chem. Soc. 140 (2018) 17597–17605.

- [39] J. Song, C. Wei, Z.-F. Huang, C. Liu, L. Zeng, X. Wang, Z.J. Xu, Chem. Soc. Rev. 49 (2020) 2196–2214.
- [40] A. Lončar, D. Escalera-López, S. Cherevko, N. Hodnik, Angew. Chem. Int. Ed. 61 (2022) e202114437.
- [41] N.-T. Suen, S.-F. Hung, Q. Quan, N. Zhang, Y.-J. Xu, H.M. Chen, Chem. Soc. Rev. 46 (2017) 337–365.
- [42] Z. Lei, T. Wang, B. Zhao, W. Cai, Y. Liu, S. Jiao, Q. Li, R. Cao, M. Liu, Adv. Energy Mater. 10 (2020) 2000478.
- [43] I.C. Man, H.Y. Su, F. Calle-Vallejo, H.A. Hansen, J.I. Martínez, N.G. Inoglu, J. Kitchin, T.F. Jaramillo, J.K. Nørskov, J. Rossmeisl, ChemCatChem 3 (2011) 1159–1165.
- [44] A. Grimaud, A. Demortière, M. Saubanère, W. Dachraoui, M. Duchamp, M.-L. Doublet, J.-M. Tarascon, Nat. Energy 2 (2016) 1–10.
- [45] X. Wang, S. Xi, P. Huang, Y. Du, H. Zhong, Q. Wang, A. Borgna, Y.-W. Zhang, Z. Wang, H. Wang, Nature 611 (2022) 702–708.
- [46] N. Han, W. Zhang, W. Guo, H. Pan, B. Jiang, L. Xing, H. Tian, G. Wang, X. Zhang, J. Fransaer, Nano-Micro Lett. 15 (2023) 185.
- [47] P. Liu, S. Farid, M. Liu, J. Wang, Catal. Surv. Asia 28 (2024) 361-374.
- [48] S. Gong, T. Zhang, J. Meng, W. Sun, Y. Tian, Mater. Chem. Front. 8 (2024) 603–626.
- [49] J. Han, J. Guan, Nano Res. 16 (2023) 1913-1966.
- [50] R.L. Doyle, M.E.G. Lyons, In, springer international publishing, Cham, 2016, pp. 41–104.
- [51] M. Falsaperna, R. Arrigo, F. Marken, S.J. Freakley, ChemElectroChem 11 (2024) e202300761.
- [52] J. Li, Nano-Micro Lett. 14 (2022) 112.
- [53] X. Liu, Z. He, M. Ajmal, C. Shi, R. Gao, L. Pan, Z.-F. Huang, X. Zhang, J.-J. Zou, Trans. Tian. Uni. 29 (2023) 247–253.
- [54] N. Zhang, Y. Chai, Energy Environ. Sci. 14 (2021) 4647-4671.
- [55] T. Naito, T. Shinagawa, T. Nishimoto, K. Takanabe, Inorg. Chem. Front. 8 (2021) 2900–2917.
- [56] M. Zhao, X. Zheng, C. Cao, Q. Lu, J. Zhang, H. Wang, Z. Huang, Y. Cao, Y. Wang, Y. Deng, Phys. Chem. Chem. Phys. 25 (2023) 4113–4120.
- [57] Z. Wang, W.A. Goddard, H. Xiao, Nat. Commun. 14 (2023) 4228.
- [58] J. Zheng, R. Sun, D. Meng, J. Guo, Z. Wang, J. Mater. Chem. A 11 (2023) 15044–15053.
- [59] X. Li, Z. Cheng, X. Wang, Electrochem. Energy Rev. 4 (2021) 136–145.
- [60] V. Komanicky, V. Latyshev, Role of Electrocatalysts in Water Electrolysis, Handb. Energy Mater., Springer, 2022, pp. 1–32.
- [61] X. Liu, Z. He, M. Ajmal, C. Shi, R. Gao, L. Pan, Z.-F. Huang, X. Zhang, J.-J. Zou, Trans. Tianjin Univ. 29 (2023) 247–253.
- [62] Y. Li, S. Xu, J. Rare Earths 34 (2016) 618–625.
- [63] F. Wei, J. Shen, J. Xie, Z. Luo, L. Shi, T.T. Isimjan, X. Yang, J. Qiu, B. Wu, J. Energy Chem. 98 (2024) 472–480.
- [64] F.F. Alharbi, S. Aman, M. Abdullah, A.G. Abid, S. Manzoor, R.Y. Khosa, H.M. T. Farid, M.V. Silibin, S.V. Trukhanov, T.I. Zubar, A.V. Trukhanov, Ceram. Int. 50 (2024) 8997–9006.
- [65] Y. Liao, X. Lu, X. Jin, H. Chen, X. Huang, Y. Li, J. Li, Int. J. Hydrog. Energy 72 (2024) 288–296.
- [66] M. Hussain, L. Abu El Maati, M.A. Alomar, M. Ali, M. Abdullah, S. Aman, H.M. T. Farid, Ceram. Int. 50 (2024) 19525–19533.
- [67] H. Kabir, S.H. Nandyala, M.M. Rahman, M.A. Kabir, A. Stamboulis, Appl. Phys. A Mater. Sci. Process. 124 (2018) 820.
- [68] Z. Liu, J. Wan, M. Li, Z. Shi, J. Liu, Y. Tang, Nanoscale 14 (2022) 1997–2003.
- [69] T. Munawar, A. Bashir, M.U. Nisa, R.A. Alshgari, F. Mukhtar, S. Mohammad, M. N. Ashiq, M.F. Ehsan, F. Iqbal, S.I. Allakhverdiev, Int. J. Hydrog. Energy 70 (2024) 816.
- [70] Y. Huang, J. Hu, J. Li, W. Xie, H.-S. Xu, K. Tang, Langmuir 40 (2024) 9965–9974.
 [71] S. Swathi, R. Yuvakkumar, P. Senthil Kumar, G. Ravi, M. Thambidurai, C. Dang,
- D. Velauthapillai, Fuel 310 (2022) 122319.
- [72] F. Liang, Y. Yu, W. Zhou, X. Xu, Z. Zhu, J. Mater. Chem. A 3 (2015) 634–640.
- [73] D.D. Matienzo, T. Kutlusoy, S. Divanis, C.D. Bari, E. Instuli, Catalysts 10 (2020) 1387.
- [74] K. Wu, D. Wang, Q. Fu, T. Xu, Q. Xiong, S.G. Peera, C. Liu, Inorg. Chem. 63 (2024) 11135–11145.
- [75] Q. Zhou, L. Zhang, X. Wang, Appl. Surf. Sci. 610 (2023) 155551.
- [76] T. Munawar, A. Bashir, M.S. Nadeem, F. Mukhtar, S. Manzoor, M.N. Ashiq, S. A. Khan, M. Koc, F. Iqbal, Fuel 355 (2024) 129485.
- [77] H. Zhang, L. Xia, Y. Li, J. Tang, L. Wang, S. Zhong, Inorg. Chem. Commun. 141 (2022) 109531.
- [78] L. Kashinath, K. Byrappa, Front. Chem. 10 (2022) 889579.
- [79] J. Xian, H. Jiang, Z. Wu, H. Yu, K. Liu, M. Fan, R. Hu, G. Fang, L. Wei, J. Cai, W. Xu, H. Jin, J. Wan, J. Energy Chem. 88 (2024) 232–241.
- [80] Z. Zhang, X. Wu, Z. Kou, N. Song, G. Nie, C. Wang, F. Verpoort, S. Mu, Chem. Eng. J. 428 (2022) 131133.
- [81] W. Li, L. Zhao, C. Wang, X. Lu, W. Chen, ACS Appl. Mater. Interfaces 13 (2021) 46998–47009.
- [82] M.B. Kale, R.A. Borse, A. Gomaa Abdelkader Mohamed, Y. Wang, Adv. Funct. Mater. 31 (2021) 2101313.
- [83] H. Liu, Z. Yan, X. Chen, J. Li, L. Zhang, F. Liu, G. Fan, F. Cheng, Research 2020 (2020) 11.
- [84] M. Jiang, Z. Tan, M. Cao, Int. J. Hydrog. Energy 46 (2021) 15507–15516.
- [85] Z. Lyu, S. Yu, M. Wang, P. Tieu, J. Zhou, Q. Shi, D. Du, Z. Feng, X. Pan, H. Lin, S. Ding, Q. Zhang, Y. Lin, Small 20 (2024) 2308278.
- [86] M. Akbar, A. Akbar, U. Saddozai, M. Khan, M. Zaheer, M. Badar, Mater. Adv. 4 (2023).

- [87] M. Akbar, S. Khattak, M. Khan, U. Saddozai, N. Ali, A. Alasmari, M. Zaheer, M. Badar, Front. Pharmacol. 14 (2023) 1265440.
- [88] H. Liu, J. Yu, J. Lin, B. Feng, M. Sun, C. Qiu, K. Qian, Z. Si, B. Huang, J.-
- J. Delaunay, Y. Ikuhara, S. Yang, EES Catal. 1 (2023) 720–729. [89] P. Zhou, G. Hai, G. Zhao, R. Li, X. Huang, Y. Lu, G. Wang, Appl. Catal. B Environ.
- Energy 325 (2023) 122364.
- [90] X. Wang, W. Pi, S. Hu, H. Bao, N. Yao, W. Luo, Nano-Micro Lett. 17 (2024) 11.
- [91] J. Huang, H. Sheng, R.D. Ross, J. Han, X. Wang, B. Song, S. Jin, Nat. Commun. 12 (2021) 3036.
- [92] S. Pan, H. Li, T. Wang, Y. Fu, S. Wang, Z. Xie, L. Wei, H. Li, N. Li, ACS Catal. 14 (2024) 13814–13824.
- [93] L. Yin, S. Zhang, Y. Huang, C. Yan, Y. Du, Coord. Chem. Rev. 518 (2024) 216111.
 [94] J. Bai, C. Chen, Y. Lian, Y. Deng, M. Xiang, Q. Zhou, Y. Tang, Y. Su, J. Colloid Interface Sci. 663 (2024) 280–286.
- [95] Y. Cheng, A. Yuan, Y. Zhang, H. Liu, J. Du, L. Chen, J. Colloid Interface Sci. 660 (2024) 166–176.
- [96] L. Li, S. Liu, L. Ying, D. Yang, M. Han, L. Zhang, Int. J. Hydrog. Energy 85 (2024) 818–831.
- [97] D. Gielen, M. Lyons, Int. Renew. Energy Agen. (2022) 1-48.
- [98] F. Tesfaye, H. Peng, M. Zhang, JOM 73 (2021) 16-18.
- [99] G. Tessitore, G.A. Mandl, S.L. Maurizio, M. Kaur, J.A. Capobianco, RSC Adv. 13 (2023) 17787–17811.
- [100] Y. Wu, Y. Liu, A.S. Namini, S. Jung, S.A. Delbari, C. Xia, Q.V. Le, H.W. Jang, A. T-Raissi, M. Shokouhimehr, D. Kim, J. Alloys Compd. 1000 (2024) 174792.
- [101] Y. Zhang, S. Liu, Z.-S. Zhao, Z. Wang, R. Zhang, L. Liu, Z.-B. Han, Inorg. Chem. Front. 8 (2021) 590–619.
- [102] Z.-H. Pan, Z.-Z. Weng, X.-J. Kong, L.-S. Long, L.-S. Zheng, Coord. Chem. Rev. 457 (2022) 214419.
- [103] C. Sposato, E. Catizzone, A. Blasi, M. Forte, A. Romanelli, M. Morgana, G. Braccio, G. Giordano, M. Migliori, Processes 9 (2021) 1369.
- [104] D.M.F. Azevedo, J.A.S. Silva, E.F.C. Servulo, V.L.A. Frescura, J. Dognini, F.J. S. Oliveira, J. Environ. Sci. Health Part A 54 (2019) 686–693.
- [105] Y. Sun, T. Zhang, C. Li, K. Xu, Y. Li, J. Mater. Chem. A 8 (2020) 13415–13436.
- [106] S. Naik Shreyanka, J. Theerthagiri, S.J. Lee, Y. Yu, M.Y. Choi, Chem. Eng. J. 446 (2022) 137045.
- [107] R.R. Salunkhe, Y.V. Kaneti, Y. Yamauchi, ACS Nano 11 (2017) 5293–5308.
- [108] Y. Peng, S. Sanati, A. Morsali, H. García, Angew. Chem. Int. Ed. 62 (2023) e202214707.
- [109] C. Ni, H. Zheng, W. Liu, L. Wu, R. Li, K. Zhou, W. Zhang, Adv. Funct. Mater. 33 (2023) 2301075.
- [110] J. Hu, Q. Xu, X. Wang, X. Huang, C. Zhou, Y. Ye, L. Zhang, H. Pang, Carbon Energy 5 (2023) e315.
- [111] Z. Huang, M. Liao, S. Zhang, L. Wang, M. Gao, Z. Luo, T.T. Isimjan, B. Wang, X. Yang, J. Energy Chem. 90 (2024) 244–252.
- [112] B. Shabbir, K. Jabbour, S. Manzoor, M.F. Ashiq, K.F. Fawy, M.N. Ashiq, Heliyon 9 (2023) e20261.
- [113] Y. Liao, Y. Xiao, Z. Li, X. Zhou, J. Liu, F. Guo, J. Li, Y. Li, Small 20 (2024) 2307685.
- [114] N.K. Shrestha, S.A. Patil, J.H. Seok, A.S. Salunke, S. Cho, A.I. Inamdar, Y. Park, S. U. Lee, H. Kim, H. Im, Mater. Today Phys. 38 (2023) 101252.
- [115] Y. Ma, Y. Miao, G. Mu, D. Lin, C. Xu, W. Zeng, F. Xie, Nanomaterials 11 (2021) 1847.
- [116] J.A. Dias, M.A.S. Andrade Jr., H.L.S. Santos, M.R. Morelli, L.H. Mascaro, ChemElectroChem 7 (2020) 3173–3192.
- [117] J. Liu, E. Jia, K.A. Stoerzinger, L. Wang, Y. Wang, Z. Yang, D. Shen, M. H. Engelhard, M.E. Bowden, Z. Zhu, S.A. Chambers, Y. Du, J. Phys. Chem. C 124 (2020) 15386–15390.
- [118] W.-J. Yin, B. Weng, J. Ge, Q. Sun, Z. Li, Y. Yan, Energy Environ. Sci. 12 (2019) 442–462.
- [119] M. Qu, X. Ding, Z. Shen, M. Cui, F.E. Oropeza, G. Gorni, V.A. de la Peña O'Shea, W. Li, D.-C. Qi, K.H.L. Zhang, Chem. Mater. 33 (2021) 2062–2071.
- [120] M.A. Spackman, D. Jayatilaka, CrystEngComm 11 (2009) 19-32.
- [121] L. Williams, A. Mukherjee, K. Rajan, J. Phys. Chem. Lett. 11 (2020) 7462–7468.
- [122] K.P. Shinde, H.S. Chavan, A.S. Salunke, J. Oh, A.T. Aqueel Ahmed, N.K. Shrestha, H. Im, J. Park, A.I. Inamdar, Nanomaterials 13 (2023) 3076.
- [123] S. Kumar, M. Singh, R. Pal, U.P. Azad, A.K. Singh, D.P. Singh, V. Ganesan, A. K. Singh, R. Prakash, Int. J. Hydrog. Energy 46 (2021) 17163–17172.
- [124] I. Rodríguez-García, J.L. Gómez de la Fuente, D. Galyamin, Á. Tolosana-Moranchel, P. Kayser, M.A. Salam, J.A. Alonso, F. Calle-Vallejo, S. Rojas, M. Retuerto, J. Mater. Chem. A 12 (2024) 16854–16862.
- [125] O. Diaz-Morales, S. Raaijman, R. Kortlever, P.J. Kooyman, T. Wezendonk, J. Gascon, W.T. Fu, M.T.M. Koper, Nat. Commun. 7 (2016) 12363.
- [126] S. Somdee, M. Rittiruam, T. Saelee, P. Khajondetchairit, A. Ektarawong, S. Kheawhom, B. Alling, P. Praserthdam, S. Praserthdam, Adv. Theory Simul. 7 (2024) 2301235.
- [127] P. Bag, D. Wang, Z. Chen, R. Cao, Chem. Commun. 52 (2016) 3669–3672.
- [128] Y. Yan, B.Y. Xia, B. Zhao, X. Wang, J. Mater. Chem. A 4 (2016) 17587-17603.
- [129] Z. Fang, S. Li, Y. Zhang, Y. Wang, K. Meng, C. Huang, S. Sun, J. Phys. Chem. Lett. 15 (2024) 281–289.
- [130] X. Wan, Z. Zhang, H. Niu, Y. Yin, C. Kuai, J. Wang, C. Shao, Y. Guo, J. Phys. Chem. Lett. 12 (2021) 6111–6118.
- [131] M. Secor, A.V. Soudackov, S. Hammes-Schiffer, J. Phys. Chem. C 127 (2023) 15246–15256.
- [132] X. Liao, R. Lu, L. Xia, Q. Liu, H. Wang, K. Zhao, Z. Wang, Y. Zhao, Energy Environ. Mater. 5 (2022) 157–185.

- [133] Z.W. Seh, J. Kibsgaard, C.F. Dickens, I. Chorkendorff, J.K. Nørskov, T. F. Jaramillo, Science 355 (2017) eaad4998.
- [134] Y. Wu, Y. Liu, A.S. Namini, S. Jung, S.A. Delbari, C. Xia, Q. Van Le, H.W. Jang, T. Ali, M. Shokouhimehr, J. Alloys Compd. 1000 (2024) 174792.
 [135] H.-M. Ren, H.-W. Wang, Y.-F. Jiang, Z.-X. Tao, C.-Y. Mu, G. Li, Top. Curr. Chem.
- 380 (2022) 9.
- [136] M.M. Sirati, S. Sirati, U. Amara, A. Hussain, D. Hussain, M. Hanif, K. Mahmood, H. M. Asif, M. Khalid, M. Tariq, Fuel 362 (2024) 130812.
- [137] Y. Wang, B. Wang, X. Liu, Y. Wang, Y. Wang, Z. Liu, ACS Appl. Energy Mater. 5 (2022) 8686–8696.
- [138] C.-L. Chen, C. Wang, X.-Y. Zheng, R. Zhang, Y. Xu, G.-L. Zhuang, L.-S. Long, L.-S. Zheng, X.-J. Kong, Y. Cao, J. Am. Chem. Soc. 145 (2023) 16983–16987.
- [139] S. Lyu, C. Guo, J. Wang, Z. Li, B. Yang, L. Lei, L. Wang, J. Xiao, T. Zhang, Y. Hou, Nat. Commun. 13 (2022) 6171.
- [140] M. Mukhtar Sirati, S. Sirati, U. Amara, A. Hussain, D. Hussain, M. Hanif, K. Mahmood, H.M. Asif, M. Khalid, M. Tariq, F. Siddique, M. Yaqub, I. Ahmad, Fuel 362 (2024) 130812.
- [141] Y. Cheng, L. Zhu, Y. Gong, Int. J. Hydrog. Energy 58 (2024) 416-425.
- [142] S. Maghool, A.A. Asgharinezhad, A. Larimi, C. Ghotbi, F. Khorasheh, Surf. Interfaces 54 (2024) 105108.
- [143] X. Wei, S. Yu, J. Li, T. Liu, S. Li, S. Hata, Z. Wu, Y. Shiraishi, Y. Du, J. Mater. Chem. A 12 (2024) 29291–30100.
- [144] Y. Ma, Y. Miao, G. Mu, D. Lin, C. Xu, W. Zeng, F. Xie, Nanomaterials 11 (2021).
- [145] Y. Cheng, X. Xiao, X. Guo, H. Yao, H. Pang, A.C.S. Sustain, Chem. Eng. 8 (2020) 8675–8680.
- [146] P.F. Santos, J. Ribeiro, P.P. Luz, Solid State Sci. 110 (2020) 106479.
- [147] X. Duan, N. Zhang, Z. Li, L. Zhang, F. Sun, Z. Zhou, H. Liu, Y. Guo, X. Sun, J. Jiang, J. Colloid Interface Sci. 632 (2023) 171–178.
- [148] L.-B. Liu, C. Yi, H.-C. Mi, S.L. Zhang, X.-Z. Fu, J.-L. Luo, S. Liu, Electrochem. Energy Rev. 7 (2024) 14.
- [149] A. Grimaud, K.J. May, C.E. Carlton, Y.-L. Lee, M. Risch, W.T. Hong, J. Zhou, Y. Shao-Horn, Nat. Commun. 4 (2013) 2439.
- [150] P. Li, B. Wei, Z. Lü, Y. Wu, Y. Zhang, X. Huang, Appl. Surf. Sci. 464 (2019) 494–501.
- [151] H. Wang, X. Chen, D. Huang, M. Zhou, D. Ding, H. Luo, ChemCatChem 12 (2020) 2768–2775.
- [152] H. Jo, Y. Yang, A. Seong, D. Jeong, J. Kim, S.H. Joo, Y.J. Kim, L. Zhang, Z. Liu, J.-Q. Wang, S.K. Kwak, G. Kim, J. Mater. Chem. A 10 (2022) 2271–2279.
- [153] X. Zhou, L. Qiu, R. Fan, H. Ye, C. Tian, S. Hao, Y. Yang, J. Power Sources 473 (2020) 228556.
- [154] Q. Li, Y. Zhang, G. Zhang, Y. Wang, H. Pang, Natl. Sci. Open 2 (2023) 20220065.
 [155] S.C. Paul, S.C. Dey, M.A.I. Molla, M.S. Islam, S. Debnath, M.Y. Miah,
- M. Ashaduzzaman, M. Sarker, Polyhedron 193 (2021) 114871. [156] S. Wen, J. Huang, T. Li, W. Chen, G. Chen, Q. Zhang, X. Zhang, Q. Qian,
- K. Ostrikov, Appl. Catal. B Environ. Energy 316 (2022) 121678.
 [157] M. Dinari, H. Allami, M.M. Momeni, J. Electroanal. Chem. 877 (2020) 114643.
- [157] M. Bhiari, H. Ahani, M.M. Molleni, S. Electroanal, Chem. 877 (2020) 114045.
 [158] L. Ma, M. Zhang, Z. Wei, X. Meng, R. Chen, M. Qin, L. Zhu, Y. Wang, X. Huang,
- M. Feng, P. He, D. Jia, Y. Zhou, X. Duan, Ceram. Int. 50 (2024) 52159–53524. [159] L. Wang, Y. Liu, X. Liu, W. Chen, Dalton Trans. 52 (2023) 12038–12048.
- [160] L. Guo, J. Liu, F. Quan, S. Zhang, T. Yu, Y. Mo, R. Guo, X. Liu, Y. Liu, W. Mu, X. Lei, J. Alloys Compd. 920 (2022) 165898.
- [161] S. Hao, M. Liu, J. Pan, X. Liu, X. Tan, N. Xu, Y. He, L. Lei, X. Zhang, Nat. Commun. 11 (2020) 5368
- [162] M. Li, X. Pan, M. Jiang, Y. Zhang, Y. Tang, G. Fu, Chem. Eng. J. 395 (2020) 125160
- [163] Y.-C. Zhang, Y.-K. Liu, L. Zhang, X.-F.-F.E.L. Pan, X. Zhang, A. Fazal e, D.-R. Zou, S.-H. Liu, J.-J. Zou, Appl. Surf. Sci. 452 (2018) 423–428.
- [164] J. Liu, Y. Gao, Y. Wei, X. Chen, S. Hao, X. Ding, L. Pan, Chem. Commun. 56 (2020) 4228–4231.
- [165] A. Rajapriya, S. Keerthana, A. Rebekah, C. Viswanathan, N. Ponpandian, Int. J. Hydrog. Energy 46 (2021) 37281–37293.
- [166] T. Dai, X. Zhang, M. Sun, B. Huang, N. Zhang, P. Da, R. Yang, Z. He, W. Wang, P. Xi, Adv. Mater. 33 (2021) 2102593.
- [167] V. Mishra, I.M. Abdullahi, D. Mumbaraddi, M. Jomaa, L. Guérin, M. Nath, A. Mar, Chem. Mater. 36 (2024) 937–948.
- [168] S. Paladugu, I.M. Abdullahi, P.R. Jothi, B. Jiang, M. Nath, K. Page, Small 20 (2024) 2305789.
- [169] A.C. Hartnett, R.J. Evenson, A.E. Thorarinsdottir, S.S. Veroneau, D.G. Nocera, J. Am. Chem. Soc. 147 (2025) 1123–1133.
- [170] L. Li, G. Zhang, C. Zhou, F. Lv, Y. Tan, Y. Han, H. Luo, D. Wang, Y. Liu, C. Shang, L. Zeng, Q. Huang, R. Zeng, N. Ye, M. Luo, S. Guo, Nat. Commun. 15 (2024) 4974.
- [171] S. Paladugu, I.M. Abdullahi, H. Singh, S. Spinuzzi, M. Nath, K. Page, ACS Appl. Mater. Interfaces 16 (2024) 7014–7025.
- [172] R.R.P. Kimaka, P. Wang, M. He, S. Meng, J. Yao, H. Li, C. Yang, Z. Li, Sci. China Chem. 67 (2024) 2586–2598.
- [173] M. Hussain, M.M. Alanazi, S.D. Alahmari, M. Abdullah, K. Ahmad, A.M.
- A. Henaish, G. Khan, A.G. Al-Sehemi, Int. J. Hydrog. Energy 69 (2024) 974–981. [174] A. Fatima, H.A. Alyousef, A.W. Alrowaily, B.M. Alotaibi, A. Dahshan, A.M.
- A. Henaish, Diam. Relat. Mater. 145 (2024) 111072.
- [175] Q. Ouyang, S. Cheng, C. Yang, Z. Lei, Inorg. Chem. 62 (2023) 1719–1727.
- [176] X. Yang, S. Li, Y. Zhang, F. Qiu, Y. Sun, W. Ning, Q. Tao, W. Li, S. Miao, J. Mater. Chem. A 12 (2024) 17574–17585.
- [177] E. Omari, M. Omari, Ceram. Int. 50 (2024) 25509-25517.
- [178] D. Ghosh, M. Manikanta Kumar, C.R. Raj, D. Pradhan, ACS Appl. Energy Mater. 5 (2022) 5666–5679.

S. Muhammad et al.

- [179] K.B. Patel, M. Mariyaselvakumar, G. Vyas, J.C. Chaudhari, R. Patidar, K. Srinivasan, D.N. Srivastava, G.R. Bhadu, Appl. Surf. Sci. 649 (2024) 159212.
- [180] Y. Huang, X. Ding, B. Huang, Z. Xie, J. Alloys Compd. 981 (2024) 173672.
 [181] T. Li, Z. Wang, L. Wang, M. Wang, Y.-O. Liu, Appl. Catal. B Environ. Energy 352
- (2024) 123990.
 [182] S. Aman, M.M. Alanazi, S.A.M. Abdelmohsen, A.G. Abid, R.Y. Khosa, S. Manzoor,
- [102] S. Anian, M.M. Ananza, S.A.M. Abdennonsen, A.G. Abid, K.F. Khosa, S. Malizoot, M.U. Nisa, A.G. Al-Sehemi, H.M.T. Farid, J. Sol-Gel Sci. Technol. 106 (2023) 226–235.
- [183] T. Hou, R. Yang, J. Xu, X. He, H. Yang, P.W. Menezes, Z. Chen, Nanoscale 16 (2024) 15629–15639.
- [184] M. Li, X. Wang, D. Zhang, Y. Huang, Y. Shen, F. Pan, J. Lin, W. Yan, D. Sun, K. Huang, Y. Tang, J.-M. Lee, H. Li, G. Fu, Nano Energy 128 (2024) 109868.
- [185] B. Shabbir, M.Z. Ansari, S. Manzoor, A.G. Abid, M.U. Nisa, A.M. Shawky, S. Znaidia, S. Aman, M.N. Ashiq, T.A. Taha, Mater. Chem. Phys. 292 (2022) 126861.
- [186] Y. Ma, G.-M. Mu, Y.-J. Miao, D.-M. Lin, C.-G. Xu, F.-Y. Xie, W. Zeng, Rare Metals 41 (2022) 844–850.
- [187] Z. Wan, Q. He, J. Chen, T.T. Isimjan, B. Wang, X. Yang, Chin. J. Catal. 41 (2020) 1745–1753.
- [188] M.M. Sirati, D. Hussain, K. Mahmood, A.H. Chughtai, M. Yousaf-Ur-Rehman, W. M.A. Malik, S. Alomairy, S.B. Ahmed, M.S. Al-Buriahi, M.N. Ashiq, J. Taibah, Univ. Sci. 16 (2022) 525–534.
- [189] A. Khan, F. Javed, S.D. Alahmari, F.F. Alhrabi, A. Dahshan, K. Ahmad, A.M. A. Henaish, M.J. Khan, M. Abdullah, Ceram. Int. 50 (2024) 30188–30198.
- [190] A.M. Tawfeek, K. Jabbour, A.G. Abid, M.U. Nisa, S. Manzoor, B. Shabbir, M.Y. U. Rehman, T. Munawar, M. Sillanpää, M.N. Ashiq, J. Sol-Gel Sci. Techn. 109 (2024) 1–14.
- [191] N. Nazar, S. Manzoor, Y.U. Rehman, I. Bibi, D. Tyagi, A.H. Chughtai, R.S. Gohar, M. Najam-Ul-Haq, M. Imran, M.N. Ashiq, Fuel 307 (2022) 121823.
- [192] S. Li, H. Chai, L. Zhang, Y. Xu, Y. Jiao, J. Chen, J. Colloid Interface Sci. 642 (2023) 235–245.
- [193] Y. Niu, X. Chang, M. Zhang, J. Mu, Ceram. Int. 50 (2024) 13014-13021.
- [194] D. Kubba, I. Ahmed, A. Roy, P. Kour, C.S. Yadav, S.K. Sharma, K. Yadav, K.
- K. Haldar, ACS Appl. Nanostruct. Mater. 7 (2024) 1536–1547. [195] R. Xie, Z. Nie, X. Hu, Y. Yu, C. Aruta, N. Yang, ACS Appl. Energy Mater. 4 (2021)
- 9057–9065.
 [196] G. Fang, K. Liu, M. Fan, J. Xian, Z. Wu, L. Wei, H. Tian, H. Jiang, W. Xu, H. Jin, J. Wan, Carbon Neutrality 2 (2023) 709–720.
- [197] Y. Khreif, M. Omari, S. Makhloufi, Inorg. Chim. Acta 566 (2024) 122028.
- [198] E. Omari, M. Omari, Int. J. Hydrog. Energy 44 (2019) 28769–28779.
- [199] P.B.A. Selvadurai, T. Xiong, P. Huang, Q. Tan, Y. Huang, H. Yang, M.S. Balogun,
- J. Mater. Chem. A 9 (2021) 16906–16916. [200] H. Wang, J. Wang, Y. Pi, Q. Shao, Y. Tan, X. Huang, Angew. Chem. Int. Ed. 131 (2019) 2338–2342.

- Coordination Chemistry Reviews 534 (2025) 216573
- [201] S. Bhowmick, A. Dhankhar, T.K. Sahu, R. Jena, D. Gogoi, N.R. Peela, S. Ardo, M. Qureshi, ACS Appl. Energy Mater. 3 (2020) 1279–1285.
- [202] Y. Zhu, Q. Lin, Z. Hu, Y. Chen, Y. Yin, H.A. Tahini, H.-J. Lin, C.-T. Chen, X. Zhang, Z. Shao, H. Wang, Small 16 (2020) 2001204.
- [203] N. Liu, D. Cao, W. Liu, H. Zhang, Y. Zhu, L. Chang, D. Wu, D. Cheng, Int. J. Hydrog. Energy 47 (2022) 14504–14514.
- [204] M. Yu, J. Zheng, M. Guo, J. Energy Chem. 70 (2022) 472-479.
- [205] Z. Cai, P. Wang, J. Zhang, J. Xu, Y. Yan, A. Chen, X. Wang, J. Alloys Compd. 933 (2023) 167743.
- [206] D. Liu, Z. Zhao, Z. Xu, L. Li, S. Lin, Dalton Trans. 51 (2022) 12839-12847.
- [207] L. Gao, Y. Li, G. Li, J. Huo, L. Jia, Chem. Eng. J. 451 (2023) 138743.
- [208] M. Li, X. Wang, K. Liu, H. Sun, D. Sun, K. Huang, Y. Tang, W. Xing, H. Li, G. Fu, Adv. Mater. 35 (2023) 2302462.
- [209] C. Shang, C. Cao, D. Yu, Y. Yan, Y. Lin, H. Li, T. Zheng, X. Yan, W. Yu, S. Zhou, J. Zeng, Adv. Mater. 31 (2019) 1805104.
- [210] X. He, X. Yi, F. Yin, B. Chen, G. Li, H. Yin, J. Mater. Chem. A 7 (2019) 6753–6765.
 [211] Z. Majie, W. Guoxiang, M. Qingwang, W. Hao, A. Boyan, G. Shuya, J. Electroanal. Chem. 975 (2024) 118650.
- [212] Y. Wang, S. Hao, X. Liu, Q. Wang, Z. Su, L. Lei, X. Zhang, ACS Appl. Mater. Interfaces 12 (2020) 37006–37012.
- [213] J. Li, Y. Kang, Z. Lei, P. Liu, Appl. Catal. B Environ. Energy 321 (2023) 122029.
 [214] X. Ding, R. Jiang, J. Wu, M. Xing, Z. Qiao, X. Zeng, S. Wang, D. Cao, Adv. Funct.
- Mater. 33 (2023) 2306786.
- [215] T. Li, J. Yin, D. Sun, M. Zhang, H. Pang, L. Xu, Y. Zhang, J. Yang, Y. Tang, J. Xue, Small 18 (2022) 2106592.
- [216] Z. Huang, X. Liao, W. Zhang, J. Hu, Q. Gao, ACS Catal. 12 (2022) 13951-13960.
- [217] Y. Liang, X. Zhao, P. Yan, L. Xue, H. Li, L. Gu, Y. Long, T. Yu, Y. Yang, J. Colloid Interface Sci. 655 (2024) 565–575.
- [218] T. Ul Haq, S.A. Mansour, A. Munir, Y. Haik, Adv. Funct. Mater. 30 (2020) 1910309.
- [219] D. Taherinia, S.H. Moravvej, M. Moazzeni, E. Akbarzadeh, Sustain. Energ Fuels 5 (2021) 2994–3000.
- [220] P. Wang, X. Wu, M. Li, X. Wang, H. Wang, Q. Huang, H. Li, Y. Tang, G. Fu, J. Rare Earths 42 (2024) 2003–2182.
- [221] H. Cheng, Y. Guan, F.-P. Wang, T. Yang, L. Huang, J. Tang, R. Hu, J. Alloys Compd. 972 (2024) 172820.
- [222] L. Zhang, Y. Lei, W. Xu, D. Wang, Y. Zhao, W. Chen, X. Xiang, X. Pang, B. Zhang, H. Shang, Chem. Eng. J. 460 (2023) 141119.
- [223] X. Chen, X. Xu, Y. Cheng, H. Liu, D. Li, Y. Da, Y. Li, D. Liu, W. Chen, Small 20 (2024) 2303169.
- [224] P.C. Nagajyothi, K. Pavani, R. Ramaraghavulu, J. Shim, Inorganics 11 (2023) 161.
- [225] M. Cao, M. Yang, Y. Xu, Y. Sun, H. Sun, Appl. Surf. Sci. 627 (2023) 157313.
- [226] S. Hao, Y. Wang, G. Zheng, L. Qiu, N. Xu, Y. He, L. Lei, X. Zhang, Appl. Catal. B Environ. Energy 266 (2020) 118643.