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# Metal–oxygen bonding characteristics dictate activity and stability differences of RuO<sub>2</sub> and IrO<sub>2</sub> in the acidic oxygen evolution reaction†

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Ruthenium dioxide (RuO<sub>2</sub>) and iridium dioxide (IrO<sub>2</sub>) serve as benchmark electrocatalysts for the acidic oxygen evolution reaction (OER), yet their intrinsic activity–stability relationships remain elusive. Herein, we employ density functional theory (DFT) calculations to systematically investigate the origin of divergent OER catalytic behaviors between RuO<sub>2</sub> and IrO<sub>2</sub> in acidic media. Mechanistic analyses reveal that RuO<sub>2</sub> follows the adsorbate evolution mechanism with superior activity (theoretical overpotential: 0.698 V vs. 0.909 V for IrO<sub>2</sub>), while IrO<sub>2</sub> demonstrates enhanced stability due to a higher dissolution energy change (>2.9 eV vs. −0.306 eV for RuO<sub>2</sub>). Electronic structure analysis reveals that RuO<sub>2</sub> exhibits ionic-dominated metal–oxygen bonds with delocalized electron distribution, facilitating intermediate desorption but promoting detrimental RuO<sub>4</sub><sup>2−</sup> dissolution. In contrast, IrO<sub>2</sub> features covalent bonding characteristics with more electron filling in Ir–oxygen bonds (2.942 vs. 2.412 for RuO<sub>2</sub>), thereby stabilizing surface intermediates against dissolution at the expense of higher OER barriers. This work establishes a clear correlation between the bonding nature and electrocatalytic performance metrics, offering fundamental insights for the rational design of acid-stable OER electrocatalysts with optimized activity–stability relationships.

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## 1. Introduction

Electrochemical water splitting technology is widely regarded as an ideal method for utilizing renewable electricity to produce clean hydrogen (H<sub>2</sub>) fuel.<sup>1,2</sup> Acidic proton exchange membrane water electrolyzers (PEMWEs), with outstanding proton conductivity, lower ohmic losses, and more compact system design, have been widely regarded as one of the most efficient technological devices for green hydrogen production, which has sparked extensive research interest.<sup>3–5</sup> However, the commercialization of PEMWEs is significantly hindered by the sluggish acidic oxygen evolution reaction (OER) kinetics, a bottleneck primarily attributed to the current lack of active, stable, and cost-effective OER catalysts.<sup>6–10</sup> To date, ruthenium (Ru)-based catalysts, particularly RuO<sub>2</sub>, and iridium (Ir)-based catalysts, notably IrO<sub>2</sub>, are commonly regarded as the preferred materials for anode catalysts due to their excellent durability and good activity in the commercial application of PEMWEs.<sup>11–14</sup>

Nevertheless, when it comes to large-scale applications, the two catalysts, RuO<sub>2</sub> and IrO<sub>2</sub>, confront three pivotal constraints. Firstly, their scarcity and high cost pose a significant barrier, as the price of Ru can reach up to \$9523 per kg, and Ir can soar to \$60 670 per kg.<sup>15,16</sup> More importantly, Ru-based catalysts still grapple with formidable challenges in terms of long-term stability during the OER in acidic environments or PEM reactors.<sup>10,17,18</sup> Additionally, Ir exhibits a relatively high overpotential during the OER, resulting in lower energy efficiency.<sup>14,19,20</sup> These intertwined limitations collectively hinder the achievement of the Department of Energy's (DOE's) goal of reducing hydrogen production costs to below \$2 per kg by 2025.<sup>21,22</sup> In recent years, great efforts have been made to improve the Ru or Ir acidic OER performance *via* strategies such as multimetal oxides or doping (Mn-doped RuO<sub>2</sub>,<sup>23</sup> Ta-RuO<sub>2</sub>,<sup>24</sup> Hf-doped IrO<sub>2</sub>,<sup>25</sup> and Re-doped IrO<sub>2</sub>,<sup>26</sup>), morphology and structure tuning (ultra-thin RuO<sub>2</sub> nanosheets,<sup>27</sup> single-atom Ru–N–C,<sup>28</sup> and Au@AuIr<sub>2</sub>,<sup>20</sup>), strain effect (Ru/RuO<sub>2</sub>@NCS<sup>29</sup> and Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2–δ</sub>,<sup>14</sup>), surface reconstruction (CaCu<sub>3</sub>Ru<sub>4</sub>O<sub>12</sub>,<sup>30</sup> A<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>, A = Y, Nd, Gd and Bi,<sup>31</sup> and SrCo<sub>0.9</sub>Ir<sub>0.1</sub>O<sub>3–δ</sub>,<sup>32</sup>) and so on, resulting in enhanced OER activity and stability compared with commercial RuO<sub>2</sub> and IrO<sub>2</sub> nanoparticles in acids.

However, the longest lifetime achieved so far for these novel catalysts is only 2000 hours under electrochemical testing conditions for Y<sub>2</sub>Ru<sub>1.2</sub>Ir<sub>0.5</sub>O<sub>7</sub>.<sup>33</sup> This falls far short of meeting the needs of practical applications, especially when compared

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to the target lifetime of 100 000–120 000 hours by 2050.<sup>34</sup> Conversely, studying and understanding the fundamental processes occurring in typical noble metal-based oxide catalysts (RuO<sub>2</sub> and IrO<sub>2</sub>) is expected to have a high degree of universality and contribute to the development of low-cost and high-efficiency materials. Mechanistically, the reaction pathways of RuO<sub>2</sub> and IrO<sub>2</sub>, especially the involvement of lattice oxygen, remain widely controversial. Macounova *et al.*<sup>35</sup> investigated the lattice oxygen participation of nanocrystalline RuO<sub>2</sub>-based catalysts, revealing that lattice oxygen contributed roughly 9% in pure RuO<sub>2</sub> and even up to 50% in Ru<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>2</sub>. However, this finding was later challenged by a study that found no evidence of oxygen exchange occurring on any of the four orientation surfaces of RuO<sub>2</sub>, regardless of whether the electrolyte is acidic or alkaline.<sup>36</sup> Similarly, researchers have also expressed differing views on the participation of lattice oxygen in IrO<sub>2</sub>. Kasian *et al.*<sup>37</sup> considered the participation of lattice oxygen to be ubiquitous in the Ir-based oxide system, and the specific structural characteristics of the catalyst significantly influence the evolution pathway of lattice oxygen. Conversely, Scott *et al.*<sup>38</sup> concluded that lattice oxygen is, at most, a negligible contribution to the overall OER activity for Ir-based catalysts in acidic electrolytes. Furthermore, the specific dissolution path and dissolved products of RuO<sub>2</sub> and IrO<sub>2</sub>, which will inevitably suffer corrosion due to the harsh acidic environment, have been widely concerned.<sup>9,39–41</sup> It is suggested that the over-oxidation of RuO<sub>2</sub>, occurring at elevated temperatures and under high O<sub>2</sub> partial pressures or as a consequence of anodic polarization, leads to the production of volatile and water-soluble RuO<sub>4</sub><sup>2–</sup>.<sup>39,42</sup> Alexandrov *et al.*<sup>41</sup> discovered the presence of two pivotal intermediates (RuO<sub>2</sub>(OH) and RuO<sub>2</sub>(OH)<sub>2</sub>) on the RuO<sub>2</sub>(110) surface, which couple the Ru dissolution process with the catalytic process at the atomic scale. Interestingly, it was computationally revealed that the dissolution of IrO<sub>2</sub> exhibits potential dependence, transforming into IrO<sub>3</sub> at high anodic potentials and into Ir(OH)<sub>3</sub> at low anodic potentials.<sup>43</sup> Nevertheless, other authors have experimentally discovered that IrO<sub>2</sub> ultimately dissolves in the form of IrO<sub>4</sub><sup>2–</sup> at high anodic potentials.<sup>44</sup> Evidently, the widespread controversies surrounding the catalytic activity and deactivation mechanisms of the two catalysts stem primarily from the lack of consensus in understanding their underlying mechanisms.

In our work, we explored the OER and the deactivation mechanisms of RuO<sub>2</sub> and IrO<sub>2</sub> in detail to understand the intrinsic differences in their activity and stability by density functional theory (DFT) calculations. Initially, we evaluated three distinct OER pathways for each catalyst to determine the thermodynamically favorable reaction routes. Subsequently, we analyzed potential deactivation mechanisms for both catalysts, with a focus on dissolution pathways, the species formed upon dissolution, and the resultant activity following the dissolution of active sites. Furthermore, we conducted a comprehensive assessment of their intrinsic electronic structures, examining orbital states and bonding characteristics, and correlated these elements with OER activity and stability. Our findings indicate that variations in metal–oxygen (M–O) bonding characteristics

are the fundamental reason for the observed differences in performance. This research not only deepens our understanding of the differing performances between OER catalysts but also offers a robust theoretical framework to guide future optimization efforts in catalyst performance.

## 2. Computational details

Spin-polarized DFT calculations were conducted using the Vienna ab initio simulation package (VASP),<sup>45,46</sup> in which the ionic cores of all atoms are described by projector augmented wave (PAW) pseudopotentials.<sup>47</sup> The generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE)<sup>48</sup> exchange-functional was applied, along with D3-dispersion correction (BJ)<sup>49,50</sup> to account for long-range van der Waals interactions. During the optimization of geometric structures using a force-based conjugate gradient method, the convergence thresholds for force and energy were set to 0.02 eV Å<sup>–1</sup> and 10<sup>–5</sup> eV, respectively. The cut-off energy for plane-wave basis was set as 450 eV.

The lattice parameters of the rutile structure were optimized to give  $a = 4.490$  Å,  $c = 3.118$  Å for RuO<sub>2</sub>, and  $a = 4.527$  Å,  $c = 3.173$  Å for IrO<sub>2</sub>, which is in agreement with a previous experimental prediction.<sup>51</sup> The Brillouin zone was sampled using the Monkhorst–Pack scheme with a  $6 \times 6 \times 8$   $k$ -point mesh for RuO<sub>2</sub> and IrO<sub>2</sub> cells. Detailed information regarding the optimized structure of the cell model is provided in Fig. S1 and Tables S1, S2 (ESI†). In our calculations, we selected the MO<sub>2</sub>(110) (M = Ru, Ir) surfaces, the most stable structure that have been extensively studied.<sup>36,38,41,43,52–54</sup> It is noteworthy that the rutile (110) surface comprises two distinct metal positions: a coordinatively unsaturated site (Cus) that is not capped by oxygen and is bound to five O atoms, and a bridge site (Bri) that is bound to six O atoms. We utilized the slab model consisting of 48 M atoms and 96 O atoms, where the first layer was fixed during geometry optimization, as depicted in Fig. 1. Tables S1 and S2 (ESI†) present the relevant parameters of the optimized geometric structures of RuO<sub>2</sub>(110) and IrO<sub>2</sub>(110). In subsequent discussions, we will uniformly adopt RuO<sub>2</sub> and IrO<sub>2</sub> to refer to the corresponding surface materials, respectively. For the calculations of the slab, the  $k$ -point mesh was set to  $3 \times 3 \times 1$ . A 20 Å thick vacuum layer was introduced perpendicular to the surface to minimize any potential interactions between periodic replicas. Due to the strong correlation of d electrons in Ru and Ir, a  $U$ – $J$  value of 2.0 eV was adopted and spin polarization was considered in our study.<sup>55,56</sup> More details regarding the calculation formulas and derivation process can be found in the ESI.†

## 3. Results and discussion

### 3.1 OER mechanism and activity of RuO<sub>2</sub> and IrO<sub>2</sub>

Three general mechanisms of OER in an acid medium, including the adsorbate evolution mechanism (AEM), lattice oxygen oxidation mechanism (LOM), and oxidation pathway mechanism (OPM), are described in Fig. 2a–c.<sup>57–60</sup> In the complete

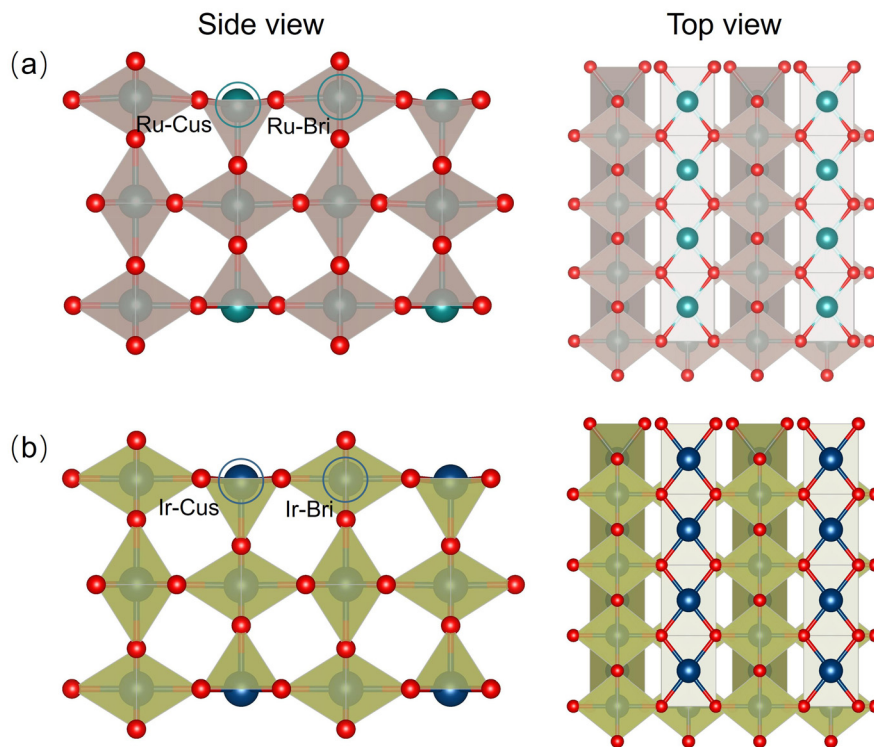


Fig. 1 Side view and top view of (a)  $\text{RuO}_2(110)$  and (b)  $\text{IrO}_2(110)$ . Ru–Cus and Ir–Cus denote the active sites. Color code: dark green balls are Ru atoms, dark blue balls denote Ir atoms, and red balls represent O atoms.

crystalline structure, we select the Cus site as the active site (Fig. S2, ESI<sup>†</sup>). When defects occur, the Bri site is also exposed to a five-coordinate environment and serves as the active site (Fig. S3, ESI<sup>†</sup>). For traditional AEM, water firstly deprotonates to a hydroxyl anion ( $\text{OH}^-$ ), oxidized to an  $^*\text{OH}$  intermediate that adsorbs on the active site (M). Afterward, the  $^*\text{OH}$  deprotonates generate an  $^*\text{O}$  intermediate, which is subsequently attacked by  $\text{OH}^-$  yielding an  $^*\text{OOH}$  intermediate. Finally, the  $\text{O}_2$  dissociates from the catalyst surface *via* deprotonation, freeing up the active site and enabling the continuation of the reaction cycle. For the LOM, while the initial two steps closely resemble the AEM, divergence emerges from the third step where  $^*\text{O}$  interacts with lattice oxygen to produce  $\text{O}_2$ , leaving an oxygen vacancy site ( $\text{O}_\text{v}$ ). Subsequently, the vacancy is occupied by  $^*\text{OH}$ , which ultimately undergoes deprotonation to drive the reaction cycle forward. Different from the single-site mechanism of the AEM and LOM, OPM demonstrates a dual-site mechanism. After an  $^*\text{OH}$  intermediate is generated at a metal site, a water molecule, acting as a nucleophile, attacks the adjacent active site once again, leading to the formation of  $^*\text{OH}$  adsorption at that location, thereby achieving a dual-site-adsorbed  $^*\text{OH}$  state ( $^*\text{OH}_2^*\text{OH}$ ). Subsequently, dehydrogenation reactions occur sequentially at the two adsorption sites, first transitioning into an  $^*\text{OH}_2^*\text{O}$  structure and then into an  $^*\text{O}_2^*\text{O}$  structure, ultimately culminating in  $\text{O}_2$  production and the perpetuation of the reaction cycle.

The reaction thermodynamics for these three mechanisms on the bare  $\text{RuO}_2$  and  $\text{IrO}_2$  facets are compared. The free energy diagrams for the OER *via* the AEM, LOM, and OPM on the  $\text{RuO}_2$

and  $\text{IrO}_2$  surfaces are respectively presented in Fig. 2d. For the AEM, forming  $^*\text{OH}$  and  $^*\text{O}$  on  $\text{RuO}_2$  is inherently spontaneous, while generating  $^*\text{OOH}$  and  $\text{O}_2$  poses relatively more challenges. Specifically, the transition from  $^*\text{OOH}$  to  $\text{O}_2$  generation serves as the potential-determining step (PDS). A similar trend is observed for  $\text{IrO}_2$ , consistent with a previous result.<sup>61</sup> Under the thermodynamic equilibrium potential of 1.23 V (*vs.* RHE), the theoretical OER overpotential ( $\eta$ ) of  $\text{RuO}_2$  is 0.698 V, significantly lower than that of  $\text{IrO}_2$ , which is 0.909 V. This demonstrates that  $\text{RuO}_2$  has higher activity and a distinct advantage over  $\text{IrO}_2$  from a thermodynamic perspective. It is attributed to the fact that the single active site of  $\text{RuO}_2$  shows a weaker interaction with  $^*\text{OOH}$  than  $\text{IrO}_2$ . Moreover, the reaction trends of both catalysts following the AEM mechanism exhibited nearly identical behaviour under both solvation and vacuum conditions (Fig. S4, ESI<sup>†</sup>). This consistency strongly supports the conclusion that solvation effects play a minimal role in the catalytic system under study.

In the case of LOM, the difficulty in forming oxygen vacancies (Table S3, ESI<sup>†</sup>) poses a significant challenge for the production of  $\text{O}_2$ , resulting in an exceptionally high theoretical overpotential, which ultimately hinders both oxides from effectively undergoing this mechanism. For the OPM featuring dual active sites, when the phenomenon of dual-site adsorption is observed, it is found that the species adsorption is too strong on both  $\text{RuO}_2$  and  $\text{IrO}_2$ , resulting in significant difficulties in the desorption process. Therefore, the OPM is not applicable. Fig. 2e compares the theoretical overpotential to the AEM, LOM, and OPM pathways on  $\text{RuO}_2$  and  $\text{IrO}_2$ , respectively.

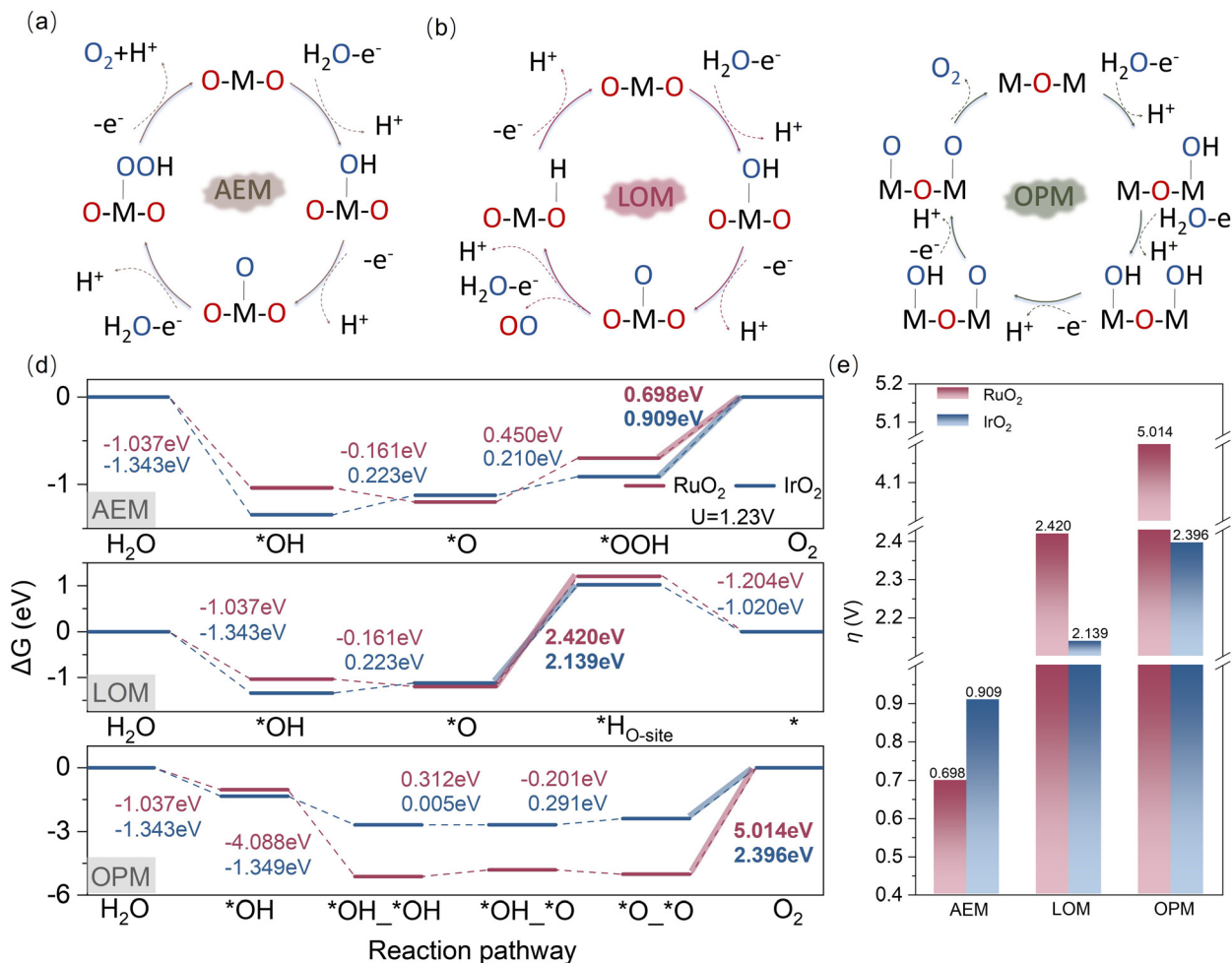


Fig. 2 (a)–(c) Schematic representations of three OER pathways (a) AEM (b) LOM (c) OPM on the surface of RuO<sub>2</sub> and IrO<sub>2</sub> considered in this study. Red oxygen and blue oxygen represent lattice oxygen and oxygen from an acidic environment, respectively. M stands for metal (Ru, Ir). (d) Gibbs free energy diagrams for the AEM, LOM, and OPM for the OER at 1.23 V on RuO<sub>2</sub> and IrO<sub>2</sub>. The thick lines in the figures represent PDS. (e) Overpotential for different reaction pathways for RuO<sub>2</sub> and IrO<sub>2</sub>.

The results suggest that the OER on the RuO<sub>2</sub> and IrO<sub>2</sub> is thermodynamically more likely to follow the AEM rather than the LOM or OPM, in good agreement with previous investigations.<sup>51,62,63</sup>

### 3.2 The OER deactivation mechanism of RuO<sub>2</sub> and IrO<sub>2</sub>

Fig. 3a illustrates the potential deactivation pathways during the OER process. The LOM pathway is less likely to occur due to the inherent presence of vacancies, while the oxygen-containing intermediates in both AEM and OPM may disrupt the structure of active sites, leading to dissolution. For instance, the adsorption of intermediates like \*OH and \*O combined with lattice oxygen results in the leaching of MO<sub>3</sub> from the active site and the formation of tetra-coordinated MO<sub>4</sub><sup>2-</sup> through further oxidation of MO<sub>3</sub> by the electrolyte. When \*OOH adsorbed, or a dual-site adsorption phenomenon occurs (*i.e.*, the adsorbed species are \*OH\_\*OH, \*OH\_\*O, or \*O\_\*O), the dissolution of tetra-coordinated MO<sub>4</sub><sup>2-</sup> can be triggered directly.

The dissolution of active sites is closely related to the stability of the RuO<sub>2</sub> and IrO<sub>2</sub> structures and their defect configurations after dissolution. The thermodynamic stability

of the defect configurations after the dissolution of catalysts has been thoroughly evaluated, as shown in Fig. S5 and S6 (ESI<sup>†</sup>). Table S4 (ESI<sup>†</sup>) presents the formation energies for all defect configurations. A smaller formation energy indicates a more stable defect structure, making it more likely to occur during dissolution. In the case of RuO<sub>2</sub>, defect configuration 6 is the most stable, formed by releasing a five-coordinated Ru and two neighbouring bridge O atoms. On the other hand, for IrO<sub>2</sub>, defect configuration 4 is the most stable and is more readily formed by the interaction of a six-coordinated Ir atom with two neighbouring bridge O atoms.

Fig. 3b and Fig. S7 (ESI<sup>†</sup>) show that the dissolution of the Ru site in RuO<sub>2</sub> mainly produces the four-coordinate RuO<sub>4</sub><sup>2-</sup> species rather than the three-coordinate RuO<sub>3</sub> species, being more thermodynamically favoured in the AEM, with distinct negative free energy changes. In comparison, the dissolution of RuO<sub>3</sub> requires an uphill free energy of over 1.5 eV. Specifically, all the intermediates in the AEM can spontaneously induce the dissolution of the Ru sites into the RuO<sub>4</sub><sup>2-</sup>. As the valence state of the Ru site increases, the more negative free energy changes

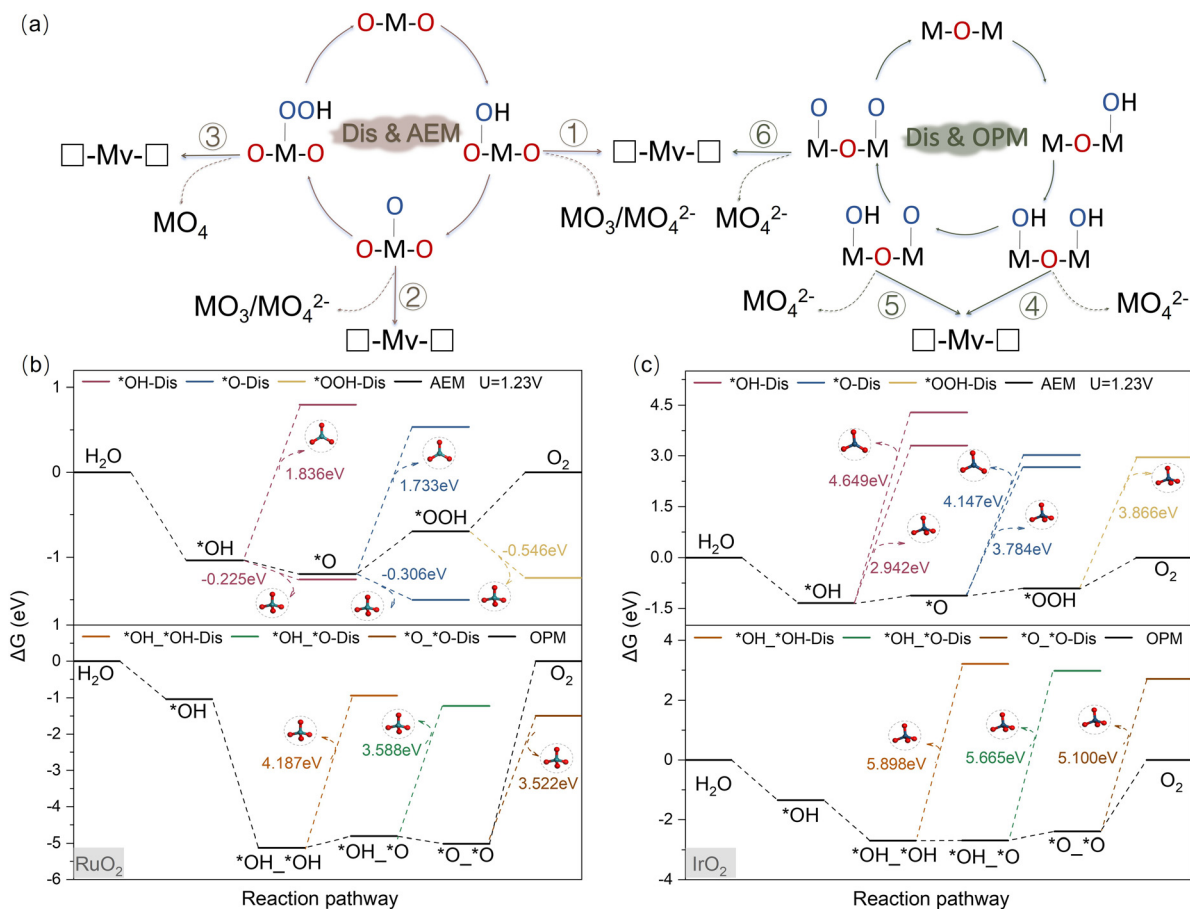


Fig. 3 (a) Schematic representations of the dissolution pathways on the surface of RuO<sub>2</sub> and IrO<sub>2</sub>. Red oxygen and blue oxygen represent lattice oxygen and oxygen from the solution, respectively. M stands for metal (Ru, Ir). Mv and square represent the formation of metal vacancies and oxygen vacancies, respectively. (b) Dissolution-free energy diagram of AEM and OPM coupling with corrosion for RuO<sub>2</sub> at 1.23 V. (c) Dissolution-free energy diagram of AEM and OPM coupling with corrosion for IrO<sub>2</sub> at 1.23 V.

become, indicating the easier dissolution of active sites. During the OPM, the dissolution pathway of RuO<sub>2</sub> is non-spontaneous, with a free energy requirement for the leaching of RuO<sub>4</sub><sup>2-</sup> exceeding 3.5 eV. These findings indicate that RuO<sub>2</sub> has a strong tendency to dissolve in the AEM of the OER. Regarding the dissolution behaviour of RuO<sub>2</sub> catalysts, the influence of solvation effects has been further investigated. By coupling the dissolution process with AEM, the dissolution pathway and trend show excellent agreement with the results obtained under vacuum conditions (Fig. S9, ESI<sup>†</sup>). This finding indicates that solvation effects have negligible impact on the dissolution behaviour of RuO<sub>2</sub> catalysts in our studied system. In addition, once the Ru defects formed on the RuO<sub>2</sub>, as illustrated in Fig. S10 (ESI<sup>†</sup>), the theoretical overpotential for the OER increases to over 1.5 V, showing a significant depression in OER intrinsic activity. It means that the dissolution of the Ru site during OER catalysis is the main reason for the deactivation of the RuO<sub>2</sub> catalyst. Preserving the integrity of the crystal structure of RuO<sub>2</sub> as much as possible is an effective strategy to maintain its high intrinsic OER activity.

In comparison to RuO<sub>2</sub>, the dissolution pathways of IrO<sub>2</sub> during AEM and OPM, as shown in Fig. 3c, are thermodynamically non-

spontaneous. The free energy changes of the dissolution step, whether dissolved as IrO<sub>4</sub><sup>2-</sup> or IrO<sub>3</sub>, are higher than 2.9 eV, indicating considerable thermodynamic non-feasibility. This highlights the remarkable stability of IrO<sub>2</sub> throughout the entire OER process. Interestingly, once IrO<sub>2</sub> has a defect, it exhibits enhanced intrinsic activity in both AEM and OPM compared to the IrO<sub>2</sub> surface (Fig. S10, ESI<sup>†</sup>). This indicates that pre-introducing oxygen vacancies in the IrO<sub>2</sub> surface is an effective way to improve the OER activity of IrO<sub>2</sub>. Upon comparing the dissolution performance of IrO<sub>2</sub> and RuO<sub>2</sub>, it is evident that IrO<sub>2</sub> exhibits higher stability during the OER process.

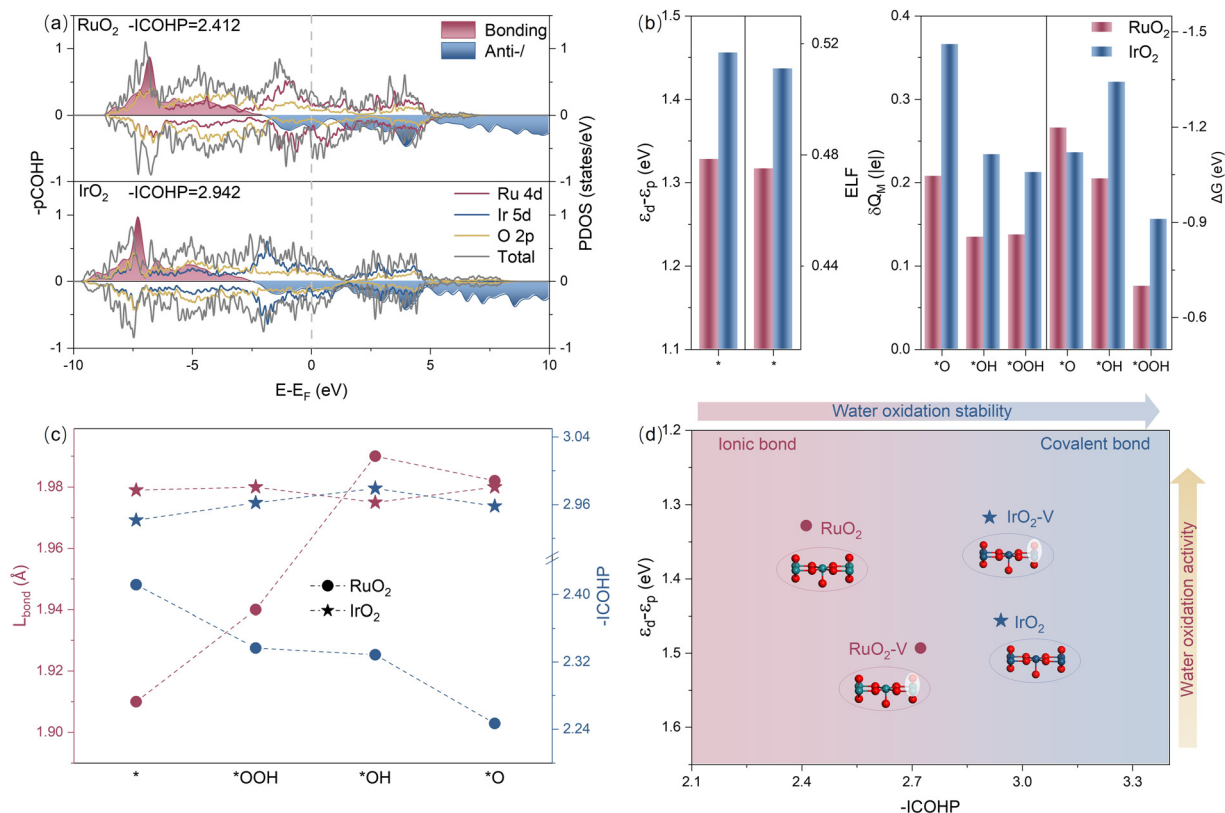
### 3.3 The descriptor of activity and stability for the OER

An investigation of the electronic structure reveals that the bonding properties of RuO<sub>2</sub> and IrO<sub>2</sub> are attributed to the contrasting trends in their activity and stability. Fig. 4a displays the projected density of states (PDOS), illustrating the overlap of the orbitals from metal and oxygen atoms and how electrons are distributed in both compounds. Notably, the energy level of the bonding orbitals in IrO<sub>2</sub> is lower than that in RuO<sub>2</sub>, whereas the energy level of the antibonding orbitals is higher in IrO<sub>2</sub>. This observation indicates that the overlap of the Ir-d orbitals

with the O-p orbitals is more significant than that of the Ru-d orbitals with the O-p orbitals, suggesting that the Ir-O bonding has a greater covalency than Ru-O bonding. Further confirmation comes from the projected crystal orbital Hamilton overlap population (pCOHP) analysis, which shows that the electron filling in the Ir-O bonds (2.942) is notably higher than in RuO<sub>2</sub> (2.412), indicating stronger covalency in the Ir-O bond. Additionally, the energy difference between the d-band of Ru and the p-band of O ( $\epsilon_d - \epsilon_p$ ) is smaller for RuO<sub>2</sub> (1.328 eV) compared to IrO<sub>2</sub> (1.456 eV), indicating more ionic bonding nature in the Ru-O bond. This is also supported by the electronic localization function (ELF) analysis, which reveals that the Ru-O bonds exhibit a lower electronic delocalization value (0.475). In contrast, the Ir-O bonds have a higher value (0.511), suggesting a more covalency bonding nature due to increased electronic localization.<sup>64,65</sup> Furthermore, the electronic distributions of RuO<sub>2</sub>-V and IrO<sub>2</sub>-V exhibit significant changes after vacancy formation (Fig. S11, ESI†). For RuO<sub>2</sub>-V,  $\epsilon_d$  shifts positively, and  $\epsilon_p$  shifts negatively, resulting in an increase in  $\epsilon_d - \epsilon_p$ . In contrast, for IrO<sub>2</sub>-V,  $\epsilon_d$  shifts negatively and  $\epsilon_p$  shifts positively, leading to a decrease in  $\epsilon_d - \epsilon_p$ , showing an opposite trend. Analysis of the pCOHP of the defective

catalysts reveals that the bonding orbital interaction of RuO<sub>2</sub>-V ( $-ICOHP = 2.723$ ) is enhanced compared to the intact catalyst, while that of IrO<sub>2</sub>-V ( $-ICOHP = 2.911$ ) is weakened. Therefore, it can be concluded that the nature of the metal-oxygen bonds may have changed after defect formation, leading to the observed changes in catalytic activity.

The covalent Ir-O bonds contribute to the stability of IrO<sub>2</sub>, even after the adsorption of OER intermediates. However, these bonds with more localized electrons also impede the release of O<sub>2</sub> by enhancing the adsorption strength of the intermediates. In contrast, the greater ionic bonding characteristics of RuO<sub>2</sub> with more delocalized electrons facilitate O<sub>2</sub> formation and desorption; nonetheless, the Ru-O structure is more susceptible to disruption by the adsorption of intermediates. Fig. 4b illustrates significant variations in the charge transfer number ( $\delta Q_M$ ) associated with active sites upon the adsorption of three intermediate species: \*O, \*OH, and \*OOH. During this adsorption process, the metal active sites of the oxides interact with the intermediates primarily through covalent interaction (orbital overlap) and electrostatic interactions. A higher degree of orbital overlap correlates with increased charge transfer and enhanced binding strength. In RuO<sub>2</sub>, its greater ionic bonding



**Fig. 4** (a) Projected crystal orbital Hamilton overlap population (pCOHP) curves and projected density of states (PDOS) plots of M-d and O-p in the RuO<sub>2</sub> and IrO<sub>2</sub> models. The dashed line refers to the Fermi level. (b) Values of the difference between d-band and p-band centers ( $\epsilon_d - \epsilon_p$ ) and electronic localization function (ELF) for RuO<sub>2</sub> and IrO<sub>2</sub>; changes in charge transfer numbers ( $\delta Q_M$ ) on the metal active after the adsorption of intermediates on RuO<sub>2</sub> and IrO<sub>2</sub>; changes in Gibbs free energy of AEM ( $\Delta G$ ) at 1.23 V on RuO<sub>2</sub> and IrO<sub>2</sub>. (c) Correlation between the calculated bond lengths between the bulk metal and oxygen, and  $-ICOHP$  of the bulk after the adsorption of intermediates on RuO<sub>2</sub> and IrO<sub>2</sub>. (d) The regular trends of  $\epsilon_d - \epsilon_p$  and  $-ICOHP$  with respect to the water oxidation activity and stability. RuO<sub>2</sub> and IrO<sub>2</sub> represent the pristine (110) crystal surfaces, while RuO<sub>2</sub>-V and IrO<sub>2</sub>-V represent the defective crystal surfaces.

leads to the adsorption of intermediate species mainly through electrostatic interactions, resulting in lower electron transfer and relatively weaker binding. In contrast, the covalent bonding nature of IrO<sub>2</sub> promotes stronger overlap between the Ir orbitals and those of the intermediate species, leading to more significant electron transfer and stronger adsorption.

As shown in Fig. 4c, while the Ir–O bond length in IrO<sub>2</sub> (1.979 Å) is notably longer than the Ru–O bond length in RuO<sub>2</sub> (1.910 Å) due to the larger radius of Ir, the Ru–O bond length of RuO<sub>2</sub> significantly elongates upon the adsorption of reaction intermediates, whereas that of IrO<sub>2</sub> remains largely unchanged. This geometric behavior highlights the tendency of RuO<sub>2</sub> to undergo deformation, indicating its lower stability. Furthermore, the –ICOHP value for RuO<sub>2</sub> decreases considerably, while that of IrO<sub>2</sub> remains relatively stable (Fig. S12, ESI†).

Fig. 4d illustrates the complex relationship between the bonding properties of RuO<sub>2</sub> and IrO<sub>2</sub> and their catalytic performance. It demonstrates that electron filling in the M–O bonds contributes to the stability of these oxides. Specifically, a higher degree of electron filling in the M–O bonds makes the catalyst less susceptible to external disturbances, as evidenced by the highly stable IrO<sub>2</sub>. In contrast, the difference between  $\epsilon_d$  and  $\epsilon_p$  in an oxide can indicate its OER activity. Smaller  $\epsilon_d - \epsilon_p$  values correlate with more delocalized electrons and weaker adsorption of intermediates at reactive sites, which is favorable for the release of oxygen. RuO<sub>2</sub> serves as a prime example of a catalyst with excellent OER activity. To enhance the stability of RuO<sub>2</sub>, it is essential to increase the electron filling degree in Ru–O bonds to maintain structural integrity. This can be achieved by doping electron-rich atoms, as demonstrated by Zhang *et al.*,<sup>66</sup> where La doping in RuO<sub>2</sub> forms a La–O–Ru local structure, optimizes Ru–O bond strength, enhances RuO<sub>2</sub> stability, and suppresses Ru dissolution, enabling stable operation for 450 hours at 100 mA cm<sup>-2</sup>. On the other hand, improving IrO<sub>2</sub> activity requires increasing the delocalized electrons on Ir, which can be realized by either reducing Ir–O orbital overlap or introducing oxygen vacancies. Wang *et al.*<sup>67</sup> exemplified this approach through their Gd-doped IrO<sub>2</sub> catalyst, synthesized *via* template-free ammonia complexation. The Gd doping optimized OER performance by regulating the Ir<sup>4+</sup>/Ir<sup>3+</sup> ratio and increasing oxygen vacancy concentration, leading to enhanced H<sub>2</sub>O adsorption and reduced \*OH dissociation energy.

## 4. Conclusions

Our comprehensive thermodynamic analysis reveals the dominant reaction pathways governing both OER mechanisms and dissolution processes in RuO<sub>2</sub> and IrO<sub>2</sub> catalysts. The AEM emerges as the predominant OER pathway for both oxides, with RuO<sub>2</sub> demonstrating superior catalytic activity compared to IrO<sub>2</sub>. Crucially, this AEM pathway drives the thermodynamically spontaneous dissolution of RuO<sub>2</sub> into soluble RuO<sub>4</sub><sup>2-</sup> species, while maintaining IrO<sub>2</sub>'s exceptional stability through non-spontaneous dissolution characteristics. Electronic structure analysis through  $\epsilon_d - \epsilon_p$  energy gaps, ELF, and –ICOHP

values uncovers fundamental bonding differences: RuO<sub>2</sub> exhibits ionic-dominated bonding with significant electron delocalization, whereas IrO<sub>2</sub> displays covalent-dominated interactions with higher electron filling. This contrast creates an intrinsic activity–stability trade-off; the ionic character in RuO<sub>2</sub> weakens intermediate adsorption to enhance OER activity but sacrifices structural integrity through labile metal–oxygen bonds. Conversely, IrO<sub>2</sub>'s covalent nature stabilizes the catalyst framework but strengthens intermediate binding, thereby limiting catalytic performance.

These atomistic insights establish a fundamental structure–activity–stability relationship. The revealed electronic origins of the RuO<sub>2</sub> and IrO<sub>2</sub> difference provide critical design principles for next-generation OER catalysts: strategic engineering of metal–oxygen bonding character through alloying, strain modulation, or heterostructure construction could potentially decouple the activity–stability correlation, enabling simultaneous optimization of both essential properties for practical water electrolysis applications.

## Author contributions

L. T. performed the theoretical calculations and the interpretation. L. T., X. C. and Z. X. were responsible for data collection and analysis. L. L. and L. T. conducted the data analysis and wrote this manuscript. Q. X. and J. L. contributed to the revision. L. L. and Z. W. directed the project and finalized the manuscript. All authors discussed the results and contributed to the final manuscript.

## Data availability

The data supporting the findings of this study are available within the article and its ESI.†

## Conflicts of interest

There are no conflicts to declare.

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