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Review

Iridium-containing water-oxidation catalysts in acidic electrolyte

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ABSTRACT

With the goal of constructing a carbon-free energy cycle, proton-exchange membrane (PEM) water electrolysis is a promising technology that can be integrated effectively with renewable energy resources to produce high-purity hydrogen. IrO₂, as a commercial electrocatalyst for the anode side of a PEM water electrolyzer, can both overcome the high corrosion conditions and exhibit efficient catalytic performance. However, the high consumption of Ir species cannot meet the sustainable development and economic requirements of this technology. Accordingly, it is necessary to understand the OER catalytic mechanisms for Ir species, further designing new types of low-iridium catalysts with high activity and stability to replace IrO₂. In this review, we first summarize the related catalytic mechanisms of the acidic oxygen evolution reaction (OER), and then provide general methods for measuring the catalytic performance of materials. Second, we present the structural evolution results of crystalline IrO₂ and amorphous IrO_x using *in situ* characterization techniques under catalytic conditions to understand the common catalytic characteristics of the materials and the possible factors affecting the structural evolution characteristics. Furthermore, we focus on three types of common low-iridium catalysts, including heteroatom-doped IrO₂ (IrO₂)_x-based catalysts, perovskite-type iridium-based catalysts, and pyrochlore-type iridium-based catalysts, and try to correlate the structural features with the intrinsic catalytic performance of materials. Finally, at the end of the review, we present the unresolved problems and challenges in this field in an attempt to develop effective strategies to further balance the catalytic activity and stability of materials under acidic OER catalytic conditions.

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1. Introduction

The booming energy demands of modern society require people to secure energy resources more wisely and widely [1]. Due to the unsustainable nature of fossil fuels, the dominant position of the global energy system needs to be substituted by renewable energy (*e.g.*, solar, wind, and water power) step by step without hassle [2,3]. The mature strategy to utilize renewable energy is its direct transformation into electricity by

photovoltaic modules, wind turbines, or hydropower dams [1,4]. In view of the intermittency of renewable sources, advanced energy-conversion and -storage solutions are urgently needed to achieve more convenient usage of this energy at any desired time [1,5–7]. Correspondingly, appropriate energy carriers should be carefully selected to empower the new integrated energy system. Hydrogen is the most promising candidate, owing to its high energy density and carbon-free features [8–11]. Fig. 1 displays an integrated energy system driven by

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renewable energy using hydrogen as the energy carrier. In this energy system, fossil fuels are not involved. Renewable energy is first gathered to produce electricity, which can be used for hydrogen production by using water electrolyzers [10,12]. The resulting hydrogen can then be stored, applied in industry, and transported as a kind of fuel. In addition, the resulting hydrogen can also actuate fuel cells to generate power for transportation and other energy-related applications.

A water electrolyzer is one of the core apparatuses that constitute the above future energy system. Related electrolysis technologies can be grouped into three main categories: the proton-exchange membrane (PEM) water electrolyzer, alkaline water electrolyzer (AWE), and solid oxide electrolyzer (SOE) [13,14]. Among these, PEM water electrolyzers and AWE are commercially available devices, whereas SOE is less developed and thus beyond further discussion. Currently, AWE is the most widely employed device at the industrial level for hydrogen production because of its cost-effective components, such as non-noble-metal catalysts. Compared with AWE, the PEM water electrolyzer exhibits higher proton conductivity, lower gas crossover, and higher efficiency owing to the use of a solid polymer membrane (commonly Nafion) as the electrolyte. PEM water electrolyzers also offer better system compactness and shorter start-up time [4]. These features, especially fast response times, make PEM water electrolyzers more suitably coupled with intermittent renewable energy sources.

In this regard, it is important to develop high-performance, long-lifetime PEM water electrolyzers with reasonable cost. However, this goal is greatly impeded by the strong acid environment of PEMs. This harsh corrosive condition limits the selection range of catalytic materials for the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER)—two half-reactions of water electrolysis that occur on the cathode and anode of the electrolyzer, respectively. Only noble metal-based catalytic materials (Pt for HER and Ir for OER) currently exhibit acceptable acidic resistance and catalytic activity for PEM water electrolyzers in commercial use. As illustrated in the center of Fig. 1, the main components of the

PEM water electrolyzer include the membrane electrode assembly (MEA), gas-diffusion layer (GDL), and bipolar plates [15]. The MEA serves as the core reaction region of the PEM water electrolyzer, and GDL together with BPP are responsible for transporting electrical current, water, and gaseous products (*e.g.*, H_2 and O_2) [15]. The MEA is composed of a PEM and anode, cathode electrocatalysts, where the PEM functions as both electrolyte and diaphragm with good proton conductivity ($0.1 \pm 0.02 \text{ S cm}^{-1}$) to separate the anode and cathode parts of the electrolyzer (Fig. 1) [4]. Different methods can be used to fabricate the MEA, while the most commonly used method for researchers is directly coating the electrocatalyst slurry on the surface of the membrane, followed by hot-pressing treatment under a certain pressure [15]. Generally, a loading amount of approximately $0.025\text{--}0.3 \text{ mg cm}^{-2}$ of Pt-based catalyst is sufficient to maintain high HER performance. However, an Ir-based catalyst needs at least a loading of 2 mg cm^{-2} to facilitate OER [4]. Moreover, the exchange current density of H^+/H_2 on a Pt-based catalyst is almost 1000 times larger than that of $\text{H}_2\text{O}/\text{O}_2$ on Ir-based catalysts [16]. This also means that the sluggish OER is the bottleneck reaction for the PEM water electrolyzer, and dominantly determines the overall efficiency of water splitting.

Recently, various catalytic materials have been developed for acidic OER, mainly including precious-metal-based catalysts (Ru, Ir, Pd, Rh, and Pt species, etc.) and nonprecious-metal-based catalysts (Co, Ni, Fe, Mn, and Mo species, etc.) [17–21]. However, most of the materials are restricted by a reverse relationship between catalytic activity and stability, and only Ir-based catalysts can somewhat balance the activity and stability as state-of-the-art OER catalysts for PEM water electrolyzers [22,23]. Ir is one of the least abundant elements in the Earth's crust, and the average mass fraction of Ir is approximately 0.001 ppm in crustal rock [16]. In contrast, platinum (Pt, 0.005 ppm) is 5 times more abundant than Ir [24]. In addition, the production output of Ir (< 9000 kg/year, in 2010) is approximately 4.5% of that of Pt, and the price of Ir is also much higher than that of Pt (\$1485 for Ir vs. \$895 for Pt per troy ounce, in 2020) [19,25]. Based on these data, a back-of-the-envelope calculation can be performed. For a PEM water electrolyzer with an Ir loading of 2 mg cm^{-2} operating at 4 W cm^{-2} , 500 kg of Ir is required to reach gigawatt of power without considering the deactivation of the catalyst. It can be expected that a higher penetration of PEM water electrolyzers into the market would dramatically exacerbate both the demand and price of Ir. Thus, the high cost and low earth abundance are other key issues of Ir catalysts and cannot be simply overlooked [25].

In this review, we summarize recent research advances in Ir-containing electrocatalysts for OER under acidic conditions. We first introduce the possible catalytic mechanisms of Ir-containing electrocatalysts under OER, and then provide basic measurement methods for evaluating the catalytic properties of materials. Subsequently, we present some important structural characterization results for pure IrO_2 and its relatives during the catalytic reaction. We then review some recent research efforts for designing low-iridium OER electrocatalysts,

Fig. 1. Schematic illustration of the electrolyzer as a key part for constructing future hydrogen energy systems.

and further try to correlate these specific structural features with intrinsic catalytic properties. Finally, we provide some unsolved issues as future challenges at the end of this review.

2. Catalytic mechanisms of OER in acidic media

The OER on the anode in acidic media can be described by the following reaction (Eq. (1)) [26,27]:

$E_{(\text{O}_2/\text{H}_2\text{O})}^0$ is the standard anode potential for water oxidation into oxygen. However, a substantial overpotential is required to drive the OER because of its sluggish four-electron-involved reaction kinetics, constraining the efficiency of the overall water electrolysis process [28]. Considering the detailed catalytic steps of OER, multistep concerted and/or non-concerted proton-electron-transfer processes are possibly involved [29,30]. There are two kinds of catalytic mechanisms presented in the OER: (1) the adsorbate evolution mechanism (AEM) and (2) the lattice-oxygen oxidation mechanism (LOM). In AEM, the catalyst itself only provides appropriate adsorption sites, and the O_2 gaseous product and all involved intermediates originate from the electrolyte. In LOM, the lattice oxygen atoms of the catalyst (mostly in the surface region) leave the lattice structure and directly participate in the formation of the dioxygen product during OER [21].

2.1. Adsorbate evolution mechanism

To determine the detailed schemes and internal influences under OER, various mechanistic steps have been proposed by different groups over the years [27]. In these proposed schemes, the OER always initializes from the discharge step of hydroxide ions at a catalytic active site (M) on the surface of the catalysts (Eq. (2)), further involving different intermediates (O^* , HO^* , HOO^* , O_2^* , * represents catalytic active sites) and various valence transitions of M.

In fact, all of these schemes can be regarded as adsorbate evolution mechanisms, as surface lattice oxygen atoms do not serve as a part of the intermediate for the catalytic reaction. In fact, AEM always refers to a well-accepted scheme for investigating various catalysts (*i.e.*, metal oxides/hydroxides) for OER under both acidic and alkaline conditions, and is also interpreted well with theoretical evaluation methods developed by the groups of Nørskov and Rossmeisl [31].

A typical AEM under acidic conditions is illustrated in Fig. 2(a). In the detailed mechanism steps, water molecules in the electrolyte first interact with the M site to form an HO^* intermediate (Eq. (3)). Then, the HO^* species deprotonates to produce M-O species by a concomitant one-electron transfer process (Eq. (4)). The M-O intermediate further reacts with water, forming adsorbed HOO^* at the M site (Eq. (5)), followed by the successive generation of O_2 and the release of the M site (Eq. (6)).

Fig. 2. Schematic illustration of (a) typical AEM scheme, (b) scaling relationship among M-OH, M-O and M-OOH, (c) a volcano plot using descriptor to represent the catalytic activity trend. (d) The volcano plot between catalytic activities and $\Delta G_{\text{O}} - \Delta G_{\text{HO}}$. Reproduced with permission [36]. Copyright 2011, Wiley-VCH. (e) The volcano plot between catalytic activities and e_g electron. Reproduced with permission [38]. Copyright 2011, American Association for the Advancement of Science. (f) The relationship between p -state center and oxygen adsorption energy for cubic ABO_3 oxides. Reproduced with permission. Copyright 2018, Royal Society of Chemistry [39].

Four concerted proton–electron-transfer processes are involved, indicating that the proposed mechanism should be independent of pH on the reversible hydrogen electrode (RHE) scale [30,32]. Due to the fact that the every separate reaction step cannot be evaluated clearly using experimental studies, the groups of Nørskov and Rossmeisl constructed an important computational standard hydrogen electrode model based on Density Functional Theory (DFT) to model the thermochemistry of electrochemical reactions [31]. This specific evaluation method for the OER is based on the as-stated mechanism scheme. More specifically, the chemical potential of ($\text{H}^+ + \text{e}^-$) in solution is related to that of $1/2\text{H}_2$ in the gas phase by setting a standard hydrogen electrode (SHE) as the reference potential. This means that the reaction free energy of $1/2\text{H}_2 \rightarrow \text{H}^+ + \text{e}^-$ is zero at standard conditions ($\text{pH} = 0$, $U = 0$, $p_{\text{H}_2} = 1$ bar, $T = 298$ K, where U is the electrode potential relative to the SHE). Under such conditions, the free energy for each elementary step (ΔG_1 , ΔG_2 , ΔG_3 , and ΔG_4) can be calculated as Eqs. (7)–(10).

$$\Delta G_1 = E(\text{HO}^*) - E(^*) - E_{\text{H}_2\text{O}} + 1/2E_{\text{H}_2} + (\Delta\text{ZPE} - T\Delta S)_1 - eU \quad (7)$$

$$\Delta G_2 = E(\text{O}^*) - E(\text{HO}^*) + 1/2E_{\text{H}_2} + (\Delta\text{ZPE} - T\Delta S)_2 - eU \quad (8)$$

$$\Delta G_3 = E(\text{HOO}^*) - E(\text{O}^*) - E_{\text{H}_2\text{O}} + 1/2E_{\text{H}_2} + (\Delta\text{ZPE} - T\Delta S)_3 - eU \quad (9)$$

$$\Delta G_4 = E(^*) - E(\text{HOO}^*) + E_{\text{O}_2} + 1/2E_{\text{H}_2} + (\Delta\text{ZPE} - T\Delta S)_4 - eU \quad (10)$$

where the energies of $E(^*)$, $E(\text{HO}^*)$, $E(\text{HOO}^*)$, E_{H_2} , and $E_{\text{H}_2\text{O}}$ are calculated according to DFT calculations, and the differences in the zero-point energy (ΔZPE) and entropy ($T\Delta S$) are obtained from the calculations of vibrational frequencies using DFT and the standard tables for gas molecules, respectively. Moreover, to avoid calculations of O_2 , which may not be described accurately using DFT, the free energy change of the total reaction ($2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$) is fixed at 2.46 eV per water molecule according to experimental value [31]. Accordingly, every ΔG for the above four elementary steps can be obtained, and the larger the ΔG , the more energy should be consumed to make the step happen. This means that the step with the largest ΔG value in ΔG_{1-4} ($\max[\Delta G_{1-4}]$) is the last step to become downhill with the increased additional potential, and the corresponding step is regarded as the potential-determining step (PDS). The theoretical overpotential (η^{OER}) can be calculated using Eq. (11).

$$\eta^{\text{OER}} = \frac{\max[\Delta G_{1-4}]}{e} - 1.23 \text{ V} \quad (11)$$

This potential is also termed the thermodynamic overpotential. At this potential, all thermodynamic barriers are removed and each substep in the reaction should be thermodynamically neutral or downhill [27]. Note that the theoretical overpotential η^{OER} is a prediction of the thermodynamic limits of the OER, and it does not contain any electrokinetic terms. Thus, its value should not be directly comparable with the experimental result [33].

As classical models for OER, Rossmeisl *et al.* [34] investigated the theoretical electrocatalytic properties and adsorption behaviors of (110) surfaces of three rutile-type oxides (RuO_2 , IrO_2 , and TiO_2) according to the above methods. An activity trend of $\text{RuO}_2 > \text{IrO}_2 > \text{TiO}_2$ was observed under OER conditions. From the binding energy results, RuO_2 binds oxygen a little too weakly ($\Delta E_{\text{O}^*} = 2.66$ eV), leading to a relatively low

overpotential of 0.37 V. On the other hand, IrO_2 binds O^* rather too strongly with a binding energy of 1.66 eV, and the as-calculated overpotential is 0.56 V, demonstrating the same trend as the experimental observation [35]. Due to the strong O^* adsorption of IrO_2 , the PDS of IrO_2 is identified as the formation of HOO^* ($\text{O}^* \rightarrow \text{HOO}^*$), and it is rational to conclude that the catalytic activity of IrO_2 can be enhanced by effective strategies that can reasonably weaken the adsorption of O^* on the catalytic sites. In addition, the authors also found a universality of scaling relations among different intermediates, and this universality was further extended to rutile, perovskite, spinel, rock salt, and bixbyite oxides [28,36]. To be specific, as shown in Fig. 2(b), there is constant energy difference around 3.2 (± 0.2) eV between ΔG_{HO^*} and ΔG_{HOO^*} , and the slope of scaling relation between ΔG_{HO^*} (or ΔG_{HOO^*}) and ΔG_{O^*} is about 0.5–0.6 [34]. The scaling relation between two intermediates a and b can be further summarized using Eq. (12) [37]:

$$\Delta G_b = A_{a,b}\Delta G_a + B_{a,b} \quad (12)$$

where some of the slopes $A_{a,b}$ and the intercepts $B_{a,b}$ are assumed to be constant values for three O-containing intermediates ($A_{a,b} = 1$, $B_{a,b} = 3.2$ for ΔG_{HO^*} and ΔG_{HOO^*} , and $A_{a,b} = 0.5$ – 0.6 for ΔG_{HO^*} and ΔG_{O^*}). From Eq. (12), it can be concluded that if the values of ΔG_{O^*} and $B_{a,b}$ for ΔG_{O^*} and G_{HO^*} of one specific catalyst can be calculated, the values of ΔG_{HO^*} and ΔG_{HOO^*} can be predicted to some extent according to the scaling relation.

When seeking the internal origin of the scaling relation, it has been shown that the slope of these scaling relations correlates with the number of bonds to the adsorptive site for every intermediate [27]. Both OH^* and OOH^* bond M with a single bond, and the slope of the scaling relation is 1. In another case, M–O connects the surface with two bonds, and the corresponding slopes between OH^* and O^* or between OOH^* and O^* are around 0.5. The bonding patterns of intermediates actually depend on the electron-counting rule (*i.e.*, the octet rule). This demonstrates that these scaling relations originate from intermediates rather than catalytic active sites, further leading to the corresponding universality among various metals and oxides. Based on the universal limit of the scaling relation, it is difficult to design an ideal catalyst with minimal thermodynamic overpotential under the framework of AEM. The constant binding energy of 3.2 eV between M–OH and M–OOH actually confines at least 0.37 ± 0.10 V thermodynamic overpotential of OER, considering that every step should consume 1.23 eV with the transfer of one electron and one proton at optimum [28]. This may be the reason why numerous reported OER catalysts exhibit an overpotential in the range of 0.3–0.4 V, and the overpotentials cannot be further reduced easily [5]. Therefore, in the framework of AEM, how to break the scaling relationship is a crucial issue for the development of OER catalysts, and strategies that can change the slope $A_{\text{O}^*,\text{OH}^*}$ (the relation between O^* and OH^*) and/or the intercept $B_{\text{OH}^*,\text{OOH}^*}$ (the relation between OH^* and OOH^*) should be explored to circumvent this internal issue.

Many recent research efforts have been made to find rational descriptors of OER—a single microscopic parameter to describe the catalytic activities of different electrode materials. A descriptor could be any internal property of the catalyst or

catalyst-reactant interaction. Successful descriptors can always describe the interaction strength between key intermediates involving catalytic reaction and the catalytic active sites in the surface region [27]. According to such descriptors, a volcano plot can be obtained (Fig. 2(c)), and the maximum activity can be achieved at an optimum descriptor value with moderate interaction. Because of the scaling relation between M-O, M-OH, and M-OOH, it has been proven that both ΔG_0 and $\Delta G_0 - \Delta G_{OH}$ can serve as appropriate descriptors for OER, representing the internal oxygen affinity of catalytic surfaces [31,36]. Fig. 2(d) displays a volcano plot, which shows the trend in the catalytic activity of various oxides as a function of $\Delta G_0 - \Delta G_{OH}$ [36]. The optimum value of $\Delta G_0 - \Delta G_{OH}$ is approximately 1.6, which means that at such values, the catalysts bind the intermediates neither too weakly nor too strongly. Additionally, the PDS of the catalysts can also be concluded using such volcano plots through different O binding strengths. On surfaces that bind O strongly (left region of the volcano plot), the PDS is the formation of M-OOH ($O^* \rightarrow HOO^*$). Correspondingly, when O binds the surfaces too weakly, PDS is the formation of M-OH ($* \rightarrow HO^*$, when $\Delta G_1 > \Delta G_2$ in Eqs. (7) and (8)) or the oxidation of M-OH ($HO^* \rightarrow O^*$, when $\Delta G_2 > \Delta G_1$). This is determined by the relative free energy differences of ΔG_1 and ΔG_2 .

In addition to direct intermediate adsorption interaction, several electronic structure-related descriptors have also been developed under the concepts of orbital occupancy and electron counting. Motivated by the successful application of the *d*-band theory to describe the catalytic activities of pure transition metals, Suntivich *et al.* [38] correlated the estimated e_g occupancy of transition metal sites in perovskites with corresponding OER activities, obtaining a volcano-shaped dependence (Fig. 2(e)). The authors proposed that the e_g filling of surface transition metal cations greatly influenced the binding energy of OER intermediates, as e_g -orbitals in σ -bonding formed stronger overlaps with the oxygenated adsorbates. In addition, the Shao-Horn group also pointed out that the O 2*p* bands in perovskite oxides reflected the covalency character between metal sites and oxygen, and these values were further relevant to the relative activities of O-containing adsorbates with catalytic active sites [40]. Moreover, the Vojvodic group screened ternary ABO₃ perovskite oxides as OER catalysts using high-throughput computation and revealed the universal scaling relation between ΔG_{HOO} and ΔG_{HO} for perovskite-type catalysts [39]. By correlating the electronic structure of the perovskite surface with the corresponding free energy of oxygen adsorption, the authors reported that the center of the *p*-projected density of states (DOS) for surface oxygen atoms served as a more general parameter to reflect the adsorption behavior of O* adsorbates on the B site (Fig. 2(f)). Additionally, the parameters evaluated from the *d*-band model (total *d*-state filling, e_g -state filling, and t_{2g} -state filling) were not appropriate to describe the bond energy when the *d*-states of the B site are completely filled or unfilled.

2.2. Lattice-oxygen oxidation mechanism

The LOM of OER has recently been developed to bypass the

adsorption scaling relation involved in AEM. In fact, due to the enhancement of characterization techniques at the molecular level, some catalysts have revealed that at least some degree of lattice oxygen atoms participate during the OER, including Ru-/Ir-based catalysts, perovskites with high metal-oxygen covalency, and some Co-based catalysts [41]. As a newly identified mechanism, the detailed scheme of LOM is not clear enough, and the internal origin of LOM is not fully understood.

Fig. 3(a) summarizes three previously reported possible reaction pathways for LOM. The main differences among the three pathways lie in the binding pattern between lattice oxygen and the as-formed intermediate. In pathway 1, the HO* derived from the water molecule first interacts with metal adsorption site M, followed by an oxidation process to form O*. This process is similar to the initial step of the AEM. In the next step, the O* species directly reacts with lattice oxygen to produce a dioxygen species (OO*), releasing the O₂ product and leaving an oxygen vacancy on the catalyst surface. The oxygen vacancy might be refilled by the adsorption of HO*, and this restoration step prevents the structure of the catalyst from collapsing. In pathway 2, the as-formed HO* intermediate chooses the lattice-oxygen site as the initial adsorption site, rather than the metal site. This means that HO* directly combines with lattice-oxygen to form HOO*. The HOO* species subsequently dissociates to generate O₂ and H⁺. The lattice oxygen also partially contributes to the final O₂ product. In pathway 3, two lattice oxygen atoms may couple with each other under OER conditions (step 1–step 2), forming two oxygen vacancies simultaneously on the catalyst surface.

In the framework of LOM, some non-concerted proton–electron-transfer processes (*e.g.*, direct O–O coupling step) may be involved in the OER. This is a noticeable difference between the LOM and AEM. The Shao-Horn group reported that LOM-involved perovskite catalysts (*e.g.*, La_{0.5}Sr_{0.5}CoO_{3-δ}, Pr_{0.5}Ba_{0.5}CoO_{3-δ}, and SrCoO_{3-δ}) exhibited pH-dependent catalytic behavior for the OER [30]. This phenomenon implies that the redox activity of lattice oxygen might be associated with pH conditions, and the rate-determining step of these catalysts might be limited by the concentration of protons. Additionally because of the involvement of the direct O–O coupling step, LOM can fundamentally circumvent the scaling relation limitation of OER adsorbates. As a result, catalysts based on LOM potentially have lower reaction barriers and faster reaction kinetics than those based on AEM [19,21].

Isotope labeling methods using ¹⁸O together with *in situ* mass spectrometry are a powerful characterization combination for splitting the contributions of AEM and LOM for a given catalytic material. Mayrhofer and coworkers synthesized crystalline Ir¹⁸O₂ and hydrous Ir¹⁸O_x as model materials, and traced their atomic structural evolution and O₂ product during OER. The authors found that crystalline Ir¹⁸O₂ and amorphous Ir¹⁸O_x behave in different ways under catalytic conditions [42,44]. Atom probe tomography (APT) revealed that the ¹⁶OH groups interacted with Ir¹⁸O₂ only in the surface region, and online electrochemical mass spectrometry (OLEMS) analyses demonstrated that molecular oxygen was generated totally from H₂¹⁶O rather than from lattice ¹⁸O. These results suggest that the OER

Fig. 3. (a) Schematic illustration of three possible LOM schemes. (b) APT data of the near-surface region of hydrous Ir^{16}O_x . (c) Local mass spectrum of oxide cluster in (b). (b,c) Reproduced with permission [42]. Copyright 2019, Royal Society of Chemistry. (d) Colored HRTEM image of $\text{La}_2\text{LiIrO}_6$ after 50 CV measurements. (e) XAS spectra of pristine $\text{La}_2\text{LiIrO}_6$, $\text{La}_2\text{LiIrO}_6$ after oxidation and IrO_2 . (d,e) Reproduced with permission [43]. Copyright 2017, Nature Publishing Group.

in the presence of crystalline IrO_2 followed the AEM. In the case of amorphous Ir^{18}O_x , the high density of defects and the porous nature allowed the ^{16}OH groups to easily permeate into its loose structure, as demonstrated by the APT results (Figs. 3(b,c)). As for the oxygen products, $^{16}\text{O}^{16}\text{O}$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}^{18}\text{O}$ were detected using OLEMS. The formation of $^{18}\text{O}^{18}\text{O}$ also indicated that both oxygen atoms were derived from the oxide matrix. These results demonstrated that both AEM and LOM were involved in the Ir^{18}O_x -catalyzed OER.

In another example, Grimaud *et al.* [43] reported that $\text{La}_2\text{LiIrO}_6$ exhibited 50 times enhancement in OER activity compared with IrO_2 at pH 1. Using differential electrochemical mass spectrometry (DEMS) in an organic solvent, the authors captured a surface oxygen loss process. In addition, the authors also observed the migration of bulk oxygen to the surface and the reduced oxidation state of the Ir species during the OER (Figs. 3(d,e)). [43]. In addition to the experimental results, the DFT results also showed that O species could be activated in the delithiated phase of $\text{La}_2\text{LiIrO}_6$, and some surface oxygen atoms exhibited an electrophilic nature. Based on the experimental and theoretical results, the authors postulated the involvement of LOM to explain the superior catalytic activity of $\text{La}_2\text{LiIrO}_6$ for the OER. The electrophilic surface oxygen was believed to be prone to interaction with water for the for-

mation of OOH^* intermediates, followed by the simultaneous generation of molecular dioxygen and oxygen vacancies on the surface.

In contrast to AEM, the theoretical research on LOM is only at the initial stage, and the lattice oxygen participation during OER for various catalysts is still debated. The Alexandrov group compared the thermodynamic overpotential of AEM and LOM for rutile RuO_2 and IrO_2 catalysts using DFT calculations, further demonstrating the possible promotions of structural defects (vacancies and transition metal dopants) for the involvement of LOM [45]. The results showed that for perfect (110) and (211) surfaces of RuO_2 and IrO_2 , AEM exhibited a much lower thermodynamic limit than LOM. This implied that perfect crystalline RuO_2 and IrO_2 followed a pathway of AEM, in agreement with the above experimental results. However, when structural defects were introduced into the surfaces of RuO_2 and IrO_2 , the LOM pathway started to become competitive with a significantly reduced OER overpotential. In the case of RuO_2 , both surface vacancies and Ni/Co dopants can switch the favorable OER mechanism from the AEM to the LOM, demonstrating that RuO_2 is sensitive to structural defects. For IrO_2 , things become slightly different. Although the overpotential of LOM was also reduced in the presence of vacancies (from 2.40 to 0.33 V for IrO_2 (110)), IrO_2 surfaces with low defect

concentrations still preferred to follow AEM rather than LOM, demonstrating that LOM had a weaker destabilizing effect on the lattice of IrO₂. These results demonstrate the reason why IrO₂ exhibits a much better structural stability than RuO₂ under OER electrochemical conditions. Additionally, by correlating the O 2p-band center of the catalyst with OER overpotential, the authors suggested that this important parameter correlated well with the OER overpotential for both AEM and LOM, and the LOM became more competitive than the AEM when the O-2p band center of the catalyst moved closer to the Fermi level. In another theoretical work on perovskites, Yoo *et al.* [46,47] also demonstrated the importance of the involvement of LOM on the catalytic activities of ABO₃ perovskites, and the theoretical overpotentials of OER were much more explainable when the LOM was considered. The authors further reported that under LOM, the lattice oxygen in ABO₃ participated in the formation of reaction intermediates through the reversible formation of surface oxygen vacancies (V_O).

It can be concluded that many structural properties of catalytic materials, including crystallinity, composition, defects, and crystal structure, can influence which reaction mechanism (AEM or LOM) is adopted under OER conditions [19], and there is also another reasonable possibility, which is that both AEM and LOM may occur on a given catalytic material simultaneously. Moreover, it should also be noted that the reversible oxygen vacancy refilling process of LOM seems to be closely associated with the structural stability of the catalyst. When the kinetics of refilling oxygen vacancies is slow, the restoration step of HO* adsorption cannot catch up the generation rate of oxygen vacancies, and thereby structural degradation or cation dissolution may occur. Relevant experimental results also demonstrate that LOM-active perovskites generally undergo rapid surface amorphization and suffer from cation dissolution during OER operation, further leading to poor OER catalytic stability [40]. Therefore, besides catalytic activity, the structural stability of catalyst may also correlate with the involved mechanism during OER, and the corresponding surface structural evolution of catalyst should be carefully examined for both mechanism understanding and catalyst design.

3. Experimental methods for evaluating catalytic performance of OER electrocatalysts

Electrocatalysis is generally defined as a catalytic reaction occurring at the electrode-electrolyte interface, and the corresponding catalytic activity demonstrates the ability of an electrode surface or electrocatalyst material to facilitate the rate of the electrochemical process. For any research on electrochemical reactions, the core parameters should be the kinetic parameters that can describe the electro-transfer reactions under the purpose of fundamental investigation, together with the internal parameters that can represent the catalytic activity and stability of electrocatalysts from an application perspective. Current (*i*) and potential (*V*) are the most observable parameters for any electrochemical measurement. Generally, the current represents the rate of the interfacial reaction, and the potential can be regarded as the driving force for the electro-

catalysis process. The current value is dependent on the applied potential from any given electrochemical process. The relationship between current and potential and some specific parameters for describing the intrinsic catalytic properties of catalysts are summarized in the following section.

3.1. Experimental methods for evaluating catalytic activity

3.1.1. Overpotential

Overpotential (η) is one of the most effective parameters for evaluating the catalytic activity of materials. By performing a linear sweep voltammetry (LSV) measurement for a specific catalyst under a potential above 1.23 V vs. RHE (Fig. 4(a)), the polarization curve of the OER and the corresponding overpotential can be obtained. It should be noted that, for the accuracy of measurement, the scan rate of the LSV should be set as approximately 1 mV/s, or a steady-state polarization curve should be conducted to eliminate the influence of the non-Faraday current. Additionally, due to the fact that different current values can be obtained by verifying the surface areas of the electrode, under a purpose of carrying out parallel comparisons for various catalysts, the measured catalytic current (*i*, mA) during OER is generally normalized by the geometric area of the electrode (*A*, cm²) to get the geometric current density (*j*_{geo}, mA/cm_{geo}²), as shown in Eq. (13).

$$j_{\text{geo}} = \frac{i}{A} \quad (13)$$

The overpotential to achieve a geometric current density of 10 mA/cm_{geo}² is usually considered an important criterion for the assessment of catalytic activity with a lab-scale electrochemical testing system. This particular current density originates from the estimated current density generated by a solar water-splitting device with a 10% solar-to-fuel efficiency under an energy input of 1 sun illumination [48,49]. This parameter represents the apparent OER activity of the catalyst, which can also be estimated by the geometric current density at a given overpotential (*e.g.*, $\eta = 300$ mV vs. RHE). However because the geometric current density does not contain detailed information about the loading mass and/or surface area of the catalysts, this value fails to reflect the intrinsic activity of the nanostructured catalyst.

3.1.2. Tafel slope and exchange current density

Steady-state Tafel plot analysis is one of the most prevalent techniques for describing the electro-transfer process involved in electrocatalytic reactions. Generally, the relationship between the apparent catalytic current (*i*) and overpotential (η) can be described mathematically using the Butler-Volmer equation (Eq. (14)).

$$i = i_0 \cdot \left\{ \exp \left[\frac{\alpha_a n F \eta}{RT} \right] - \exp \left[\frac{\alpha_c n F \eta}{RT} \right] \right\} \quad (14)$$

where *i*₀ is the exchange current representing the rate of forward and reverse reactions at the equilibrium potential [27], *T* is the absolute temperature, *n* is the total electron number involved in the reaction, *F* is Faraday's constant, and *R* is the universal gas constant. α_a and α_c are the transfer coefficients for the anodic and cathodic reactions, respectively, and the sum of

Fig. 4. (a) A polarization curve for OER. η_{10} is the overpotential at 10 mA/cm². (b) A Tafel plot converted from (a). The red dashed line depicts the least potential deviation for determining the linear region. (c) Schematic diagrams of Tafel plot analysis for two specific catalysts. (d) CV plots with different scan rates under the non-Faradic range. (e) A linear trend conducted from the difference of Δj against different scan rates. (f) CV plot of SrZrO₃-SrIrO₃ solid solution at a potential region of 0.4–1.4 V vs. RHE.

α_a and α_c is 1 ($\alpha_a + \alpha_c = 1$). From Eq. (14), the Butler-Volmer equation includes the contribution of both the anode reaction and the cathode reaction on one electrode surface. Note that in the potential range of OER, the anodic reaction dominates the total electrochemical reaction, and the cathode reactions can be ignored. Thus, under such conditions, the Butler-Volmer equation can be simplified to the Tafel equation (Eq. (15)).

$$i = i_0 \cdot \exp \left[\frac{\alpha_a n F \eta}{RT} \right] \quad (15)$$

By expressing the current in logarithmic form, the Tafel equation can be further depicted using Eqs. (16–18).

$$\eta = a + b \log |i| \quad (16)$$

$$a = \frac{2.303RT}{\alpha_a nF} \log |i_0| \quad (17)$$

$$b = \frac{2.303RT}{\alpha_a nF} \quad (18)$$

It is clear that there is a linear relationship between η and $\log |i|$ predicted from Eq. (16) and the slope b of the linear relation is well-known as the Tafel slope with a unit of millivolts per decade of current (mV/dec). a is the intercept of the linear relation, and the corresponding exchange current i_0 can be obtained by Eq. (17). Additionally, by normalizing the i_0 using geometric area of the electrode, the exchange current density (j_0) can be obtained.

To correlate the Tafel equation with the actual experimental result, a general Tafel plot can be converted from the polarization curve by setting the $\log |j_{\text{geo}}|$ as the x axis and the overpotential as the y axis (Fig. 4(b)). The Tafel slope b and exchange

current density j_0 related to the catalytic reaction can be extracted by fitting the linear region in the Tafel plot. In addition because there may be more than one linear region in the Tafel plot, the potential range of the linear region should be chosen carefully and needs to satisfy two implicit requirements. (1) The potential range of the linear region in the Tafel plot should roughly correspond to the potential range where the current density starts to increase rapidly in the corresponding polarization curve [50], as illustrated by the light yellow region in Figs. 4(a,b). (2) The potential range of the linear region should deviate from the equilibrium potential for at least ~50 mV (Fig. 4(b)), considering that at this potential range, the contribution of the cathode reaction in the Butler-Volmer equation (Eq. (14)) can be eliminated to follow the establishing condition of the Tafel equation.

The Tafel slope is a multifaceted parameter that can provide rational interpretation for both catalytic activity and reaction mechanism. For basic catalytic activity evaluation, the Tafel slope can represent the rate of change of the current density with the electrode potential. From Eq. (16), a low Tafel slope indicates that the current density can increase rapidly with a small overpotential voltage change, demonstrating fast reaction kinetics. For fundamental mechanism characterization, the Tafel slope can demonstrate the rate-determining step (RDS) of the catalytic reaction. The RDS is actually highly correlated with the transfer coefficient α_a , which is experimentally estimable using Eq. (18) from the value of the Tafel slope. α_a can be further deconstructed according to Eq. (19).

$$\alpha_a = n_f/v + n_r\beta \quad (19)$$

where n_f is the number of electrons transferred before the RDS, and n_r is the number of electrons participating during the RDS [27]. For the proton-electron-transfer process in OER, the value of n_r can be assumed to be 1. v is the number of times for RDS in the overall reaction, and β is the symmetry factor generally considered to be 0.5. By combining Eqs. (18) and (19), the RDS of the OER can be rationally evaluated. For example, if the first step of the OER (Eq. (3)) is RDS, the value of α_a should be 0.5, considering that n_f and n_r should be 0 and 1, respectively. Thus, the value of the Tafel slope can be inferred as 120 mV/dec. This means that when the actual value of the Tafel slope is close to ~120 mV/dec, the RDS should be the formation of M-OH. Additionally, because the determination of RDS is a kinetic analysis of the catalytic reaction, it is important to distinguish the RDS from the concept of the PDS, as mentioned in Section 2.1. Note again that the PDS represents the predicted thermodynamic barrier for OER. The RDS as a kinetic concept includes the contribution of the activation barrier; therefore, the PDS and RDS should not necessarily be the same.

In addition to the Tafel slope, the exchange current density j_0 can also reflect the kinetics of the catalytic reaction. Generally, a large j_0 value indicates fast reaction kinetics and high catalytic performance. Thus, an effective catalyst generally exhibits a low Tafel slope with a high exchange current density. However, in the actual experimental case, a special situation exists where the Tafel slope b does not correspond to the j_0 value, as illustrated in Fig. 4(c) [27]. Catalyst I exhibits a low Tafel slope with a low j_0 value, while catalyst II possesses a high j_0 value with a high Tafel value. More complicated explanations need to be conducted to describe these two catalysts. According to the physical interpretation of Eq. (14), j_0 may refer to the kinetics at the thermodynamic potential. It may not represent the reaction kinetics at a higher potential range, which is more meaningful for practical applications. Therefore, compared with the exchange current density, the Tafel slope is more important for determining the favorable catalytic properties. Catalyst I is more suitable for practical applications because it exhibits a higher current density at a lower overpotential than catalyst II.

3.1.3. Mass activity, turnover frequency and specific activity

As mentioned before, comparing the overpotential at a given geometric current density is a universal method for evaluating the catalytic performance. However, this geometric activity is largely dominated by the loading amount of the catalyst, and it cannot reflect the surface reaction behavior of the catalysis process, especially for nanostructured catalysts with roughened interfaces. Thus, other important parameters, including mass activity, turnover frequency, and specific activity, are summarized in this section, with the aim of providing a comprehensive activity evaluation for a particular catalyst.

The mass activity was obtained by normalizing the catalytic current to the loading mass of the catalysts or the total amount of active metal species in the catalysts at a given potential. This parameter correlates with the cost efficiency of the catalyst. A high mass activity demonstrates that a small amount of such catalyst would exhibit an efficient catalytic performance. Thus,

considering the severe scarcity of Ir, iridium mass activity (j_{Ir} , A/g_{Ir}) of iridium-based catalysts is an important parameter for evaluating iridium utilization in the catalyst. The corresponding equation is presented in Eq. (20).

$$j_{\text{Ir}} = \frac{i}{m_{\text{loading}} \times \text{Ir}(\text{wt}\%)} \quad (20)$$

where Ir (wt%) is the mass fraction of iridium in catalyst and m_{loading} (mg) represents the loading mass of catalyst. Note that the mass activity is not a parameter that represents the intrinsic activity of the catalyst. In view of the fact that the catalytic reaction generally occurs on the surface region of catalysts, a nanostructured catalyst with a high number of surface-active sites would exhibit higher mass activity than their bulk counterparts, but the two materials may possess similar intrinsic catalytic activity.

Turnover frequency (TOF) is defined as the number of products produced for a single catalytic site per unit of time at a given potential [51]. TOF is a reasonable parameter for describing the intrinsic activity of a catalyst. However, owing to the fact that it is difficult to obtain the real active site number of catalysts, the precise assessment of TOF values for heterogeneous electrocatalysts is still a challenge. Currently, there are three main methods for a compromise to evaluate TOF. The first involves converting the surface area of the catalysts to the number of active sites through a specific coefficient [52]. This coefficient defines the active site number per unit surface area, which is always determined according to the literature. The second is evaluating the number of active sites of the catalysts through cyclic voltammetry (CV) measurements. For materials with clear redox CV features, the corresponding coulombic charge (Q) can be quantified by integrating the specified CV peak, further obtaining the number of possible participating atoms in the catalysts during the reaction. The last one assumes that all atoms in the catalyst serve as the active sites for the catalytic reaction, and the active site number is obtained by normalizing the loading amount of the catalyst with molecular weight. Unlike the previous two methods, the last method cannot reflect the intrinsic activity of the catalyst, whose value is essentially correlated with the mass activity of the catalyst.

The specific activity was estimated by normalizing the catalytic current with the surface area of the catalyst. As a more convenient alternative to TOF, it can reflect the intrinsic activity of the catalyst. Accordingly, this parameter can be used to demonstrate the internal differences among various catalysts, further revealing the fundamental structure-activity relationship of the catalysts. As a crucial variable for specific activity, the surface area of the catalyst refers to the real surface region that participates in the catalytic reaction. Thus, rational evaluation of specific activity calls for experimental approaches to determine the surface area of the catalyst. These methods can be roughly split into non-electrochemical methods and electrochemical methods.

For non-electrochemical methods, using adsorption and desorption measurements of probe gas molecules (N₂ for most frequently, or CO, O₂, H₂, etc.) together with the corresponding Brunauer-Emmett-Teller (BET) adsorption isotherm studies is a method to evaluating the available surface area for

nanostructured materials. The so-called BET-normalized specific activity (j_{BET} , mA/cm_{BET}²) can then be calculated using Eq. (21).

$$j_{\text{BET}} = \frac{i}{\text{BET} \times 10 \times m_{\text{loading}}} \quad (21)$$

where BET (m²/g) is the BET surface area. Owing to the universality of this measurement, this parameter is easily reproducible and provides a meaningful expression for intrinsic activity. However, it is difficult to monitor the structural changes of the catalyst during OER. In addition, the BET surface area of the material is not sufficiently reliable when the catalyst possesses a small surface area (e.g., < 20 m²/g). In addition to the BET method, atomic force microscopy (AFM) and electron microscopy measurements (transmission electron microscopy and scanning electron microscopy) can also be used to evaluate the surface area of materials. AFM is capable of measuring the surface areas of thin-film electrodes, and it is appropriate to use electron microscopy measurements to evaluate materials with regular shapes [52].

As for electrochemical methods, the as-measured surface area of the catalyst should be more rational in terms of the electrochemical active surface area (ECSA, cm²). Then, the ECSA-normalized specific activity (j_{ECSA} , mA/cm_{ECSA}²) can be obtained through Eq. (22).

$$j_{\text{ECSA}} = \frac{i}{\text{ECSA}} \quad (22)$$

To estimate ECSA, the double layer capacitance (C_{dl} , mF/cm²) of the catalyst is the most universal indicator for extracting the surface area of the catalyst accessible to the electrolyte ions. Generally, a series of cyclic voltammetry (CV) measurements with different scan rates (e.g., 20, 40, 60, 80, and 100 mV/s) are performed first in a potential window in the non-Faradic range (Fig. 4(d)). Then, a linear trend can be obtained by plotting the difference in the geometric current density ($\Delta j = j_{\text{anodic}} - j_{\text{cathodic}}$) at the middle position of the potential range against the scan rate, as shown in Fig. 4(e). The half value of the resulting slope for the fitting line is the as-estimated C_{dl} of the catalyst. Finally, the ECSA can be obtained from C_{dl} according to Eq. (23)

$$\text{ECSA} = \frac{C_{\text{dl}}}{C_s} \times A \quad (23)$$

where C_s (mF/cm²) is the specific capacitance of the sample, which represents the capacitance of an atomically smooth planar surface of the material per unit area under identical electrolyte conditions [48]. Besides C_{dl} measurement, utilizing specific redox reactions occurring on the surface of the catalyst is another effective alternative to obtain the corresponding ECSA. The specified surface reactions include hydrogen underpotential deposition (HUPD), CO stripping reaction, underpotential deposition (UPD) of metal, surface redox reaction of the catalyst, and the coulombic charge (Q , C) can be quantified from the corresponding redox region in characteristic CV peaks [52]. The ECSA can then be converted from Q through a known specific charge, which is mostly determined by experimentally measured values or calculated results based on simplified models [52]. For example, Fig. 4(f) presents a CV plot that demonstrates the surface redox reaction of the SrZrO₃-SrIrO₃ solid solution [53]. A potential region of 0.4–1.4 V vs. RHE is set

for this CV plot, assuming that only Ir species undergo *in situ* oxidation and reduction under such potential range. The value of Q can then be extracted by integrating the backward reduction peak, reflecting the surface-active concentration of Ir sites. Additionally, rather than using specific charge to evaluate the corresponding ECSA, the Q -normalized specific activity (j_Q , A/C) can be calculated by Eq. (24).

$$j_Q = \frac{i}{Q} \quad (24)$$

This is another parameter for obtaining comparable intrinsic activities. Both j_{ECSA} and j_Q are sensitive for diagnosing the structural changes of catalysts during OER. However, they all suffer from poor reproducibility, considering that many practical factors such as catalyst mass loading, measurement configuration, electrode effect, and/or potential window range could influence the as-calculated value of ECSA and Q . Because of this limitation, a comparison of the intrinsic activity of various catalysts using j_{ECSA} or j_Q is recommended to be carried out under the same testing conditions. The as-calculated j_{ECSA} or j_Q from different reports could hardly be compared based on the above considerations, even for the same catalyst.

3.1.4. Faradaic efficiency

In addition to obtaining various parameters through the reaction current to evaluate the catalytic activity of materials, it is also important to determine if all the transferred electrons (charge) participate in the catalytic reaction of OER, or if some portions are consumed by other side reactions. Faradaic efficiency describes the efficiency of electron involvement for a specific reaction. The Faradaic efficiency can be obtained by calculating the ratio of the measured amount of evolved product (experimental value) to the expected amount of product based on Faraday's law (theoretical value). In the case of OER, the product is an as-generated O₂ gas, and a 100% Faradaic efficiency means that 100% of the current output during electrolysis is derived from the OER without any side reactions. Additionally, there might be two main factors affecting the Faradaic efficiency of the OER. The first factor is derived from specific materials with reduced states (alloy materials, chalcogenides, phosphides, etc.) [5]. Due to the oxidation condition of OER, these catalytic species cannot remain stable, and some oxidation reactions together with irreversible valance increments would occur on the surface region of the materials. Accordingly, some of the electrons are consumed by these surface reactions. This would reduce the Faradaic efficiency of the OER, further generally accompanied by a transformation of the catalytic active phase. The other factor originates from some competitive redox couples in the electrolyte. For example, if there are certain amounts of chloride ions (Cl⁻) in the acidic electrolyte, the chlorine evolution reaction (CER) will theoretically start to occur when the applied potential reaches 1.36 V (equilibrium potential of CER) [54]. This means that the CER would tend to simultaneously occur at high current densities with OER, further influencing the calculated Faradaic efficiency of the OER.

3.2. Experimental methods for evaluating catalytic stability

In general, the electrocatalytic stability of a material is examined by a combination of many kinds of electrochemical measurements, such as chronoamperometry (CA), chronopotentiometry (CP), and LSV curves. However, these stability evaluation techniques are insensitive to the possible structural changes of materials. The catalytic stability of the OER catalyst may not necessarily correlate with its corresponding structural stability. In order to uncover possible structural variations of the catalysts, various characterization techniques should be used under *in situ* conditions, such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), energy-dispersive X-ray spectroscopy (EDS), inductively coupled plasma atomic emission spectroscopy (ICP-OES), Raman spectroscopy, and high-resolution transmission electron microscopy (HRTEM) [55].

Under acidic OER conditions, the inevitable dissolution of cations often occurs in all cases of various catalytic materials, and this is the core concern related to catalyst stability. In a notable example, the Markovic group investigated a series of monometallic oxides for acidic OER, and pointed out that the activity and stability trends of these oxides were actually reversed [56]. The activity followed a trend of $\text{Os} \gg \text{Ru} > \text{Ir} > \text{Pt} \gg \text{Au}$, while the catalytic stability increased in the order $\text{Au} \gg \text{Pt} > \text{Ir} > \text{Ru} \gg \text{Os}$ (Fig. 5(a)). Ir oxide was identified to achieve promising activity with acceptable stability. Recently, different types of Ir-based materials have been developed for acidic OER, including amorphous and hydrous oxides [57–59], perovskites, pyrochlores, and hollandites with different chemical composi-

tions and crystal structures. In fact, all of these Ir-based materials generally followed the reverse catalytic activity-structural stability relationship.

In order to better evaluate the catalytic properties of an OER catalyst, it is desirable to develop a common, simple, and comprehensive method to describe the activity-stability relation of an OER catalyst. Geiger et al. [60] investigated the dissolution behaviors of amorphous IrO_x , crystalline IrO_2 , SrIrO_3 perovskite, and A_2BIrO_6 ($\text{A} = \text{Ba}, \text{Sr}$; $\text{B} = \text{Nd}, \text{Pr}, \text{Y}$) double perovskite. Geiger et al. [60] built an independent stability parameter, the so-called stability number (S-number), to define the intrinsic structural stability of the catalyst. The S-number can be calculated as the amount of evolved O_2 divided by the amount of dissolved Ir, as shown in Eq. (25).

$$\text{S-number} = \frac{n_{\text{O}_2(\text{OER})}}{n_{\text{Ir}(\text{dissolved})}} \quad (25)$$

where $n_{\text{O}_2(\text{OER})}$ is the moles of produced O_2 , and $n_{\text{Ir}(\text{dissolved})}$ is the number of moles of leached Ir species. Based on this method, a promising electrocatalyst would exhibit a relatively high stability number, and the S-number of IrO_2 is evaluated to be approximately $1.0 \text{ E}+6$ to $1.0 \text{ E}+7$ (Fig. 5(b)). Moreover, the authors also proposed that the value of S-number was not influenced by the mass loading of the catalyst, surface area of the working electrode, and/or applied potential (Fig. 5(c)), demonstrating the potential universality of this specific parameter.

In another attempt, the Markovic group tried to quantify the activity-stability relationship of materials by proposing a parameter called the activity stability factor (ASF), which can be

Fig. 5. (a) The inverse relationship between the stabilities of monometallic oxides and their reactivities for OER. Reproduced with permission [56]. Copyright 2014, American Chemical Society. (b) Stability number presented for iridium containing catalysts in thin film or powder form. (c) Stability number plotted versus mass specific current density for some iridium containing powder catalysts. (b,c) Reproduced with permission [60]. Copyright 2018, Nature Publishing Group. (d) The activity stability factor (ASF) for Ir-poly and dft-Ir₂₅Os₇₅. Reproduced under the terms of the Creative Commons Attribution License.

Fig. 6. Iridium dissolution profiles for (a) Ir black (red), electrochemically oxidized iridium (blue) and (b) thermally prepared IrO₂ when cycling the catalysts from 0.05 to 1.2 V. (a,b) Reproduced with permission [62]. Copyright 2017, American Chemical Society. (c) CV curves (left axis) and Ir oxidation state value at applied potentials (right axis) of EIROF. Reproduced with permission [65]. Copyright 2014, Royal Society of Chemistry. Ir 4f (d) and O 1s (e) XPS spectrum under open circuit and oxygen evolution conditions. (d,e) Reproduced with permission [66]. Copyright 2014, Wiley-VCH.

calculated by Eq. (26).

$$\text{ASF} = \frac{J - S}{S} \Big|_{\eta} \quad (26)$$

where J is the catalytic current density, which is employed to represent the O₂ production rate, S is the dissolution current density, which is equivalent to the metal dissolution rate during OER, and η stands for a constant overpotential [61]. A material with a higher ASF value tends to possess both superior activity and stability, suggesting that its balance of activity and stability may be closer to ideal. In their work, they used dealloyed Ir₂₅Os₇₅ thin films (dtf-Ir₂₅Os₇₅) as an example (Fig. 5(d)), which exhibited a factor of ~30 improvement for ASF compared with Ir-based oxide materials (Ir_{poly}). However, it should be noted that the determination of J and S from experimentally measured faradaic currents is conducted using an *in situ* stationary probe rotating-disk electrode (SPRDE) coupled to an inductively coupled plasma-mass spectrometer (ICP-MS). This obvious equipment limitation may substantially impede the promotion of such parameters.

4. Recent insights in structural evolution of Ir oxides under OER electrocatalysis

Nanosized IrO₂ is an OER electrocatalyst that is currently employed for commercial PEM water electrolyzers. With the substantial development of *in situ* characterization techniques,

some new insights into the structural evolution of Ir oxides, including IrO₂ and its relative IrO_x, under OER electrocatalysis have been achieved recently.

The dissolution behavior of various Ir oxides under OER conditions is rather complicated. The influence factors include not only the nature of OER catalysts, such as crystallinity and composition, but also the external working environment (*e.g.*, electrolyte and applied potential). Jovanović *et al.* [62] systematically investigated the electrochemical dissolution of (1) pure metallic iridium (A-Ir), (2) electrochemically oxidized iridium (E-Ir), and (3) thermally prepared IrO₂ (T-IrO₂) under a high-sensitivity electrochemical flow cell (EFC) [62]. The results demonstrated that the corrosion stability increased in the order of A-Ir < E-Ir < T-IrO₂. Metallic iridium particles exhibited the most unstable nature, and the dissolution concentration of T-IrO₂ was two orders of magnitude lower than those of A-Ir and E-Ir. The authors further pointed out that both cathodic and anodic dissolutions were detected for Ir-based materials (Figs. 6(a,b)). Three possible dissolution pathways were proposed, including reduction dissolution (Eq. (27)), direct dissolution (Eq. (28)), and oxidation dissolution (Eq. (29)).

Both A-Ir and T-IrO₂ were inferred to dissolve predominantly through the generation of unstable Ir species with a

valence state $> +4$. The dissolution mechanism of E-Ir exhibited a different pathway, which mainly proceeded *via* the transient formation of Ir(IV) to Ir(III). In another work, Kasian *et al.* [63] monitored the degradation products of Ir and Ir oxides using a scanning flow cell coupled with online electrochemical mass spectrometry (OLEMS). The formation of IrO_3 was observed for all the studied anodes, and IrO_3 was considered to be one of the active phases for Ir-based materials. IrO_3 either decomposes into IrO_2 and O_2 to generate an O_2 product or interact with water to form soluble $\text{IrO}_2\text{-4}$, leading to one of the major dissolution pathways for Ir oxides.

The valence state variations of Ir and O species in Ir oxides during catalytic reactions need to be carefully considered, and the actual existential forms of both Ir and O species are highly correlated to the corresponding mechanism for OER [64–70]. In order to identify the valence state of the Ir species, Minguzzi *et al.* [64] applied *in situ* X-ray absorption spectroscopy (XAS) to monitor the signal change and position shift at the Ir-L_{III} edge under oxygen evolution conditions. Electrodeposited iridium oxide film (EIROF) was chosen as the study object, and its highly hydrated property ensured that a considerable part of EIROF participated in the catalytic reaction. Using the spectra of powdered IrCl_3 and IrO_2 as a reference, the authors pointed out that Ir species in EIROF were present in both the Ir(III) and Ir(V) oxidation states during the OER (Fig. 6(c)), while there was no direct evidence to support the presence of Ir(IV) under water oxidation conditions. The same group further investigated three Ir oxides with different hydration degrees for the OER [65]. The coexistence of Ir(III) and Ir(V) was observed under $E \geq 1.3$ V for various Ir oxides. The hydrated nanoparticles exhibited higher intrinsic activity and might possess an enhanced ability to generate Ir(V) sites and/or enhance proton mobility. In another study, Casalongue *et al.* [66] used ambient-pressure X-ray photoelectron spectroscopy to probe the change of Ir oxidation state for IrO_2 nanoparticles. The Ir 4f XPS spectra showed that a fraction of the surface Ir(IV) sites transformed into Ir(V) species during the OER (Fig. 6(d)). Their results also demonstrated that the valence state variation was confined to the catalyst surface, and both Ir(IV) and Ir(V) oxidation states were present for IrO_2 nanoparticles. In addition, the change in the Ir 4f spectra was only detected under oxygen-evolving conditions, demonstrating the electrochemical reversibility of the Ir species. Moreover, by examining the O 1s spectra during OER (Fig. 6(e)), the authors monitored the reduction of adsorbed hydroxide on the catalyst surface. This result indicated that IrO_2 nanoparticles favored a deprotonation pathway and went through the conversion from hydroxide to oxide.

The presence of a mixed-valence state of oxygen species in Ir oxides was first reported by Pfeifer *et al.* [67]. In contrast to rutile IrO_2 , a distinct resonance was identified for amorphous IrO_x at 529 eV of O K-edge spectra using near-edge X-ray absorption fine structure (NEXAFS) measurements (Fig. 7(a)), and this resonance was associated with O^{1-} . Based on this finding, the authors claimed that electrophilic O^{1-} might play a key role in OER catalysis for amorphous IrO_x . O^{1-} could be susceptible to the nucleophilic attack of water during OER, further

leading to the enhancement of catalytic kinetics compared with rutile IrO_2 . The authors further confirmed the electrophilic nature of O^{1-} species by introducing CO(g) to interact with rutile IrO_2 and amorphous IrO_x in an O_2 -free reactor [68]. The results demonstrated that CO reacted with amorphous IrO_x through stoichiometric oxidation to generate CO_2 , but it did not react with rutile IrO_2 . Moreover, by using a PEM-based *in situ* technique combined with X-ray photoemission and absorption spectroscopy to investigate an initially metallic iridium model electrode [69], the authors found that O^{1-} species were generated reversibly when an anodic bias was imposed (Fig. 7(b)), and the concentration of O^{1-} increased with the magnitude of the OER reactivity (Fig. 7(c)). A detailed mechanism was proposed by the authors, as shown in Eq. (30). This mechanism further emphasizes the crucial role of O^{1-} sites of amorphous IrO_x in the OER catalytic cycle.

In another interesting work, Li *et al.* [44] investigated the first few atomic layers of electrochemically grown iridium oxide using atom probe tomography, and found that the as-formed amorphous Ir oxides gradually transformed into crystalline IrO_2 by prolonging the anodic polarization, together with a loss of catalytic activity and stability enhancement. By combining with the isotope-labeled electrolyte, the authors further observed different interaction behaviors of hydroxy groups for amorphous Ir oxides and crystalline IrO_2 islands. Hydroxy groups permeated into the electrochemical oxide particles after anodic oxidation for 4 h, while water and hydroxyl groups only covered the surface of the electrochemical oxide after anodic polarization for 120 h. An activity increase during the first 4 h was also captured by the authors, who pointed out that the as-identified non-stoichiometric IrO_x species would make the adsorption of oxygen-containing radicals more energetically favored, further resulting in higher OER electrocatalytic activity.

The determination of the structural evolution of $\text{IrO}_2(\text{IrO}_x)$ during OER is a prerequisite for the identification of the catalytic mechanism involved in the OER. However, it is quite difficult to obtain comprehensive information about the structural evolution of $\text{IrO}_2(\text{IrO}_x)$ during the OER because of the complexity of solid-liquid interfacial electrocatalysis, the mutability of material microstructures, and the lack of high sensitivity for operando characterization technologies. Therefore, a commonly accepted understanding of both the structural evolution and catalytic mechanism for $\text{IrO}_2(\text{IrO}_x)$ is still not available, and a more advanced characterization combination is needed to solve this crucial issue.

5. Low-iridium oxygen evolution electrocatalysts

For the development of acidic OER catalysis, several effective strategies have been reported to enhance the catalytic performance of Ir-based catalysts, including (1) investigating the morphology effect to enlarge the surface-active sites, (2) introducing heteroatoms into pure iridium oxides, and (3) combining with support materials to build catalyst/support

Fig. 7. (a) O K-edge spectra of IrO₂ and amorphous IrO_x. Reproduced with permission [67]. Copyright 2016, Royal Society of Chemistry. (b) O K-edge spectra of Ir-coated PEM during and after OER. (c) O K-edge spectra of Ir-coated PEM at successively applied potentials. (b,c) Reproduced with permission [69]. Copyright 2017, Royal Society of Chemistry.

systems, and (4) constructing iridates with complex crystal structures to design low-iridium catalysts. The as-designed low-iridium catalysts generally exhibit high iridium utilization efficiency, adjustable electronic structure, and enriched connection pattern of IrO₆ subunits. In this section, representative examples are presented to demonstrate the structure-activity relationship of low-iridium catalysts.

5.1. Heteroatoms-containing IrO₂(IrO_x)-based catalysts

Introducing Ru species into pure iridium oxides is the most common strategy to enhance the catalytic activity of Ir-based catalysts. Ru oxides have a superior OER intrinsic activity compared to Ir oxides, but they suffer from poor stability due to the generation of soluble species with a high oxidation state (*e.g.*, RuO₄²⁻) under acidic OER conditions [71]. In order to combine the advantages of Ir and Ru oxides, Ir-Ru bimetallic oxides have been continually investigated since the early the 1990s [23]. The reported Ir-Ru bimetallic catalysts always exhibit better catalytic activity than pure iridium oxides. However, the investigation of the dissolution behavior during the catalytic reaction is insufficient, and the possible stabilizing effect of Ir species for specified materials is also ambiguous.

Kötz *et al.* [72] observed that even a small amount of IrO₂ (~20 wt%) could significantly enhance the corrosion stability of bimetallic Ir-Ru oxides, and they claimed that the stability enhancement originated from the electronic effect. The authors

thought that the IrO₂ domains in the material shared electrons with the constituent RuO₂, and thereby inhibited the formation of soluble RuO₄²⁻ under electrocatalysis conditions. This viewpoint is a general explanation to rationalize this stabilizing effect, but it is not the only one. By using a surface segregation strategy to design stable Ru-Ir oxides, the Markovic group pointed out that the stabilization of Ru by Ir was probably governed by *in situ* formed IrO_x protective skins [73]. In another example, the Qiao group designed a core-shell Ru@IrO_x heterostructured nanomaterial for acidic OER [71]. For comparison, the authors synthesized a Ru-Ir oxide alloy (RuIrO_x). The trend in OER specific activity was found to be Ru@IrO_x > RuO₂ > RuIrO_x > IrO₂. The remarkable activity of Ru@IrO_x was ascribed to a strong charge redistribution between Ru and IrO_x, generating an electron-deficient IrO_x shell. In addition to its high catalytic activity, Ru@IrO_x exhibited good catalytic and structural stability. The concentration of Ru species in the electrolyte for the Ru@IrO_x-catalyzed OER was found to be 30-fold lower than that for the RuIrO_x-catalyzed OER (Figs. 8(a,b)). The good structural stability of Ru@IrO_x was mainly due to the protective function of the IrO_x shell. In addition, Wang *et al.* [74] synthesized low-crystalline Ir_{0.7}Ru_{0.3}O_x (EC) from metallic Ir_{0.7}Ru_{0.3} using electrochemical oxidation and high-crystalline Ir_{0.7}Ru_{0.3}O₂ (TT) through thermal oxidation. Their catalytic results demonstrated that Ir_{0.7}Ru_{0.3}O_x (EC) exhibited approximately 13 times higher activity than Ir_{0.7}Ru_{0.3}O₂ (TT) (Fig. 8(c)), but the former gave much worse corrosion stability than the

Fig. 8. Dissolved Ru and Ir for (a) Ru@IrO_x and (b) RuIrO_x at different times. Reproduced with permission [71]. Copyright 2019, Elsevier. (c) Mass activity comparison between Ir_{0.7}Ru_{0.3}O_x (EC) and Ir_{0.7}Ru_{0.3}O₂ (TT). Reproduced with permission [74]. Copyright 2017, Elsevier. (d) Schematic illustration of the Ni leaching from the surface of Ir-Ni mixed oxides. Reproduced with permission [75]. Copyright 2015, American Chemical Society. (e) Schematic illustration of catalytic sites in IrNiO_x nanoparticles. Reproduced with permission [76]. Copyright 2018, Nature Publishing Group.

latter, revealing the importance of the high degree of crystallinity in Ru(Ir)O₂ to achieve high structural stability.

In addition to Ru, several nonprecious metals have also been introduced in IrO₂(IrO_x)-based oxides to enhance catalytic activity and/or stability. Transition metals, especially Ni and Co, are the most prominent ones to be investigated [50], but these transition metals cannot remain stable during acidic OER, and surface self-reconstruction always occurs during the OER. For instance, Reier *et al.* [75] presented a class of Ir-Ni oxide thin films with tunable compositions as model catalysts for acidic OER. The Ir-Ni mixed oxides were shown to offer a 20-fold improvement in the Ir mass-based OER activity over pure IrO_x. The effect of Ni on the activity enhancement was explained by a rational speculation that the unstable Ni dissolution for Ir-Ni mixed oxides during OER facilitated the formation of OH groups on the surface structure, which served as reactive surface intermediates for promoting OER (Fig. 8(d)). To understand the effect of nickel at the atomic level, Nong *et al.* [76] systematically compared the local geometric ligand environment and electronic states of oxygen-coordinated iridium centers in Ir@IrO_x and IrNi@IrO_x using operando techniques under OER conditions. The operando measurement results revealed that compared with IrO_x and rutile-type IrO₂, IrNiO_x exhibited more *d*-band holes and uniquely shortened Ir-O bond lengths after Ni dissolution, and the covalency trend of the Ir-O bond increased in the order of rutile-type IrO₂ < IrO_x < IrNiO_x. These results were further strengthened by DFT calculations, which revealed that introducing metal defects into theoretical models would increase the formal number of iridium *d*-band holes (Δd) to-

gether with decreasing the average Ir-O bond length. The DFT results also showed that an increase in the iridium vacancy density could lead to an increase in unoccupied oxygen 2*p* states, resulting in the formation of O¹⁻ or O^{(II-δ)-} species. The presence of electrophilic O¹⁻ or O^{(II-δ)-} species was believed to endow a faster OER process through the nucleophilic acid-base O-O formation process, as illustrated in Fig. 8(e).

In another example, the Liu group reported a simple lithium incorporation method that broke long-range order of [IrO₆] octahedrons in iridium oxide to form highly efficient amorphous Li-IrO_x [77]. The overpotential at 10 mA/cm₂_{geo} for amorphous Li-IrO_x is 290 mV, which is much lower than that (435 mV) for IrO₂. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and EXAFS results confirmed that similar [IrO₆] octahedral units resided in both Li-IrO_x and IrO₂, while the [IrO₆] octahedron connection modes of the two samples were quite different. More specifically, the [IrO₆] octahedrons in rutile IrO₂ were supposed to interconnect periodically with each other in a corner-/edge-sharing form, while in the case of Li-IrO_x, [IrO₆] octahedrons are interconnected randomly, and lithium ions reside inside the structure. In addition, an increase in the iridium oxidation state for Li-IrO_x and shrinkage of the Ir-O bond distance were observed during OER, owing to the flexible structure of Li-IrO_x. In contrast, no difference was observed in rutile IrO₂ under the same conditions, suggesting that the redox behavior of Ir was largely limited by the rigid structure. Based on the above results, the authors believed that the higher oxidation state of iridium species and short Ir-O distance made the

iridium species more electrophilic and benefited the oxidation of hydroxyls and the formation of O–O bonds.

5.2. Perovskite-type iridium-based catalysts

Designing and synthesizing complex iridium-based oxides is another effective strategy for enlarging the atom utilization of iridium in iridium-based materials. The exploration of appropriate Ir-based crystal structures for OER can be traced back to 1995 [78]. This field did not attract enough attention until Seitz's report about SrIrO₃ in 2016 [79]. After this work, a number of Ir-based perovskites with various distinct structures have been studied for acidic OER (see Table 1). Through this strategy, alkaline-earth metals and/or rare-earth metals are introduced in various crystal structures, and the content of iridium can be largely diluted. Moreover, the intrinsic activity of the iridium active site could be further improved by rational electronic modulation.

Orthorhombic SrIrO₃ with a pseudo-cubic structure is a type of typical perovskite [80]. This phase of SrIrO₃ is actually metastable in nature, and a high-pressure, high-temperature condition is usually needed to achieve this unique structure [81]. As mentioned before, Seitz *et al.* [79] synthesized epitaxial SrIrO₃ films deposited on SrTiO₃ substrates using pulsed laser deposition. During electrochemical measurements, they found that the OER activity of SrIrO₃ needed approximately two hours to reach the optimum, and outperformed the rutile IrO₂ film by two orders of magnitude. By using combined characterizations, a leaching of Sr species was captured on the surface of SrIrO₃, and the Sr content decreased to about 20% of its original value after 24 h of testing, with the content of Ir remaining constant. The results demonstrated that the *in situ*-formed IrO_x/SrIrO₃ was the real active phase for the OER. Their systematic DFT calculations showed that the formation of a surface phase with a structure similar to that of anatase IrO₂ or IrO₃ was responsible for the experimentally excellent activity [79].

The additional introduction of nonprecious metals into pseudo-cubic SrIrO₃ to form double perovskites, denoted as (AA')B₂O₆ or A₂(BB')O₆, could further enhance the catalytic performance and reduce the Ir content in the catalysts [40]. Through the adjustment of the A' or B' sites in double perovskites, an optimized orbital filling of the catalytic sites would be reached with appropriate charge distribution and firm crystal architecture [82–85]. For the B' site adjustment, Diaz-Morales *et al.* [82] reported a family of iridium double perovskites (Ba₂MIrO₆, with M = Y, La, Ce, Pr, Nd, and Tb) containing 32 wt% less iridium than IrO₂ as acidic OER catalysts. All Ir-based double perovskites exhibited more than threefold higher OER catalytic performances compared with IrO₂, in an activity order of Ce ≈ Tb ≈ Y < La ≈ Pr < Nd. Surface enrichment in iridium was observed after testing, and the surface Ba content was reduced three- to fourfold in the pristine compound. The authors pointed out that a lattice strain caused by lanthanides or yttrium substitution at the B' site improved the OER activity of perovskites by weakening the oxygen adsorption energy. Their results also suggested that a 3D network of corner-shared octahedra in perovskites as prerequisites was necessary for en-

hanced Ir intrinsic activity, and Ba leaching further led to exposure of these highly active iridium centers [82].

Despite their high activity, these double perovskites often undergo great dissolution of non-noble elements at the A and B sites during the OER in acid, leading to unsatisfactory structural stability. Therefore, more stable species such as Ti or Zr are intended to alloy into SrIrO₃. Based on this consideration, our group synthesized porous SrTiO₃-SrIrO₃ solid solution nanotubes through an electrospinning method. The SrTiO₃-SrIrO₃ catalysts with 56 wt% less Ir than IrO₂ exhibited more than 10 times higher OER catalytic activity, and could retain the original perovskite structure during testing. We found that the catalysts generated Sr-deficient surfaces on SrTiO₃-SrIrO₃ solid solutions under acidic electrocatalysis, and *in situ* formed IrO_x-TiO_x solid solutions were the active species for the OER. To understand the origin of their high activities, we theoretically investigated the OER performances of rutile- and anatase-type TiO₂-IrO₂ solid solutions [86]. DFT results revealed that anatase-type TiO₂-IrO₂ solid solutions had more active Ir catalytic sites (around the top of the OER volcano plot) than the benchmark IrO₂ catalysts, while rutile-type TiO₂-IrO₂ solid solutions do not possess. These results suggest that Sr-etching-induced anatase-type TiO₂-IrO₂ on the perovskite surface was the activity origin of SrIrO₃-SrTiO₃ solid solutions. This work also inspired us to alloy catalytically inert SrZrO₃ in SrIrO₃ to form a perovskite-type solid solution electrocatalyst for OER [53]. Similarly, the SrZrO₃-SrIrO₃ electrocatalyst was considered to generate an anatase-type ZrO₂-IrO₂ solid solution on the surface as the active phase. The catalyst was among the most active Ir-based OER electrocatalysts in acid. Furthermore, elemental analysis during electrochemical testing confirmed that the alloying effects of the oxide solid solutions resulted in an improved structural stability relative to Zr-free catalysts.

6H-SrIrO₃ with a monoclinic structure is another promising Ir-based perovskite for acidic OER, which exhibits distortion of the hexagonal BaTiO₃ structure [81,87,88], and can be classified into the class of hexagonal perovskites [89]. As shown in the structural representation (Fig. 9(a)), alternated face-sharing IrO₆ octahedral dimers and corner-sharing IrO₆ octahedra along the c axis constitute the B-O framework of 6H-SrIrO₃ [87]. Moreover, the Ir-O bond distances in the face-shared octahedral dimers are much larger than those in isolated IrO₆ octahedra or in IrO₂ (2.005–2.885 Å vs. 1.978–1.982 Å), demonstrating a weaker bond energy, which may exhibit unique catalytic features for O-relevant adsorbates. Our group first identified the superior OER performance of 6H-SrIrO₃, which could achieve 10 mA/cm²_{geo} at a small overpotential of ~248 mV. The geometric area-normalized catalytic activity of 6H-SrIrO₃ is about four times higher than that of IrO₂ at 1.525 V, and the corresponding mass activity is approximately seven times higher than that of IrO₂. We further compared 6H-SrIrO₃ with pseudo-cubic SrIrO₃ (3C-SrIrO₃) under similar synthesis conditions, and the results showed that 6H-SrIrO₃ had a higher catalytic activity and structural stability than 3C-SrIrO₃. Similar to the observations of Seitz *et al.* [79], ~24% of the Sr content was deviated from the material with surface amorphization formed in the case of 3C-SrIrO₃ during

Fig. 9. (a) Crystal structure of 6H-SrIrO₃. Reproduced with permission [87]. Copyright 2018, Nature Publishing Group. (b) Crystal structure of Ba₃M'Ir₂O₉ triple perovskites. (c) XRD patterns of Ba₃M'Ir₂O₉. (b,c) Reproduced with permission [91]. Copyright 2020, American Chemical Society. (d) The crystal structure and (e) electron location function (ELF) of 12L-perovskites (Ba₄MlIr₃O₁₂). (d,e) Reproduced with permission [90]. Copyright 2020, Elsevier. (f) The structure of Ruddlesden-Popper (RP) phases with (ABO₃)_{n-1}/(AO) formula. Reproduced with permission [93]. Copyright 2014, American Chemical Society. (g) Specific OER activity of Sr iridates in 0.1 M HClO₄. Reproduced with permission [94]. Copyright 2017, American Chemical Society.

the OER, while only ~1.3 % of the total Sr content leached for 6H-SrIrO₃ with a well-preserved crystal structure. In combination with the DFT calculations, a smaller theoretical overpotential of the Ir site in face-shared octahedra suggested that such dimers made a main contribution to the catalytic performance of 6H-SrIrO₃, and the weakened surface Ir-O binding facilitated the transition from O* to HOO* as the potential-determining step of 6H-SrIrO₃ [87].

Our group also performed some interesting works for searching more Ir-based perovskites comprising face-shared octahedral dimers [90–92]. To further identify the possible structure-activity relationship under the scale of subunit, we synthesized a family of Ba₃M'M''₂O₉ triple perovskites with different B-site coordination environment (isolated M'O₆ octahedra and face-shared M''₂O₉ dimers) and tunable B-site elemental composition (M' = Ti, In, Zn; M''₂ = IrIr, TiIr, IrRu, RuRu) (Figs. 9(b,c)) [91]. Electrocatalytic measurements together with theoretical results revealed that face-shared M''₂O₉ dimers governed the OER activity and stability for Ba₃M'M''₂O₉ under acidic conditions, and M'O₆ octahedra as auxiliary subunit regulated the metal-oxygen covalency and oxygen p states in the structure. Among them, Ba₃TiIr₂O₉ containing essential Ir₂O₉ subunits exhibited the best catalytic performance, which was 28 times higher iridium mass activity than that of IrO₂. It should also be noted that a thin amorphous layer (~1 nm) formed on the surface of Ba₃TiIr₂O₉ during the OER, with about 2.1% and 1.6% of the total Ba and Ti contents leached into the electrolyte, while the bulk structure of the perovskite was well

preserved [91]. Following this, we then examined a series of Ba₃LnIr₂O₉ (Ln = lanthanides) using DFT calculations. Ir sites in the Ir₂O₉ dimer were found to be the active sites for OER, and their intrinsic activity could be regulated by the LnO₆ octahedra [92].

In another work, we synthesized a class of iridium-based 12L-perovskites (Ba₄MlIr₃O₁₂, M = Pr, Bi, Nb) with unique trinuclear Ir₃O₁₂ subunits [90]. The Ir₃O₁₂ trimers and MO₆ octahedra are corner-shared connected along the *c* axis in Ba₄MlIr₃O₁₂, forming a 12-layer structure (Figs. 9(d,e)). The acidic treatment result (0.1 M HClO₄, 30 d) showed that this kind of perovskite retained its bulk structures under acidic conditions due to the firm Ir₃O₁₂ subunits in the structure. Further electrochemical measurements showed that the OER activity of this polymorphic structure followed a sequence of Ba₄PrIr₃O₁₂ > Ba₄BiIr₃O₁₂ > Ba₄NbIr₃O₁₂, and the mass activity of Ba₄PrIr₃O₁₂ was 15.6 times higher than that of IrO₂. As for the surface reconstruction, we found that the 7 nm-depth surface region became amorphous during the OER in the case of Ba₄PrIr₃O₁₂, and around 95% of Ba and 74% Pr leached in the electrolyte. MlIrO_x (M = Pr, Bi, Nb) covered the surface of Ba₄MlIr₃O₁₂ after the OER, and a large fraction of highly under-coordinated Ir⁵⁺ species generated during testing were supposed to contribute to the superior activity of Ba₄PrIr₃O₁₂ [90].

In addition to the pseudo-cubic and monoclinic structures of Ir-based perovskites, some novel subunits and possible relationships between specific subunits and catalytic performance under the framework of perovskites have also been investigat-

ed. Ruddlesden-Popper (RP) phases $[(\text{ABO}_3)_{n-1}/(\text{AO})]$ are a type of perovskite that consists of alternating layers of AO rock salt and ABO_3 perovskite block, and exhibit a distinct layered two-dimensional topology (Fig. 9(f)) [93–95]. Strickler *et al.* [94] examined the acidic OER activity of Sr_2IrO_4 , Sr_4IrO_6 , and monoclinic SrIrO_3 with similar micrometer-scale sizes. The results showed that specific catalyst activities normalized to the BET surface area increased in the order of commercial Ir/C < Sr_4IrO_6 < SrIrO_3 < Sr_2IrO_4 (Fig. 9(g)), and Sr_2IrO_4 exhibited a 40-fold increase in mass activity compared to IrO_x . Moreover, all Sr iridates displayed higher activity than IrO_x , although all of those suffered from both Sr and Ir dissolution, demonstrating the essential roles of the starting crystal structure and the initial presence of Sr for OER activity. By investigating the structure transition during OER, the authors also found that the higher initial Sr content the starting crystal structure possess, the higher amounts of Sr and Ir dissolution the corresponding surface underwent. The reason behind this phenomenon was that the phase with higher initial Sr content was more vulnerable to Sr dissolution, leading to relatively high dissolution of both Sr and Ir [94].

As a substitution of the A site, the Grimaud group reported a novel protonated perovskite-like phase $\text{H}_{3.6}\text{IrO}_4 \cdot 3.7\text{H}_2\text{O}$ starting from Sr_2IrO_4 through a $\text{Sr}^{2+}/\text{H}^+$ cation-exchange synthetic route [85]. The corresponding structural analyses suggested that this new protonated iridate contained layers of corner-sharing IrO_6 octahedra with a large amount of structural water. This specific structural feature made $\text{H}_{3.6}\text{IrO}_4 \cdot 3.7\text{H}_2\text{O}$ exhibit an improved catalytic stability via reversibly exchanging protons in acid. The enhanced OER activity of $\text{H}_{3.6}\text{IrO}_4 \cdot 3.7\text{H}_2\text{O}$ was explained by the corner-sharing IrO_6 octahedral network together with the structural water in its structure. In addition, the authors also pointed out that an irreversible loss of structural water for this structure during OER, and the oxidation state of the iridate was modified with a change in the oxidation potential [85].

5.3. Pyrochlore-type iridium-based catalysts

Pyrochlore oxides with a general formula of $\text{A}_2\text{B}_2\text{O}_{7-\delta}$ are another kind of promising complex oxides with high stability and sufficient conductivity (Table 1). The earliest evaluation of the OER performance of pyrochlores was traced back to Goodenough's work in 1990 [96]. Fig. 10(a) presents a common structure of pyrochlore, which exhibits a cubic structure in a space group of $\text{Fd}\bar{3}\text{m}$. Generally, the large A cations occupy the 16d site (0.5, 0.5, 0.5) and connect eight O anions in the scalenohedron mode, which contains two O atoms at short distances and six O atoms at longer distances. The small B cations reside in the 16c site (0, 0, 0) and coordinate with six O atoms to form corner-shared BO_6 octahedra. A is Bi, Pb, alkaline earth metal (Ae), or rare earth metal (Ln) in pyrochlores, and B could be Ir, Ru, Os, Ti, Sn, or Nb. B sites in $\text{A}_2\text{B}_2\text{O}_{7-\delta}$ generally serve as catalytic active sites for the OER, and A sites in the structure can alter the electronic properties of B sites and thereby regulate their catalytic performance [97–103].

For example, Sun *et al.* [98] compared two metal pyro-

chlores, $\text{Bi}_2\text{Ir}_2\text{O}_7$ and $\text{Pb}_2\text{Ir}_2\text{O}_{6.5}$, with IrO_2 for acidic OER. They found that their specific activity trend followed: $\text{Pb}_2\text{Ir}_2\text{O}_{6.5} > \text{IrO}_2 > \text{Bi}_2\text{Ir}_2\text{O}_7$, and this activity trend could be correlated with the distortion degree of the IrO_6 octahedra. The valence band spectra revealed that distorted IrO_6 in $\text{Pb}_2\text{Ir}_2\text{O}_{6.5}$ induced the disappearance of $J = 1/2$ subbands in the valence band (Fig. 10(b)), while $\text{Bi}_2\text{Ir}_2\text{O}_7$ exhibited a similar electronic structure to IrO_2 . The DFT calculations further demonstrated that owing to the distorted IrO_6 coordination, $\text{Pb}_2\text{Ir}_2\text{O}_{6.5}$ possessed a broader Ir-5d bonding region (7.8 eV bandwidth in DOS) compared with IrO_2 (7 eV) and $\text{Bi}_2\text{Ir}_2\text{O}_7$ (6 eV). Obviously, the trend in the d-band widths was in accordance with the trend in OER activity. The authors believed that the broadened Ir-5d bands in $\text{Pb}_2\text{Ir}_2\text{O}_{6.5}$ improved the orbital overlap between Ir-5d and O-2p, optimized the adsorption of OER intermediates, and thus gave rise to enhanced OER activity (Fig. 10(c)).

In another example, Zeng and coworkers [99] reported a family of pyrochlore oxides, $\text{R}_2\text{Ir}_2\text{O}_7$ (R = Ho, Tb, Gd, Nd, and Pr) as acidic OER catalysts. The authors found that the intrinsic OER activity of pyrochlore oxides showed a strong dependence on the types of R ions. The catalytic activity increased with an increase in the R ionic radius, and $\text{Pr}_2\text{Ir}_2\text{O}_7$ exhibited the highest mass activity. The authors found that an increase in the R ionic radius led to an increase in the Ir-O-Ir bond angle in the pyrochlore structure and an increase in the bandwidth. Consequently, the effective electron correlations of $\text{R}_2\text{Ir}_2\text{O}_7$ could be weakened by increasing the R ionic radius, further inducing the enhanced conductivity and enhanced covalency of Ir-O bonds (Figs. 10(d,e)). As a result, $\text{Pr}_2\text{Ir}_2\text{O}_7$ exhibited metallic behavior and strengthened hybridization between the Ir 5d and O 2p orbitals, both of which promoted the OER reaction kinetics.

Additionally, the catalytic activities and structural stabilities of pyrochlores could also be influenced by various discrepancies such as synthetic methods, compositions, bulk thermodynamic properties, etc. The Thomas group initially used a computational approach to evaluate the phase stability, electrochemical stability, and conductivity of rare-earth pyrochlore oxides, and then synthesized these predicted materials using the spray-freeze freeze-drying approach [100]. In their work, $\text{Yb}_2\text{Ir}_2\text{O}_7$ and the ruthenium series ($\text{Gd}_2\text{Ru}_2\text{O}_7$ and $\text{Nd}_2\text{Ru}_2\text{O}_7$) displayed superior catalytic activities, while $\text{Gd}_2\text{Ir}_2\text{O}_7$ and $\text{Nd}_2\text{Ir}_2\text{O}_7$ exhibited comparable mass activities to IrO_2 (Fig. 10(f)). As for structural stability, A-site cation leaching was detected for all materials, and B-site dissolution mainly occurred for materials containing Ru and Nd. The obvious dissolution of Nd-based pyrochlores was due to the structural metastability, and the instability of Ru-based pyrochlores originated from the unstable nature of the Ru species.

6. Conclusions and outlook

In conclusion, PEM water electrolyzers, as a promising water electrolysis technique, can be effectively integrated with renewable energy to construct future carbon-free energy cycles. Under the brilliant blueprint and corresponding growing demand of PEM water electrolyzers, a proportionately increased requirement for noble-metal catalysts, especially irid-

ium-based OER catalysts, substantially restricts the scale-up progress of PEM water electrolyzers. In this review, we have summarized recent research advances in iridium-containing OER catalysts and our understanding of the relationship between the microstructure and catalytic properties. We first discuss two catalytic mechanisms involved in OER (*i.e.*, AEM and LOM) for Ir-based catalysts, and review general methods to evaluate the catalytic performance for OER. We then present some recent insights into the structural evolution of IrO₂ and its relatives under OER electrocatalysis. Finally, we review three

important kinds of low-iridium OER electrocatalysts, including heteroatom-containing IrO₂(IrO_x)-based catalysts and perovskite- and pyrochlore-type iridium-based catalysts. From the summarized works, it can be concluded that the specific activity of Ir species can be finely tuned by regulating the electronic structures of materials, and the catalytic stability of materials can also be correlated with the specific structural features. Although many efforts have been devoted to this field, there are still several important issues that need to be solved, as illustrated in Fig. 11.

Table 1

List of structure information, measurement parameters and catalytic performances of complex iridium-based oxides.

Catalyst	Structural information	Electrolyte solution	Mass loading (mg/cm ²)	η at $j_{\text{geo}}=10$ mA/cm _{geo} ² (mV)	Specific activity	Mass fraction of dissolved ions	Ref.
IrO _x /SrIrO ₃	Orthorhombic perovskite	0.5 M H ₂ SO ₄	—	270–290 (AFM normalized)	1.53 V ~12 mA/cm _{AFM} ²	CV @ 30 min (ICP) Sr-30%–50%	[79]
Ba ₂ PrIrO ₆	Cubic perovskite	0.1 M HClO ₄	0.95	~400 (~425 @ 1 h)	1.53 V ~1 mA/cm _{ECSA} ²	1.55 V @ 1 h (ICP) Ba-14.2% Ir-0.8% Pr-11.3%	[82]
Pr ₃ IrO ₇	Fluorite	0.1 M HClO ₄	0.95	—	1.53 V ~0.1 mA/cm _{ECSA} ²	—	[82]
SrCo _{0.9} Ir _{0.1} O ₃₋₆	Orthorhombic perovskite	0.1 M HClO ₄	0.255	~330	1.53 V ~10 mA/cm _{BET} ²	10k cycles CV (ICP) Sr-64.11% Co-67.08% Ir-35.5%	[83]
Ir doped SrTiO ₃	Cubic perovskite	0.1 M HClO ₄	0.21	247	1.525 V 820 A/g _{Ir} 0.125 mA/cm _{ECSA} ² 0.455 mA/cm _{BET} ²	—	[84]
SrZrO ₃ -SrIrO ₃ solid solution	Orthorhombic perovskite	0.1 M HClO ₄	0.13	240	1.53 V 1540 A/g _{Ir} 0.22 mA/cm _{ECSA} ² 1.2 mA/cm _{BET} ² 1.35 A/C	10 mA/cm _{geo} ² @ 10h (ICP) Sr-12% Ir-1%	[53]
3C-SrIrO ₃	Orthorhombic perovskite-3C	0.5 M H ₂ SO ₄	0.9	270	1.525 V 38 A/g _{Ir}	10 mA/cm _{geo} ² @ 30h (ICP) Sr-24%	[87]
6H-SrIrO ₃	Monoclinic perovskite-6H	0.5 M H ₂ SO ₄	0.9	248	1.525 V 76 A/g _{Ir}	10 mA/cm _{geo} ² @ 30h (ICP) Sr-1%	[87]
Co-doped SrIrO ₃ (6H)	Monoclinic perovskite-6H	0.1 M HClO ₄	0.45	235	1.525 V 286.7 A/g _{Ir}	10 mA/cm _{geo} ² @ 1h (ICP) Sr-12% Co-0.5% Ir-0.1%	[104]
BaIrO ₃ polycrystalline particles	Monoclinic perovskite	0.5 M H ₂ SO ₄	0.5	—	1.58 V 90 A/g _{oxide} ~4 A/F _{ECSA}	100-cycle CV (EDS) Ba-100%	[105]
La ₂ LiIrO ₆	Monoclinic perovskite	0.1 M H ₂ SO ₄	0.25	~300	1.53V ~40 A/g _{oxide} ~2.5 mA/cm _{BET} ²	1.65 V @ 10 min (XPS) Ir-26.7% La-94.5% Li-100%	[43]
Ba ₄ PrIr ₃ O ₁₂	Monoclinic perovskite-12L	0.1 M HClO ₄	0.562	278	1.55 V 145 A/g _{Ir} 2.63 mA/cm _{ECSA} ²	10 mA/cm _{geo} ² @ 10 h (ICP) Ba-32% Pr-32% Ir-1.18%	[90]
Ba ₃ TiIr ₂ O ₉	Hexagonal perovskite	0.1 M HClO ₄	0.281	275	1.53 V 0.89 mA/cm _{ECSA} ² 250 A/g _{Ir}	10 mA/cm _{geo} ² @ 10 h (ICP) Ba-2.1% Ti-1.6%	[91]
Sr ₂ IrO ₄	Tetragonal perovskite	0.1 M HClO ₄	0.08 mg _{Ir} /cm ²	286	1.55 V 394 A/g _{Ir} 6.1 mA/cm _{BET} ²	10 mA/cm _{geo} ² @ 6h (ICP) Sr-74% Ir-4%	[94]
Sr ₄ IrO ₆	Hexagonal perovskite	0.1 M HClO ₄	0.08 mg _{Ir} /cm ²	287	1.55 V 274 A/g _{Ir} 0.7 mA/cm _{BET} ²	10 mA/cm _{geo} ² @ 6h (ICP) Sr-90% Ir-30%	[94]
Ca ₂ IrO ₄	Hexagonal perovskite	0.1 M HClO ₄	0.20	370	—	—	[95]
H _{3.6} IrO ₄ ·3.7H ₂ O	Tetragonal perovskite	0.1 M HClO ₄	0.255	—	1.53 V ~3.5 mA/cm _{BET} ²	1 mA/cm _{geo} ² @ 1 h (ICP) Ir-0.08%	[85]
Sr ₂ CoIrO ₆	Orthorhombic perovskite	0.1 M HClO ₄	0.255	330 (BET normalized)	1.55 V 3.5 mA/cm _{BET} ²	1 mA/cm _{BET} ² @ 24 h (ICP) Sr-5% Co-4% Ir-2.8%	[106]
Sr ₂ FeIrO ₆	Triclinic perovskite	0.1 M HClO ₄	0.255	420 (BET normalized)	1.55 V 1.8 mA/cm _{BET} ²	1 mA/cm _{oxide} ² @ 24 h (ICP) Sr-7% Fe-6% Ir-3%	[106]
Sr ₂ Fe _{0.5} Ir _{0.5} O ₄	Tetragonal perovskite	0.1 M HClO ₄	0.255	410 (BET normalized)	1.55 V 2.5 mA/cm _{BET} ²	1 mA/cm _{oxide} ² @ 24 h (ICP) Sr-4% Fe-6% Ir-8%	[106]
Pb ₂ Ir ₂ O _{6.5}	Cubic pyrochlore	0.1 M HClO ₄	0.2	~470	1.55 V ~150 A/g _{Ir} cm ²	—	[98]
Bi ₂ Ir ₂ O ₇	Cubic pyrochlore	0.1 M HClO ₄	0.2	—	1.6 V ~30 A/g _{Ir} cm ²	—	[98]
Pr ₂ Ir ₂ O ₇	Cubic pyrochlore	0.1 M HClO ₄	0.285	~290	1.53 V 424.5 A/g _{Ir}	—	[99]
K _{x=0.25} IrO ₂	Monoclinic hollandite	0.1 M HClO ₄	0.2	350	1.53 V 12.2 A/g _{Ir}	—	[107]
CaIrO ₃	Cubic perovskite	0.1 M HClO ₄	0.2	—	1.55 V 30 A/g _{Ir}	—	[108]
β-H ₂ IrO ₃	Orthorhombic	0.1 M H ₂ SO ₄	0.5	345	1.53 V 1.0 mA/cm _{BET} ²	50 h@1.55 V Ir-0.2 %	[109]

Fig. 10. (a) The crystal structure of pyrochlore. Reproduced with permission [97]. Copyright 2017, American Chemical Society. (b) Valence band spectra of Pb-Ir, Bi-Ir pyrochlores and IrO_2 . (c) Schematic illustration of the broadening Ir-5d band induced by the distortion of octahedra. (b,c) Reproduced with permission [98]. Copyright 2016, Nature Publishing Group. (d) Electronic phase diagram and corresponding band structure of Ir 5d orbitals. (e) O K-edge XAS of different pyrochlores. (d,e) Reproduced with permission [99]. Copyright 2018, Wiley-VCH. (f) Geometric current density and iridium mass activity of the different pyrochlores. Reproduced with permission [100]. Copyright 2019, American Chemical Society.

(1) Specific structural design and synthesis

According to the high correlation between the material structure and catalytic performance for acidic OER, it is undoubtedly that we can modulate the catalytic performance of one specific material by changing the structural features of the materials. Using complex iridium-based oxides as an example, the crystal structures of materials can be deconstructed into several subunits, and the geometry variations for these catalytically active ones (mainly IrO_6 for iridates) including connection mode, structural distortion, bonding distances, and/or chemical valence states, together with the as-induced electronic structure changes internally influence the adsorption behaviors of the involved intermediate for OER. In addition, for catalytically inactive species in the structure, the corresponding element types, atomic radius, and/or mass fraction can also affect the structural features of materials, further leading to different catalytic performances, which suggest irreplaceable roles for all subunits. However, the general structure-activity relationships for acidic OER are not clear enough. It is necessary to combine theoretical calculation analysis together with high-throughput screening methods to construct universal structural design principles, and further develop effective synthetic methods to achieve the as-predicted structural design.

(2) Investigation of OER mechanism

The development of a catalysis mechanism influences the explanation and design principle of the corresponding catalysts. As a newly developed OER mechanism, both the clarity and acceptance of LOM are much lower than those of AEM. Thus, although both AEM and LOM are verified to be involved in OER in some cases, most studies generally limited their

scope under the framework of AEM. It is important to determine the possible tendency of LOM involvement for specific catalysts, and the participation of LOM during OER may serve as an internal factor that influences the catalytic activity and structural stability of the material. As for the Ir-containing catalyst, there is also another reasonable possibility that both AEM and LOM may occur on one catalytic material simultaneously, considering the fact that IrO_x always forms *in situ* on the surface of iridium-based oxides during acidic OER. Accordingly, it is

Fig. 11. Important perspectives for balancing the activity and stability of catalysts under acidic OER condition.

necessary to find effective indicators for reflecting the possible contributions of AEM and LOM in one specified material. More comprehensive mechanistic investigations though experimental measurements and/or theoretical analyses should be conducted thoroughly for the development of both catalysis mechanisms and catalyst design.

(3) Quantitative analysis of catalytic performance

Universal quantitative analyses are the prerequisites for describing the catalytic performance of materials. Because a reversed activity-stability relationship generally exists among related catalysts for acidic OER, a catalyst with only enhanced activity does not mean that it is suitable enough for OER. Instead, the catalytic activity and catalytic stability of one specific material are equally important, and we should not focus on one feature and ignore another. Thus, it is important to construct comparable parameters for both intrinsic activity analysis and catalytic stability evaluation, in an attempt to extract the potential structure-activity relationship for as-designed catalysts. Currently, catalytic activity-related parameters with different features (as mentioned in Section 3.1) are suitable for different types of catalysts. These parameters have both advantages and disadvantages, and at the current investigation stage, it is important to perform an effective combination of these parameters to describe the intrinsic catalytic analysis of a specific material. Additionally, the evaluation metric for catalytic stability is insufficient, which means that it is currently difficult to quantitatively describe the catalytic stability features of catalysts. Therefore, obtaining a precise and integrated catalytic performance, including both the activity and stability of materials, is still a challenge at the current investigation stage for acidic OER. More parameters with simple and reproducible features need to be developed for corresponding effective quantitative analyses.

(4) Structural identification during OER

The structural variation of catalysts during OER is correlated with both the corresponding catalytic activity and catalytic stability. Specifically, the structural variations include the dissolution mechanism, valence state transition, and phase transformation of materials during OER. They may influence the involved OER catalytic mechanism internally, further leading to the similarity or diversity of catalytic performance for various catalysts. From this review, it can be concluded that the dissolution behavior of Ir-based catalysts would be influenced by synthetic conditions, chemical composition, crystal structure, and/or testing environment of materials, while the dissolution mechanism analyses for the majority of related catalysts are insufficient. Additionally, the valence state of the Ir species has been proven to undergo reversible and/or irreversible changes during the OER, but the specific valences are still ambiguous. Moreover, although the Ir sites on the surface region of Ir-based catalysts are generally considered as catalytic active sites for OER, the O species have also been proven to contribute significantly to the catalytic performance. The involvement of O active sites makes the identification of catalytic active sites rather difficult, further complicating the mechanism evaluation of the catalytic reaction. All the above unsolved issues originate from the limitations of current characterization techniques, and

advanced *in situ* characterization measurements with high sensitivity should be developed.

(5) Effective strategies for breaking the reversed relationship between activity and stability

Developing effective strategies to balance the catalytic activity and stability of the catalyst is the core requirement for the development of acidic OER. Based on the catalytic mechanisms involved, there might be two viable directions to enhance the activity and stability of catalysts simultaneously. (1) From the perspective of AEM, the scaling relation among various intermediates needs to be somehow broken with the aim of enhancing the intrinsic activity of catalysts. Additionally, the non-destructive adsorption mode of AEM should be maintained to keep the catalytic stability of the material. (2) Under the framework of LOM, owing to the involvement of lattice oxygen, it is important to prevent the structure of the catalyst from collapsing during the OER. Therefore, in order to retain the superior catalytic activity of LOM, the catalyst needs to tolerate the formation of surface oxygen vacancies, and the refilling adsorption rate of OH species must also be accelerated. Moreover, some external factors such as support passivation, catalyst detachment, and sulfate anion poisoning need to be ruled out, and a more realistic working condition for acidic OER needs to be conducted to check the catalytic performances of the materials, considering that the general measurement condition of acidic OER is not exactly the same as the working environment of commercial PEM electrolyzers.

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Graphical Abstract

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Iridium-containing water-oxidation catalysts in acidic electrolyte

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In an attempt to find effective strategies to balance the catalytic activities and stabilities of materials for acidic water oxidation, this review focuses on iridium-containing catalysts as examples, presenting recent representative advances in this field.

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铱基催化剂在酸性析氧反应中的研究进展

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摘要: 降低对化石能源依赖, 实现无碳能源需要构建以可再生能源(如太阳能、风能等)为主体的能源框架。氢气是无碳能源框架下的一种较为理想的能源载体, 而电解水制氢技术能够有效制备环境友好的高纯氢气。其中, 质子交换膜基(PEM)电解水技术相较碱性电解技术能够实现更高的质子导电性、电解效率、响应速度以及产物气体分离能力, 展现出较高的应用价值。然而, 由于PEM电解技术工作环境为高腐蚀性的强酸条件, 极大限制了催化材料的选择范围。同时, 由于PEM电解池的阳极端析氧反应效率远远低于阴极端析氢反应, 因此析氧反应作为瓶颈反应决定了PEM电解池的总体工作效率。由于其催化条件同时具有强酸性和强氧化性, 目前只有铱基催化剂能够保持较长时间催化活性。二氧化铱(IrO_2)是PEM电解水技术商用析氧催化剂。然而由于铱元素在地球上储量极低(0.001 ppm), 因此铱基催化剂的使用严重限制了PEM电解池的大规模应用。为发展PEM电解技术, 亟需研制出高活性、高稳定性的新型低铱催化剂来替代 IrO_2 。

本文首先总结了酸性析氧反应的催化机理, 并给出了衡量材料催化性能的普适方法。其次, 总结了多个课题组利用原位表征技术获得的晶化 IrO_2 以及无定形 IrO_x 在不同催化条件下的结构变化, 以期了解材料的共性催化特征及影响结构变化的可能因素。再次, 进一步重点描述了三类常见低铱催化剂, 包括异原子掺杂 IrO_2 (IrO_x)基催化剂、钙钛矿型铱基催化剂及烧绿石型铱基催化剂, 并尝试关联材料结构特征与催化本征性能。最后, 介绍了该领域尚未解决的问题与挑战, 以期在酸性析氧反应条件下进一步平衡催化材料的催化活性和催化稳定性。

关键词: 电催化; 析氧反应; 水裂解; 铱; 质子交换膜电解池

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